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**INTRODUCTION**  
**TO THE ORGANIC CHEMISTRY**

Minsk BSMU 2018

МИНИСТЕРСТВО ЗДРАВООХРАНЕНИЯ РЕСПУБЛИКИ БЕЛАРУСЬ  
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КАФЕДРА ОБЩЕЙ ХИМИИ

**В. В. Хрусталёв, Т. В. Латушко, Т. А. Хрусталёва**

**ВВЕДЕНИЕ  
В ОРГАНИЧЕСКУЮ ХИМИЮ**

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TO THE ORGANIC CHEMISTRY**

Практикум



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На английском языке

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## **PREFACE**

This book is on the introduction to the organic chemistry. The main aim of the course of organic chemistry in the pre-university department is to make future students familiar with main types of organic compounds, their structure and chemical properties, as well as with the main types of organic reactions.

This version of a book combines theoretical part and practical tasks. Students should study theoretical material for each lesson, solve practical tasks during the lesson, and then they should solve home tasks on their own and show the results to the teacher.

Authors are looking forward to receive comments and suggestions from students and colleagues.

# LESSON 1. ALKANES

## STRUCTURE OF ALKANES

The simplest organic compounds are those composed of only two elements: hydrogen (H) and carbon (C). These compounds are called hydrocarbons. The valence of carbon is always equal to IV in all the organic substances. Hydrocarbons themselves are separated into two types: aliphatic hydrocarbons and aromatic hydrocarbons. Aliphatic hydrocarbons are hydrocarbons made from chains of C atoms. There are four types of aliphatic hydrocarbons traditionally studied in the course of the introductory organic chemistry: 1) *alkanes* are aliphatic hydrocarbons with single covalent bonds only; 2) *alkenes* are hydrocarbons that contain one C=C double bond; 3) *dienes* are hydrocarbons that contain two C=C double bonds; 4) *alkynes* are hydrocarbons that contain one C≡C triple bond. There are also aliphatic hydrocarbons with at least one ring of C atoms; these hydrocarbons are called cycloalkanes. Aromatic hydrocarbons also contain at least one ring of carbon atoms, but that ring must have so-called  $\pi$ -system explained in Lesson 5.

The simplest alkanes have their C atoms bonded in a straight chain; these are called *normal* alkanes. They are named according to the number of C atoms in the chain. The smallest alkane is called methane:

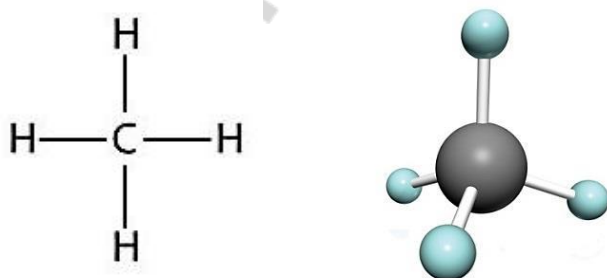


Figure 1. 2D and 3D structures of methane

The methane molecule is three dimensional, with the H atoms in the positions of the four corners of a tetrahedron (figure 1). Each carbon atom exists in a state of  $sp^3$  hybridization in alkanes.

The next alkane has two C atoms that are covalently bonded to each other. For each C atom to make four covalent bonds, each C atom must be bonded to three H atoms. The resulting molecule with the formula  $C_2H_6$  is called ethane (figure 2).

Propane (C<sub>3</sub>H<sub>8</sub>) has a backbone of three C atoms surrounded by H atoms (figure 3).

The diagrams representing alkanes are called structural formulas because they show the structure of the molecule. As molecules get larger, structural formulas become more and more complex. One way to deal with this problem is to use a condensed structural formula, which lists the formula of each C atom in the backbone of the molecule. For example, the condensed structural formula for ethane is CH<sub>3</sub>-CH<sub>3</sub>, while for propane it is CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>3</sub>.

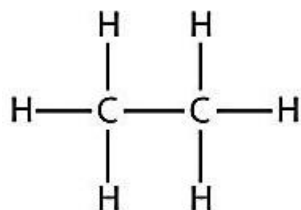


Figure 2. Structural formula of ethane

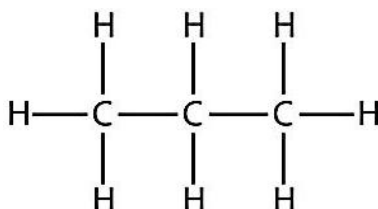


Figure 3. Structural formula of propane

Because alkanes have the maximum number of H atoms possible according to the rules of covalent bonds, alkanes are also referred to as *saturated* hydrocarbons. The common formula for all alkanes is C<sub>n</sub>H<sub>2n+2</sub>, where *n* is the number of carbon atoms.

Molecular formulas, the condensed structural formulas, and the names of the first 10 alkanes are given in the table 1.

As one can see in table 1, the heavier the alkane, the lower its boiling and melting points. At standard temperature (25 °C) an alkane made from 20 carbon atoms is already solid. However, melting and boiling points also depend on the shape of a molecule. Some hydrocarbons are not just straight chains. Many hydrocarbons have branches of C atoms attached to a chain. These branched alkanes are *isomers* of straight-chain alkanes having the same number of C atoms. However, they are different compounds with different physical and chemical properties. For example, branched alkanes have lower melting and boiling points than their linear isomers. One may try to understand it from the point of view of the number of contacts

the molecules make with each other: linear molecules are connected with each other better than branched ones.

Table 1

First ten alkanes and their characteristics

Molecular Formula	Condensed Structural Formula	Name	State of matter in normal conditions
CH <sub>4</sub>	CH <sub>4</sub>	methane	gas
C <sub>2</sub> H <sub>6</sub>	CH <sub>3</sub> -CH <sub>3</sub>	ethane	gas
C <sub>3</sub> H <sub>8</sub>	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub>	propane	gas
C <sub>4</sub> H <sub>10</sub>	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>	butane	gas
C <sub>5</sub> H <sub>12</sub>	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>	pentane	liquid
C <sub>6</sub> H <sub>14</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	hexane	liquid
C <sub>7</sub> H <sub>16</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	heptane	liquid
C <sub>8</sub> H <sub>18</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	octane	liquid
C <sub>9</sub> H <sub>20</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	nonane	liquid
C <sub>10</sub> H <sub>22</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> CH <sub>3</sub>	decane	liquid

## NOMENCLATURE FOR NAMING BRANCHED ALKANES

There are a series of rules for naming branched alkanes (and, ultimately, for all organic compounds). These rules make up the system of nomenclature for naming organic molecules. Worldwide, the International Union of Pure and Applied Chemistry (IUPAC) has developed the system of nomenclature for organic compounds. So these rules are sometimes called the *IUPAC rules of nomenclature*.

1. The longest continuous chain of C atoms should be identified. Note that the longest chain may not be drawn in a straight line. The longest chain determines the final name of the hydrocarbon. For example, in the molecule from figure 4 the longest chain of carbons has six C atoms. Therefore, it will be named as a *hexane*.

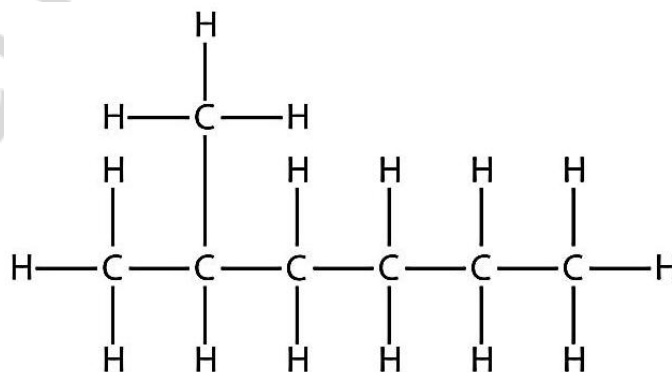


Figure 4. Structural formula of 2-methylhexane

However, in the molecule from figure 5 the longest chain of C atoms is not six, but seven, as shown by arrows. So this molecule will be named as a *heptane*.

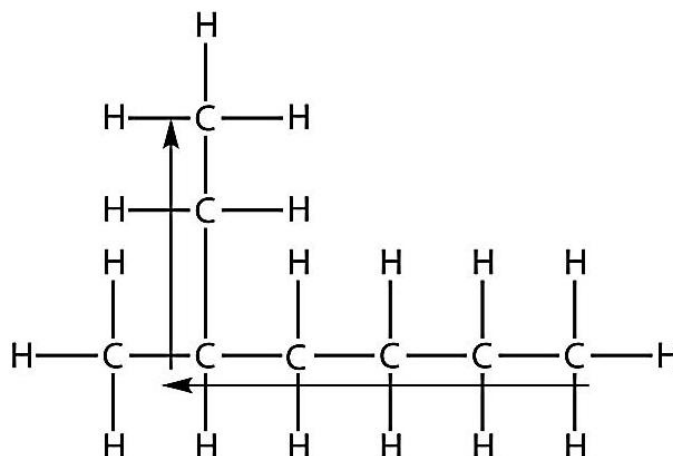


Figure 5. Structural formula of 3-methylheptane

2. All the branches, or *substituents*, of the main chain should be identified. The names of the substituents, or *alkyl groups*, are derived from the names of the corresponding hydrocarbons (table 2); however, rather than having the ending *-ane*, the substituent name has the ending *-yl*.

Table 2

Alkyl substituents names

Substituent Formula	Number of C Atoms	Name of Substituent
CH <sub>3</sub> –	1	<i>methyl-</i>
CH <sub>3</sub> –CH <sub>2</sub> –	2	<i>ethyl-</i>
CH <sub>3</sub> –CH <sub>2</sub> –CH <sub>2</sub> –	3	<i>propyl-</i>
CH <sub>3</sub> –CH <sub>2</sub> –CH <sub>2</sub> –CH <sub>2</sub> –	4	<i>butyl-</i>
CH <sub>3</sub> –CH <sub>2</sub> –CH <sub>2</sub> –CH <sub>2</sub> –CH <sub>2</sub> –	5	<i>pentyl-</i>
and so forth	and so forth	and so forth

3. The longest chain of the hydrocarbon must be numbered, and the numerical position of each substituent must be noticed. The main chain is numbered to give the substituent the lowest possible number. For example, in this alkane from figure 6 the longest chain is five C atoms long, so it is a pentane.

There is a one-carbon substituent on the third C atom, so there is a methyl group at position 3. One has to indicate the position using the number, which is followed by a hyphen, the substituent name, and the parent hydrocarbon name — in this case the name is 3-methylpentane. That name is specific to that particular hydrocarbon and no other molecule including isomers.



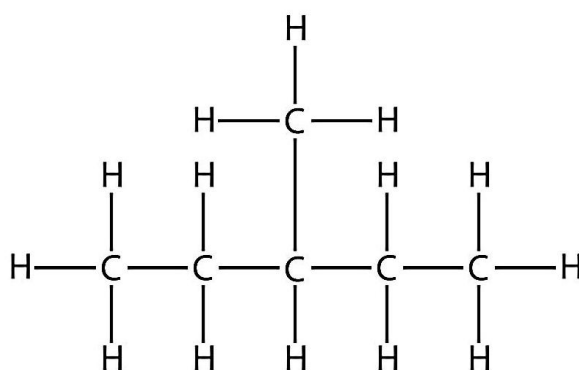


Figure 6. Structural formula of 3-methylpentane

4. If the substituents are the same, their name is used only once, but with more than one number, separated by a comma. Also, a numerical prefix should be used before the substituent name. Prefix indicates the number of substituents of that particular type.

Table 3

Names of numerical prefixes

Number of Same Substituents	Numerical Prefix
2	<i>di-</i>
3	<i>tri-</i>
4	<i>tetra-</i>
5	<i>penta-</i>

Consider the molecule of 2,3-dimethylbutane. As one can see in figure 7, there are several ways to reproduce its structure (both in 2D and 3D pictures). In figure 7, *b* one can see that the angle between two bonds is always equal to  $109.28^\circ$  in saturated hydrocarbons. This angle is explained by the  $sp^3$  hybridization of orbitals of valence electrons of carbon.

One of the simplest ways of structural formula reproduction is called representation by “smiles”: CC(C)C(C)C. The part of a molecule written in brackets is connected to the carbon atom written straight before it.

The longest chain of the molecule has four C atoms, so it is a butane. There are two substituents, each of which consists of a single C atom; they are methyl groups. The methyl groups are on the second and third C atoms in the chain (no matter which end the numbering starts from), so we would name this molecule 2,3-dimethylbutane. Note the comma between the numbers, the hyphen between the numbers and the substituent name, and the presence of the prefix *di-* before the *methyl*.

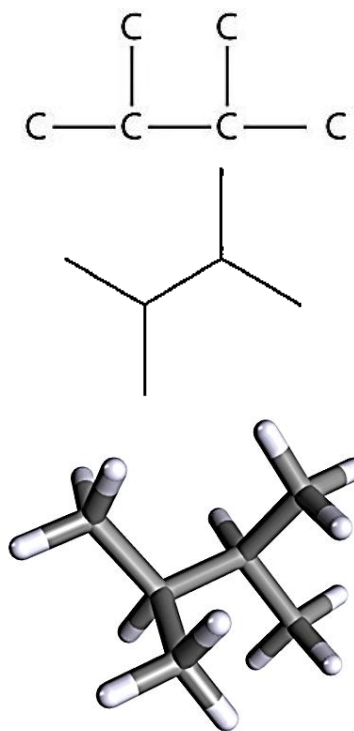
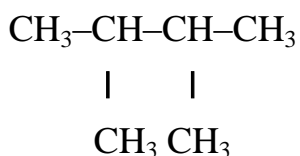


Figure 7. Three ways to represent the structure of 2,3-dimethylbutane

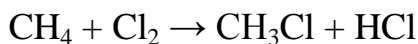
When you write the structural formula, a half-condensed way to write it is preferred. All the atoms must be written. All the bonds (and their orders) must be shown as well. Only the bonds between carbon and hydrogen may not be shown, if they are not making a part of a functional group. All the functional groups should be shown clearly in a half-structural manner. So, according to these rules, the structural formula of 2,3-dimethylbutane is as follows.



Notice that this style is very good for handwriting, but not for typesetting.

## CHEMICAL PROPERTIES OF ALKANES

Hydrocarbons are rather unreactive (compared with other compounds made from atoms of nonmetals and hydrogen), but they do participate in some chemical reactions. One common reaction is the substitution of hydrogen by a halogen atom by combining a hydrocarbon with an elemental halogen. Light is necessary to promote the reaction, such as this one between methane and chlorine:



Halogen atom (F, Cl, Br, or I) is one of the simplest functional groups. Organic compounds that contain at least one halogen atom are called alkyl halides.

The mechanism of the reaction between alkane and halogen (except fluorine) is a free radical chain reaction that leads to substitution of hydrogens by halogens in a molecule. Chlorine molecule is decomposed into two chlorine atoms ( $\text{Cl}^\cdot$  radicals) under the influence of light (initiation step). Then those radicals attack alkane molecules and gain hydrogen atoms. Remaining parts of alkanes are free radicals (alkyl radicals). These radicals attack chlorine molecules and gain chlorine atoms. Remaining chlorine radicals continue the chain reaction (this step is called the propagation of chain reaction). In general, a free radical causes the formation of another free radical. The chain may be broken when two free radicals join each other.

A simple alkyl halide can be named like an ionic salt, first by stating the name of the parent alkane as a substituent group (with the *-yl* suffix) and then the name of the halogen as if it were the anion. So,  $\text{CH}_3\text{Cl}$  has the common name of methyl chloride, while  $\text{CH}_3\text{CH}_2\text{Br}$  is ethyl bromide and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$  is propyl iodide. However, this system is not ideal for more complicated alkyl halides.

The systematic way of naming alkyl halides is to name the halogen as a substituent, just like an alkyl group, and use numbers to indicate the position of the halogen atom on the main chain. The name of the halogen as a substituent comes from the stem of the element's name plus the ending *-o*, so the substituent names are *fluoro-*, *chloro-*, *bromo-* and *iodo-*. If there is more than one of a certain halogen atom, we use numerical prefixes to indicate the number of each kind, just as with alkyl groups. For example, the molecule from figure 8 is 2-bromobutane, while the molecule from figure 9 is 2,3-dichloropentane.

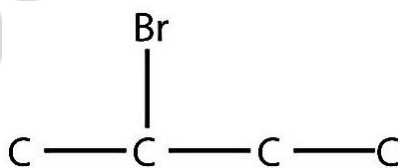


Figure 8. Structural formula of 2-bromobutane (hydrogen atoms are not shown)

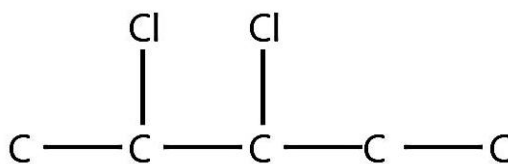
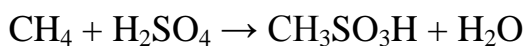
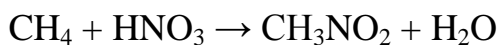


Figure 9. Structural formula of 2,3-dichloropentane (hydrogen atoms are not shown)

If alkyl groups are present, the substituents are listed alphabetically. Numerical prefixes are ignored when determining the alphabetical ordering of substituent groups.

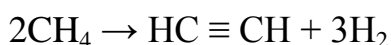
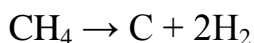
Alkanes react with diluted nitric and concentrated sulfuric and nitric acids in a way similar to the way of their reaction with halogens.



The products are nitromethane and sulfomethane. We can simplify those free radical chain reactions and say that  $\text{OH}^\cdot$  radical of nitric acid (or sulfuric acid) interacts with hydrogen from an alkane and forms water, while the remaining part of  $\text{HNO}_3$  molecule ( $\text{NO}_2^\cdot$  radical) combines with the carbon atom (the remaining part of sulfuric acid molecule is  $\text{SO}_3\text{H}^\cdot$  radical).

Reactions of alkanes with halogens and acids are substitution reactions.

Alkanes can be decomposed at high temperatures without access of oxygen. That decomposition may be complete (breaking into hydrogen and soar), or incomplete (when unsaturated hydrocarbons are formed along with hydrogen). The higher the temperature, the more complete the decomposition.



The last reaction can also go under the name dehydrogenation, since the molecule of alkane is losing hydrogen.

Another pathway of thermal decomposition is called cracking. The mixture of smaller alkanes and alkenes is produced in that reaction from longer alkanes.



One of the ways to make longer alkanes from smaller ones includes two steps: reaction with halogen producing alkyl halide; reaction between monoalkyl halide(s) and active metal (such as sodium or potassium) in which a bond between two molecules appears in the place where there were halogen atoms.

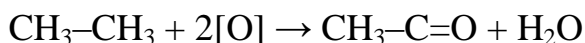
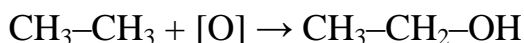


In the last reaction there will be a mixture of three products: butane (in case of reaction between two ethyl radicals), ethane (in case of reaction between two methyl radicals), and propane (in case of reaction between ethyl and methyl radicals).

The most common reaction for hydrocarbons is combustion, which is the combination of a hydrocarbon with  $O_2$  to make  $CO_2$  and  $H_2O$ . The combustion reaction for gasoline, for example, which can be represented by  $C_8H_{18}$ , is as follows:

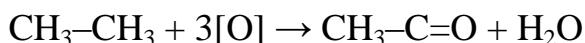


Catalytic oxidation of alkanes may produce alcohols, aldehydes and carboxylic acids. The products are listed in the order of the increase of the strength of an oxidizer.



|

H



|

OH

#### TEST FOR CLASSWORK

- What is the valence of carbon in all organic compounds?  
a) I      b) II      c) III      d) IV
- Choose the common formula for alkanes:  
a)  $C_nH_{2n-2}$       b)  $C_nH_{2n}$       c)  $C_nH_{2n+2}$       d)  $C_nH_{2n-6}$
- How many isomers can you suggest for butane molecule?  
a) 1      b) 2      c) 3      d) 4
- Choose isomers which can be described by the same  $C_5H_{12}$  formula:  
a) 2-methyl-butane      c) 2,2-dimethyl-propane  
b) 3-methyl-pentane      d) 2,2-dimethyl-pentane
- Choose alkanes existing in gaseous state in normal conditions:  
a)  $C_2H_6$       b)  $CH_4$       c)  $C_6H_{12}$       d)  $C_3H_8$
- Describe the type of chemical reaction between  $C_2H_6$  and  $Cl_2$ :  
a) addition      c) decomposition  
b) substitution      d) composition
- Which reactants can be used to synthesize  $C_{10}H_{22}$  from  $C_5H_{11}Cl$ ?  
a) potassium      c) sodium  
b) potassium chloride      d) sodium hydroxide

8. Calculate the sum of all coefficients in the redox reaction:  $C_3H_8 + O_2 \rightarrow CO_2 + H_2O$   
 a) 6            b) 10            c) 7            d) 13
9. Choose the final products of  $C_4H_{10}$  combustion in the excess of oxygen:  
 a)  $CO_2$  and  $H_2O$             c)  $C_2H_6$  and  $C_2H_4$   
 b)  $CO$  and  $H_2O$             d)  $C_4H_9OH$
10. Which substances can be produced in the reaction between three substances:  
 $C_2H_5Cl$ ,  $C_3H_7Cl$  and  $Na$ ?  
 a)  $C_4H_{10}$             b)  $C_6H_{14}$             c)  $C_5H_{12}$             d)  $C_7H_{16}$

### TEST FOR HOMEWORK

1. Choose the type of hybridization state for outer shell electron orbitals of each carbon atom in saturated hydrocarbons?  
 a)  $sp$             b)  $sp^2$             c)  $sp^3$             d) no hybridization
2. Cracking of alkanes results in formation of:  
 a) shorter alkanes            c) longer alkanes  
 b) shorter alkenes            d) longer alkenes
3. How many isomers can you suggest for pentane molecule?  
 a) 1            b) 2            c) 3            d) 4
4. Choose isomers which can be described by the same  $C_6H_{14}$  formula:  
 a) 2-methyl-butane            c) 3-methyl-pentane  
 b) 2-methyl-pentane            d) 2,3-dimethyl-pentane
5. Choose alkanes existing in solid state in normal conditions  
 a)  $C_5H_{12}$     b)  $C_6H_{14}$             c)  $C_{16}H_{34}$             d)  $C_{23}H_{48}$
6. Describe the type of the following chemical reaction:  $2CH_4 (t^\circ) \rightarrow C_2H_2 + 3H_2$   
 a) composition            c) decomposition  
 b) dehydration            d) dehydrogenation
7. Which reactants can be used to synthesize  $C_{12}H_{24}$  from  $C_6H_{13}Br$ ?  
 a) potassium            c) lithium  
 b) potassium carbonate            d) potassium permanganate
8. Calculate the sum of all coefficients in the redox reaction:  $C_4H_{10} + O_2 \rightarrow CO_2 + H_2O$   
 a) 15            b) 18            c) 25            d) 33

9. Choose the products of the reaction between  $\text{HNO}_3$  and  $\text{C}_4\text{H}_{10}$ :
- a)  $\text{C}_4\text{H}_9\text{NO}_2$  and  $\text{H}_2\text{O}$       c)  $\text{C}_3\text{H}_9\text{NO}_2$  and  $\text{H}_2\text{O}$   
 b)  $\text{C}_4\text{H}_9\text{NH}_3$  and  $\text{H}_2\text{O}$       d)  $\text{C}_4\text{H}_{11}\text{NO}_3$
10. Which substances can be produced in the reaction between three substances:  
 $\text{C}_3\text{H}_7\text{Br}$ ,  $\text{C}_4\text{H}_9\text{Br}$  and  $\text{K}$ ?
- a)  $\text{C}_8\text{H}_{18}$       b)  $\text{C}_6\text{H}_{14}$       c)  $\text{C}_5\text{H}_{12}$       d)  $\text{C}_7\text{H}_{16}$

### EXERCISES FOR CLASSWORK

#### 1. Draw structural formulas of the following compounds:

3-ethyl-3-methyl-hexane

2,2-dimethylbutane

3-ethyl-4-propylheptane

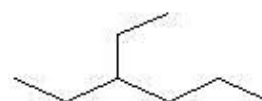
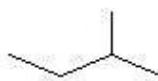
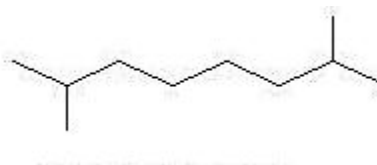
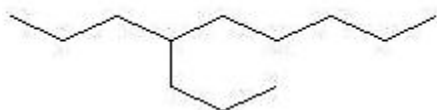
1,2-dimethylcyclopentane

3,4-diethyloctane

2,2-dimethyl-4-propylnonane

5-butyl-2,2-dimethyldecane

#### 2. Name the following alkanes



**3. Determine the volume of air that is needed to burn down a mixture composed of 3 liters of methane, 5 liters of ethane, and 20 liters of propane.**

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**4. Find the formula of a hydrocarbon. Combustion of that hydrocarbon resulted in the formation of 2 L of carbon dioxide and 1.205 g of water. The relative density of the hydrocarbon per helium is 13.5.**

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**5. The mixture made from ethane and butane has a volume of 4 L. That mixture has been completely burnt. The volume of carbon dioxide was equal to 12 L. Find the volume percentage of ethane in the initial mixture of gases.**

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**6. The mixture made from methane and propane has a volume of 6 L. That mixture has been completely burnt. The volume of oxygen used in this process was equal to 24 L. Find the volume percentage of propane in the initial mixture of gases.**

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## EXERCISES FOR HOMEWORK

### 1. Draw structural formulas of the following compounds:

2-methyl-4-propyl-octane

3,3-diethylhexane

2,3,4-trimethylpentane

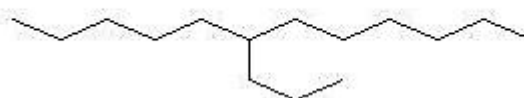
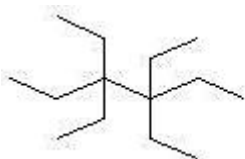
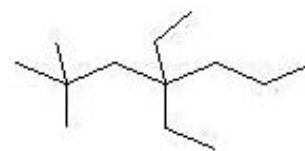
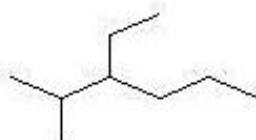
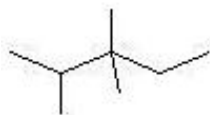
2,4-dimethylhexane

4-propyl-3-ethyl-2-methyloctane

4-isopropylheptane

4,4-diethylpentane

### 2. Name the following alkanes



### 3. Determine the volume of air which is needed to burn down a mixture composed of 6 liters of methane, 3 liters of ethane, and 1 liter of propane.

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**4. The products of the complete combustion of a hydrocarbon are: 40 L of carbon dioxide and 32.143 g of water. The relative density of this compound per oxygen is 1.75. Find the formula of a hydrocarbon.**

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**5. The mixture made from methane and butane has a volume of 5 L. That mixture has been completely burnt. The volume of oxygen used in this process was equal to 28 L. Find the volume percentage of methane in the initial mixture of gases.**

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**6. The mixture made from propane and butane has a volume of 6 L. That mixture has been completely burnt. The volume of carbon dioxide produced in this process was equal to 19 L. Find the volume percentage of butane in the initial mixture of gases.**

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## LESSON 2. STRUCTURE OF UNSATURATED HYDROCARBONS

### STRUCTURE AND NOMENCLATURE OF ALKENES

There are three types of unsaturated but not aromatic hydrocarbons traditionally studied in the introductory course of the organic chemistry: alkenes, dienes, and alkynes.

Alkenes have a double bond (C=C). The length of a double bond (0.134 nm) is just 13% shorter than the length of a single bond (0.154 nm) between two carbon atoms. Alkenes have less than the maximum number of possible H atoms, and so they are called unsaturated hydrocarbons. The common formula for all the alkenes is  $C_nH_{2n}$ . The smallest alkene (ethene) has two C atoms (figure 10) and is also known by its common name ethylene.

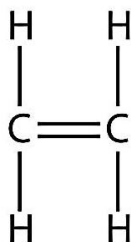


Figure 10. Structural formula of ethene (ethylene)

The next alkene (propene) has three C atoms with a C=C double bond between two of the C atoms (figure 11). It is also known as propylene.

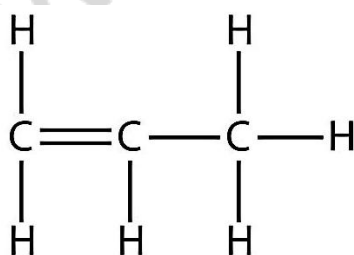


Figure 11. Structural formula of propene

The names of alkenes are the same as for their corresponding alkanes except that the ending is *-ene*, rather than *-ane*. Using a stem to indicate the number of C atoms in a molecule and an ending to represent the type of organic compound is common in organic chemistry.

With the introduction of the next alkene, butene, we begin to see a major issue with organic molecules: multiple choices.

With four C atoms, the C=C double bond can go between the first and second C atoms or between the second and third C atoms (figure 12).

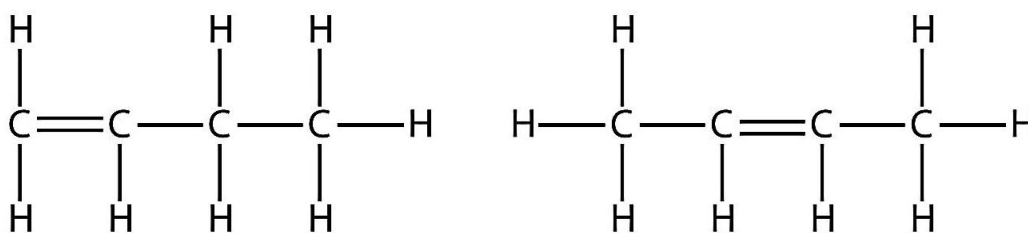


Figure 12. Structural formulas of two isomers of butene (1-butene and 2-butene)

The rules of naming in organic chemistry require that these two substances have different names. The first molecule is named *1-butene*, while the second molecule is named *2-butene*. The number at the beginning of the name indicates where the double bond is situated (if we go from left to right). The lowest possible number is used to number a feature in a molecule; hence, calling the second molecule 3-butene would be incorrect.

The compounds 1-butene and 2-butene have different physical and chemical properties, even though they have the same molecular formula —  $C_4H_8$ .

With five C atoms, we will use the *pent-* stem, and with a C=C double bond, this is an alkene, so this molecule is a pentene. In numbering the C atoms, we use the number 2 because it is the lower possible label. So this molecule is named 2-pentene (figure 13).

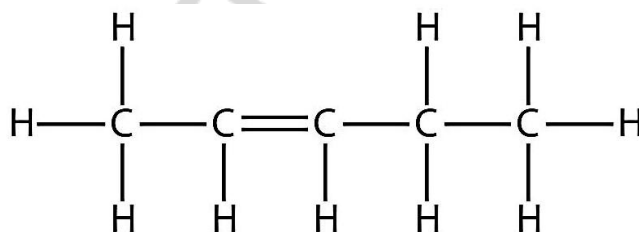


Figure 13. Structural formula of 2-pentene

Hydrocarbons with double bond may exist in *cis-* and *trans-* isomeric forms. In *cis* isomers identical substituents are situated on the same side of a double bond (figure 14). In *trans* isomers there are two different substituents on the same side of a double bond. It is clear that *cis-* and *trans-* isomers can exist only for those molecules which have different substituents on each of the two sides of their double bond. For example, in 1-butene there are two hydrogen atoms connected to the first carbon atom which participates in the double bond formation. For this reason such molecule cannot have *cis-* and *trans-* isomers.



Figure 14. Structural formulas of 2-*cis*-butene and 2-*trans*-butene

Electron orbitals of carbon atoms connected by the double bond should be in the  $sp^2$  hybridization state. For these reason two carbon atoms and the four substituents connected to them are situated in the same plane. The angle between two bonds at the carbon atom making a double bond is equal to  $120^\circ$ .

### STRUCTURE AND NOMENCLATURE OF DIENES

**Diene** is a hydrocarbon that contains two double bonds between carbon atoms. Conjugated dienes are widely used as monomers in the polymer industry.

Dienes can be divided into three classes, depending on the relative location of the double bonds:

1. **Cumulated dienes** have the double bonds sharing a common atom.
2. **Conjugated dienes** have conjugated double bonds separated by one single bond (figure 15).

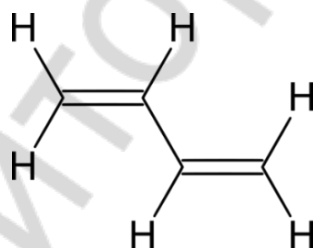


Figure 15. Structural formula of 1,3-butadiene

3. **Unconjugated dienes** have the double bonds separated by two or more single bonds. They are usually less stable than isomeric conjugated dienes.

Compounds that contain more than two double bonds are called polyenes. Polyenes and dienes share many of their chemical properties.

### STRUCTURE AND NOMENCLATURE OF ALKYNES

**Alkynes**, hydrocarbons with a  $C\equiv C$  triple bond, are named similarly to alkenes except their names end in *-yne*. The smallest alkyne is ethyne (figure 16), which is also known as acetylene:

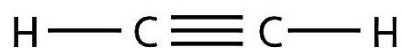


Figure 16. Structural formula of ethyne (acetylene)

Propyne has the structure shown in figure 17.

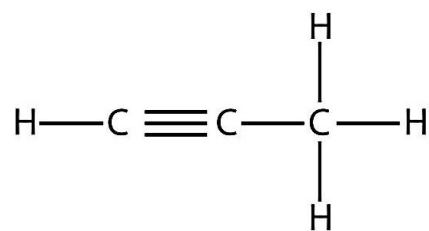


Figure 17. Structural formula of propyne

With butyne, we need to start numbering the position of the triple bond (figure 18), just as we did with alkenes.

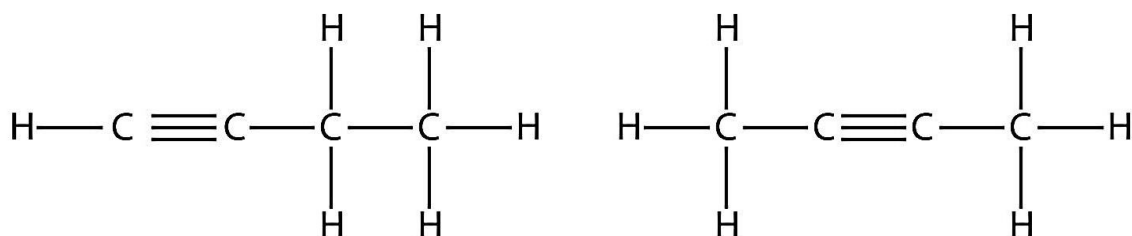


Figure 18. Structural formulas of two isomers of butyne (1-butyne and 2-butyne)

Branched alkenes and alkynes are named in a similar fashion as alkanes. The biggest difference is that when identifying the longest carbon chain, it *must* contain the double or triple bond. Furthermore, when numbering the main chain, the double or triple bond gets the lowest possible number. This means that there may be longer or higher-numbered substituents than may be allowed if the molecule was an alkane. For example, the molecule from figure 19 is 2,4-dimethyl-3-heptene (note the number and the hyphens that indicate the position of the double bond).

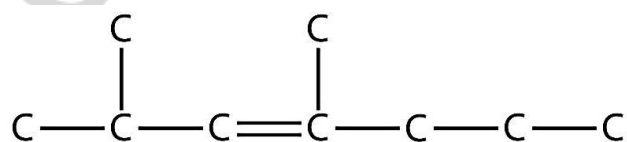


Figure 19. Carbon backbone of 2,4-dimethyl-3-heptene (hydrogen atoms are not shown)

The longest chain of the molecule from figure 20 containing the  $\text{C} \equiv \text{C}$  triple bond has six C atoms, so this is a hexyne molecule. The triple bond starts at the third C atom, so this is a 3-hexyne. Finally, there are two methyl groups on the chain; to give them the lowest possible number, we number the chain from the left side, giving

the methyl groups the second position. So the name of this molecule is 2,2-dimethyl-3-hexyne.

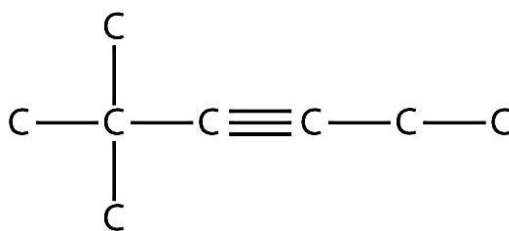


Figure 20. Carbon backbone of 2,2-dimethyl-3-hexyne (hydrogen atoms are not shown)

Electron orbitals of carbon atoms forming the triple bond are in the  $sp^1$  hybridization state. Because of this, the angle between two bonds of a carbon atom making a triple bond is equal to  $180^\circ$ . Two atoms making a triple bond, and two substituents at them are forming a linear fragment of a molecule. The length of a triple bond is just 10.45 % shorter (0.120 nm) than the length of a double bond (0.134 nm) between two carbon atoms.

#### EXERCISES FOR CLASSWORK

1. Draw structures of all the isomers (including interclass ones) of pentene:

2. Draw structures of all the isomers (including interclass ones) of hexene:

3. Draw structures of the following compounds:

5-methyl-trans-2-hexene

3-methyl-1-pentyne

3,4-dimethyl-cis-3-hexene

1,3-hexadiene

3-ethyl-4-methyl-3-heptene

5,5-diethyl-1,3-octadiene

3,4-diethyl-1-hexyne

**4. Are there cis- and trans- isomers for the following compounds? Draw their structures.**

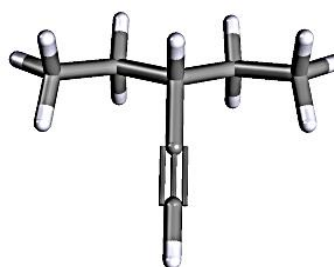
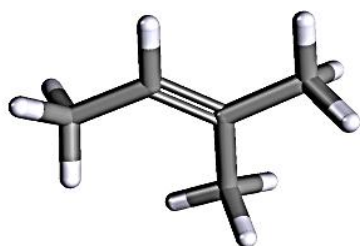
2,3-dimethyl-2-butene

1-butene

2-methyl-2-butene

2-hexene

**5. Name the following compounds:**





## EXERCISES FOR HOMEWORK

1. Draw structures of all the isomers (including interclass ones) of 1,3-butadiene:

2. Draw structures of all the isomers (including interclass ones) of heptyne:

3. Draw structures of the following compounds:

2-methyl-2-pentene

3-ethyl-4-octyne

4,4-dimethyl-cis-2-pentene

2-methyl-1,3-butadiene

1,3,7-heptatriene

6,7-dimethyl-2-octene

cyclohexene

**4. Are there cis- and trans- isomers for the following compounds? Draw their structures.**

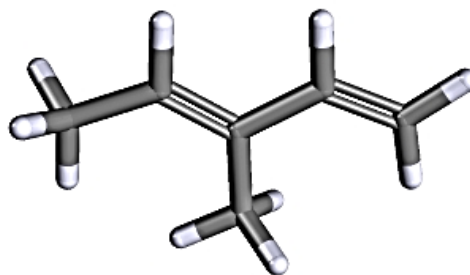
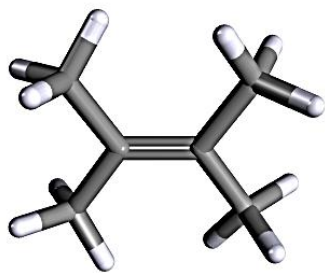
3,4-dimethyl-3-hexene

3,4-dimethyl-2-hexene

3,4-dimethyl-1-hexene

3-ethyl-2-pentene

**5. Name the following compounds:**



## LESSON 3. PROPERTIES OF UNSATURATED HYDROCARBONS

### CHEMICAL PROPERTIES OF UNSATURATED HYDROCARBONS

Halogens can react with alkenes and alkynes. The halogen reacts with the double or triple bond and inserts itself onto each C atom involved in the multiple bonds. This reaction is called an **addition reaction**. One example is given in figure 21.

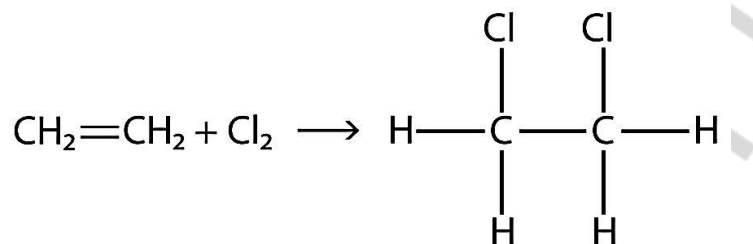
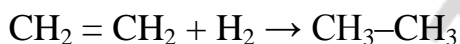


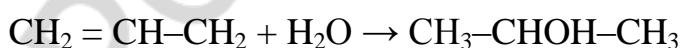
Figure 21. Reaction between ethene and chlorine

The reaction conditions are usually mild; in many cases, the halogen reacts spontaneously with an alkene or an alkyne.

Hydrogen can also be added across a multiple bond; this reaction is called a hydrogenation reaction. In this case, however, the reaction conditions may not be mild; high pressures of  $\text{H}_2$  gas may be necessary. A platinum or palladium catalyst is usually employed to get the reaction to proceed.



Hydrogen chloride, hydrogen bromide, hydrogen iodide and water can also participate in addition reactions with alkenes, dienes and alkynes. In those reactions a hydrogen atom from an inorganic compound more frequently goes to that carbon atom which already has a higher number of hydrogen atoms, while halogen atom or  $-\text{OH}$  group goes to the less hydrogenated carbon atom. So, among products of the reaction between propene and  $\text{HCl}$  the mass percentage of 2-chloropropane is higher than that of 1-chloropropane.

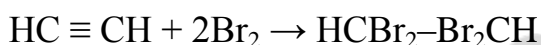


The rule described above is explained well by the mechanism of such reaction that is known as “electrophilic addition”. For example,  $\text{HCl}$  molecule is polar: hydrogen atom has a partial positive charge, and so it is an electrophile (it seeks for

electrons). Electrons from carbon atoms that make a double bond are good targets for electrophiles. So, hydrogen gains a pair of electrons from carbon (or better to say from both carbons making a double bond). After that event the bond between hydrogen and chlorine breaks down (the pair of electrons goes to chlorine), and the anion of chlorine is formed. That anion makes a dative bond with another carbon atom that has just acquired a positive charge.

Carbon atoms are more electronegative than hydrogen atoms. Because of this, electrons are situated closer to carbon atoms than to hydrogen atoms. The higher the number of hydrogens connected to carbon atom, the higher the magnitude of its partial negative charge. In other words, carbon from “CH<sub>2</sub>=” group is more negatively charged than carbon from “=CH-” group. Because of this reason electrophiles attack that more negatively charged carbon atom more frequently than they attack its less negatively charged partner.

Reaction with bromine water (intense yellow mixture containing diatomic bromine — Br<sub>2</sub> — of 2.8 % by mass dissolved in H<sub>2</sub>O) is used to determine the presence of alkenes, dienes or alkynes. Bromine water becomes colorless after the reaction with hydrocarbons containing double or triple bonds.



The same reaction of the addition of a bromine is possible in another solvent, such as CCl<sub>4</sub>. In the last case bromine cannot react with its solvent.

Alkynes react with water in a special manner in the presence of a catalyst. At first an unstable substance with double bond and hydroxyl group is formed. Then it becomes a more stable aldehyde (in case of acetylene hydration) or ketone molecule.



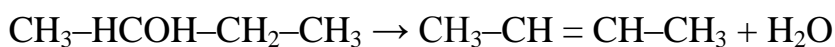
## PRODUCTION OF ALKENES, DIENES AND ALKYNES

Double bond may be formed in a saturated hydrocarbon in the *dehydrogenation* reaction.

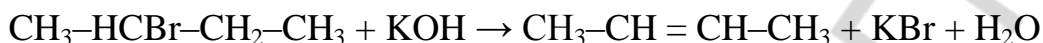


*Dehydration* is a reaction in which a water molecule is taken away from alcohols. As a result, a double bond forms. A hydrogen atom from the less hydrogenated carbon atom more frequently participates in water molecule formation together with -OH group. To perform a dehydration one needs to use high

temperature ( $t^\circ > 170\text{ }^\circ\text{C}$ ) and concentrated sulfuric acid as a substance that provides  $\text{H}^+$  cations that bind  $-\text{OH}$  groups. After such protonation event water molecule leaves the hydrocarbon. Then hydrogen atom preferably from the less hydrogenated carbon is taken away by the anion of an acid, and a double bond is formed.



In a similar way hydrogen chloride or hydrogen bromide may be taken away from alkyl chloride or alkyl bromide, respectively. To perform that reaction one needs to use alkali in the solution of alcohol.



This kind of reaction is known as elimination reaction. The mechanism of this reaction includes the formation of dative bond between  $\text{OH}^-$  anion and hydrogen atom from alkyl halide. As a result, hydrogen cation (i.e. the proton) is taken away from the alkyl halide. After this event the bond between halogen and carbon polarizes and finally halide anion leaves the molecule of hydrocarbon. The last one turns to alkene. Once again, the less hydrogenated carbon atom loses its hydrogen more frequently than more hydrogenated one. One of the reasons for this asymmetry is in the fact that negatively charged particles are getting closer to the less negatively charged carbon and its hydrogens than to the more negatively charged one.

1,3-butadiene can be produced from ethanol (two ethanol molecules form a single 1,3-butadiene molecule, while hydrogen gas and water are taken away).

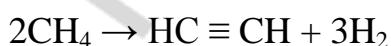


Acetylene can be produced in a hydrolysis reaction: between calcium carbide (an inorganic compound) and water.



This reaction is nothing but a hydrolysis reaction of a special kind of salt. Interestingly, acetylene shows a weak acidic activity. So, calcium carbide can be described as a salt of acetylene.

Acetylene can also be produced from methane by the way of partial thermal decomposition in the absence of oxygen. Notice that one needs to control temperature and pressure in this process to produce mostly acetylene and not ethylene.



**EXERCISES FOR CLASSWORK**

**1. Draw the structure of the product of the reaction of bromine with propene.**

**2. Draw the structure of the product of the reaction of chlorine with 2-butene.**

**3. What volume is occupied by 33 g of ethylene in normal conditions?**

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**4. Determine the volume of acetylene which can be produced from 1 kg of calcium carbide containing 30 % of impurities.**

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**5. The mixture of methane and acetylene had a volume of 6 L. That mixture has been passed through the bromine water solution. The mass of the system increased by 5 g. Find the volume percentage of methane in the initial mixture.**

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6. A mixture of ethane and acetylene has been passed through the bromine water. The mass of a glass with bromine water solution became 1.3 g higher. The same mixture of gases has been burned down. The volume of carbon dioxide was equal to 14 liters. What was the volume of the mixture of gases?

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7. The mixture of propane and propyne had a volume of 6 L (in normal conditions). The mixture reacted with 1.2 L of hydrogen. Calculate the volume percentage of propane in the initial mixture if it contains just a single substance.

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8. 9.375 g of a hydrocarbon reacted with 5 L of hydrogen up to the complete saturation and produced 5 L of an alkane. Find the formula of that compound.

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9. What is the volume of vinyl chloride produced in the following chain of chemical reactions:  $\text{CH}_4 \rightarrow \text{C}_2\text{H}_2 \rightarrow \text{CH}_2=\text{CHCl}$  from 2000 liters of gas containing 98 % of methane. The yield for the first step of the process is equal to 86 %. The yield of the second step is equal to 78 %.

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**10. There is a mixture of ethene, propyne and propadiene. 2 L of that mixture reacted with 3.5 L of hydrogen until the complete saturation. Find the volume percentage of ethene in the mixture.**

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**EXERCISES FOR HOMEWORK**

**1. Draw the structure of the product of the reaction of hydrogen with 1-butene.**

**2. Draw the structure of the product of the reaction of hydrogen with 2-pentene.**

**3. How many molecules are there in 13 L of propylene in normal conditions?**

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**4. Determine the volume of methane which can be produced from 1 kg of aluminum carbide containing 12 % of impurities.**

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5. A mixture of methane and ethylene had a volume of 8 liters. 100 liters of the air required to burn that mixture completely. Determine the volume percentage of methane in that mixture of gases.

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6. The mixture of propane and propene had a volume of 8 L. That mixture has been passed through the bromine water solution. The mass of the system increased by 3 g. Find the volume percentage of propane in the initial mixture.

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7. The mixture of butane and ethene had a volume of 3 L (in normal conditions). The mixture reacted with 1.4 g of hydrogen chloride. Calculate the volume percentage of butane in the initial mixture.

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8. 2 L of an alkene added 7.2321 g of hydrogen bromide and produced 10.9821 g of an alkyl bromide. Find the formula of that alkene.

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9. What is the volume of vinyl fluoride produced in the following chain of chemical reactions:  $C_2H_6 \rightarrow C_2H_2 \rightarrow CH_2=CHF$  from 1000 liters of gas containing 88 % of ethane. The yield for the first step of the process is equal to 75 %. The yield of the second step is equal to 66 %.

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10. There is a mixture of propene, butyne and 1,3-butadiene. 2 L of that mixture reacted with 21.429 g of bromine until the complete saturation. Find the volume percentage of propene in the mixture.

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## LESSON 4. POLYMERIZATION OF HYDROCARBONS

### POLYMERIZATION OF ALKENES

Among other applications, organic chemistry has had a huge impact on the development of modern materials called polymers.

For example, ethylene (figure 22) has a double bond.

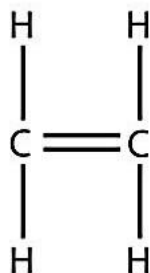


Figure 22. Structural formula of ethene (ethylene)

That double bond between the carbons can be opened up and attack another ethylene molecule (figure 23).

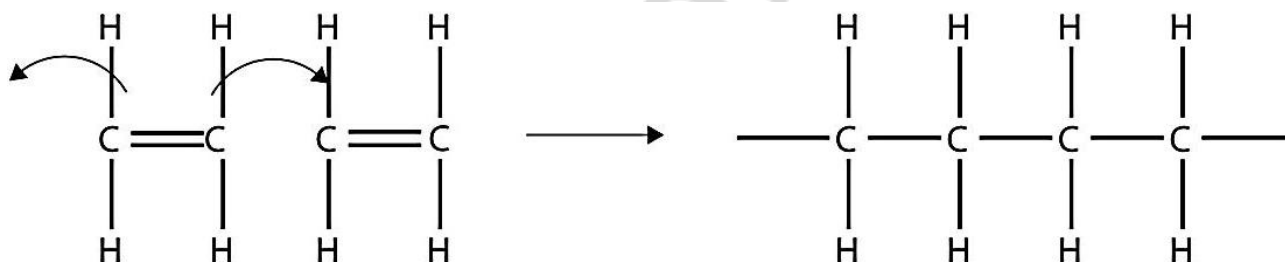


Figure 23. Polymerization of ethene

Then the second ethylene molecule's double bond opens up and attacks a third ethylene molecule, which also opens up its double bond and attacks a fourth ethylene molecule, and so forth. The final result is a long, virtually endless molecule of polyethylene (figure 24).

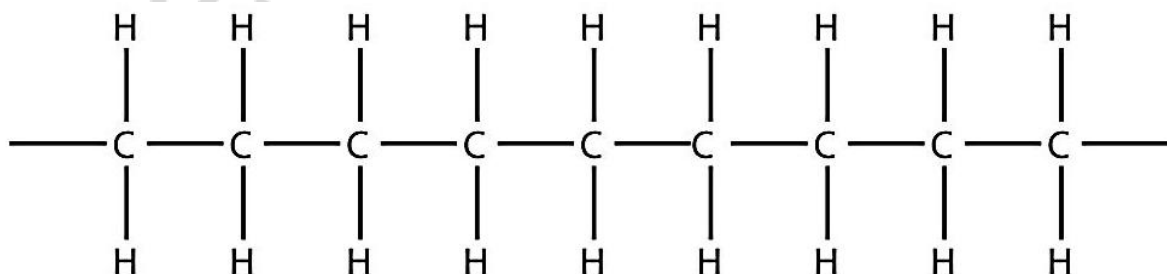


Figure 24. Structural formula of polyethylene fragment

This long, almost endless molecule is called a polymer (from the Greek word meaning “something made from many similar parts”). The part of the chain that is left from the original small molecule — ethylene — is called a monomer. Monomer means “one subunit of something made from many similar parts”. The process of making a polymer is called **polymerization**. A polymer is an example of a *macromolecule*, the name given to a large molecule.

Simple polymers are named after their monomers; the ethylene polymer is called polyethylene.

Yet another commonly used polymer is called polyvinylchloride (figure 25).

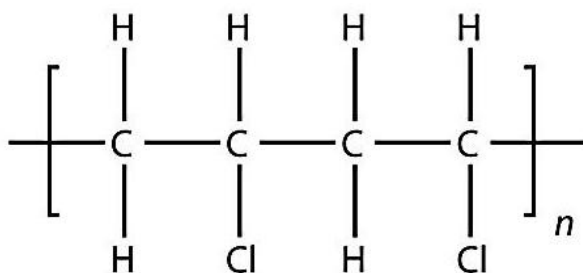


Figure 25. Structural formula of polyvinylchloride fragment

It is a product of ethylene chloride (figure 26) polymerization.

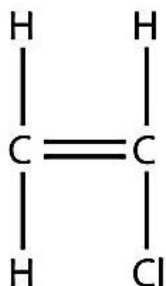


Figure 26. Structural formula of vinyl chloride

## POLYMERIZATION OF DIENES

The shortest possible diene (1,3-butadiene) also forms polymers.

Butadiene can polymerize in three different ways, called *cis*, *trans* and *vinyl*. The *cis* and *trans* forms arise by connecting the butadiene molecules in the end-to-end manner, so-called 1,4-polymerisation. The properties of the resulting isomeric forms of polybutadiene differ. For example, “high *cis*”-polybutadiene has a high elasticity and is very popular as a synthetic rubber, whereas the so-called “high *trans*”-polybutadiene is a plastic crystal with just a few useful applications. The *vinyl*

content of polybutadiene is typically no more than a few percent (such bonds make cross-links of different long polybutadiene chains). In addition to these three kinds of connectivity (figure 27), polybutadienes differ in terms of their branching and molecular weights.

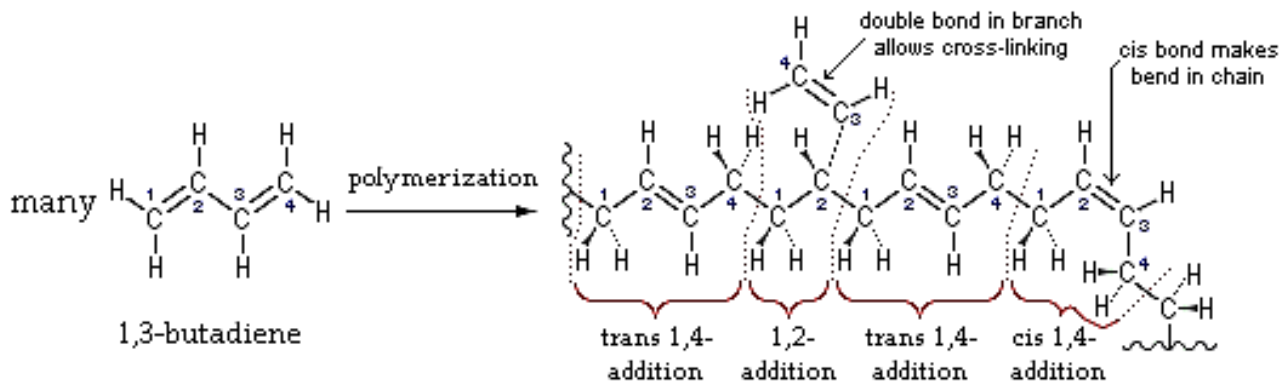


Figure 27. 1,3-butadiene polymerization

Natural rubber (figure 28) consists of isoprene (2-methyl-1,3-butadiene) and not butadiene-1,3.

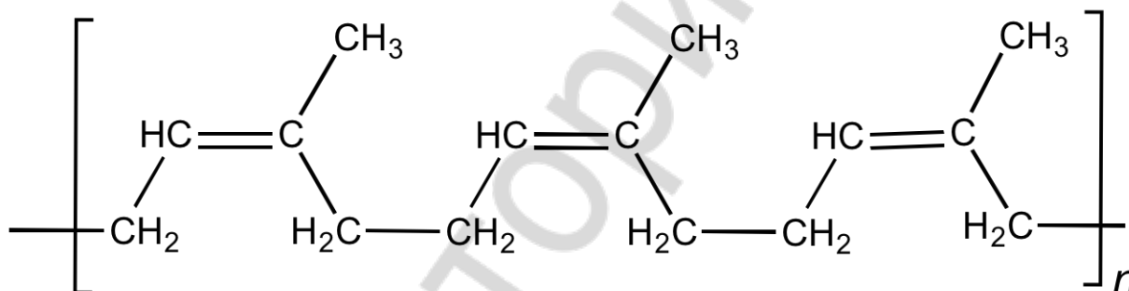
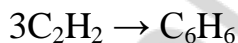


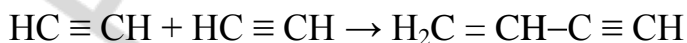
Figure 28. Structure of the cis-polyisoprene fragment

## POLYMERIZATION OF ALKYNES

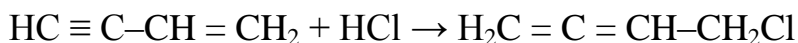
Acetylene polymerization may produce benzene molecules. This process requires three acetylene molecule and so it is called trimerization.



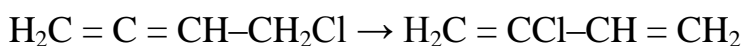
Acetylene molecules can also be dimerized. The product contains one single, one double and one triple bond. The name of that compound is vinylacetylene.



In one of the ways of synthetic rubber production vinylacetylene is used. It is combined with hydrogen chloride to produce 4-chloro-1,2-butadiene.



Then 4-chloro-1,2-butadiene (chloroprene) rearranges to the 2-chlorobuta-1,3-diene in the presence of a catalyst.



Chloroprene can be polymerized in the similar manner to the isoprene.

### EXERCISES FOR CLASSWORK

1. Write four reactions with organic compounds according to the chain of chemical reactions  $\text{Al}_4\text{C}_3 \xrightarrow{\text{H}_2\text{O}} \text{A} \xrightarrow{+1\text{Cl}_2} \text{B} \xrightarrow{+2\text{K}} \text{C} \xrightarrow{+1\text{Br}_2} \text{D}$

1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

2. Write four reactions according to the following classic chain of chemical reactions and balance them:



1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

**Draw structures of stereoisomers for 2-butene:**

3. Write four reactions according to the following classic chain of chemical reactions and balance them:



1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

4. Calculate the volume of 1,3-butadiene that is needed to make 200 g of polybutadiene.

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5. Calculate the number of monomers in 100 g of polyethylene.

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6. Find the mass of chlorine in 500 g of polyvinylchloride.

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7. Calculate the mass of acetylene that is needed to produce 1 kg of polyvinylchloride if the total yield of the process is equal to 80 %. How many steps are required for this process?

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EXERCISES FOR HOMEWORK

1. Write four reactions with organic compounds according to the chain of chemical reactions  $\text{CaC}_2 \xrightarrow{+ \text{H}_2\text{O}} \text{A} \xrightarrow{+ 1\text{H}_2} \text{B} \xrightarrow{+ \text{HCl}} \text{C} \xrightarrow{+ \text{Na}} \text{D}$

1. \_\_\_\_\_

2. \_\_\_\_\_

3. \_\_\_\_\_

4. \_\_\_\_\_

- 2. Write four reactions according to the following classic chain of chemical reactions and balance them:**

decane → pentane → 1-pentene → 2-chloropentane → 4,5-dimethyloctane

1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

**Draw the structure of the last compound:**

- 3. Write four reactions according to the following classic chain of chemical reactions and balance them:**

ethane → ethylchloride → ethene → polyethylene → carbon dioxide

1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

- 4. Calculate the volume of ethylene that is needed to make 300 g of polyethylene.**

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- 5. Calculate the number of monomers in 150 g of natural rubber.**

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**6. Find the mass of chlorine in 400 g of polychloroprene.**

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**7. Calculate the mass of ethanol required for the synthesis of 5 kg of poly-1,3-butadiene. The total yield of the process equals to 70 %.**

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РЕПОЗИТОРИЙ БГМУ

## LESSON 5. ARENES

### STRUCTURE OF AROMATIC HYDROCARBONS

Aromatic hydrocarbons (arenes) have a specific six-carbon ring called a *benzene* ring. The term “aromatic” was assigned before the physical mechanism determining aromaticity was discovered, and was derived from the fact that many of the compounds have a sweet scent. Electrons in the benzene ring form a common  $\pi$ -system that gives benzene physical and chemical properties that are markedly different from alkanes and alkenes. In modern chemistry the term *aromatic* denotes the presence of at least one ring with a  $\pi$ -system that imparts different and unique properties to a molecule. Aromatic hydrocarbons can be monocyclic or polycyclic.

Some non-benzene-based compounds called heteroarenes. In these compounds, at least one carbon atom is replaced by one of the heteroatoms: oxygen, nitrogen, or sulfur. Examples of non-benzene compounds with aromatic properties are furan, a heterocyclic compound with a five-membered ring that includes an oxygen atom, and pyridine, a heterocyclic compound with a six-membered ring containing one nitrogen atom.

The most of aromatic compounds contain the benzene unit. Benzene itself is composed of six C atoms in a ring, with alternating single and double bonds (figure 29).

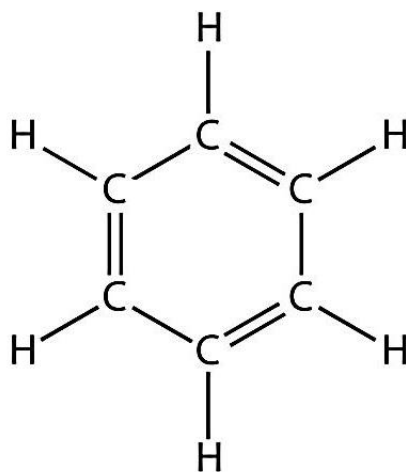


Figure 29. Structural formula of benzene with 3 double and 3 single bonds

The alternating single (C–C) and double (C=C) bonds give the benzene ring stability, and it does not react like an alkene as might be suspected. Benzene has the molecular formula  $C_6H_6$ ; in larger aromatic compounds, a different atom replaces

one or more of the H atoms. The common formula for arenes is  $C_nH_{2n-6}$ . It is obvious, that “n” should not be less than 6 in this common formula.

Each carbon atom in the hexagonal cycle has four electrons to share. One goes to the hydrogen atom, and each of two others goes to the two neighboring carbons. This leaves one electron to share with one of its two neighboring carbon atoms (this fact supports the representation of benzene molecule with alternating single and double bonds around the hexagon). The structure is also illustrated as a circle around the inside of the ring to show six electrons floating around in delocalized molecular orbitals the size of the ring itself. This also represents the equivalent nature of the six carbon-carbon bonds, each of which has the same bond order of 1.5 (figure 30). This equivalency is well explained by resonance forms. The electrons are visualized as floating above and below the ring with the electromagnetic fields they generate acting to keep the ring flat (figure 31). Each carbon atom in the benzene ring has its electron orbitals in the  $sp^2$  hybridization state. It means that the angles between bonds for those carbon atoms are equal to  $120^\circ$ . Moreover, not just 6 carbon atoms from the ring, but also the atoms directly connected to each of them are in the same plane.

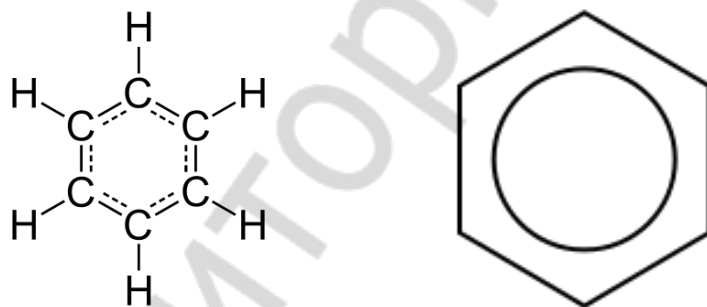


Figure 30. Structural formula of benzene with 1.5 bonds and aromatic ring

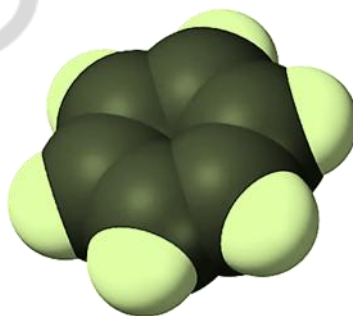


Figure 31. 3D structure of benzene

Indeed, the distance between two carbons connected by a single bond is equal to 0.154 nm. The distance between two carbons connected by a double bond is equal to 0.134 nm. All the distances between carbon atoms in benzene ring are equal to 0.14 nm.

Naming substituted benzene molecules is straightforward. If there is only one substituent, the substituent is named as a side chain on a benzene molecule, like it is shown in figure 32.

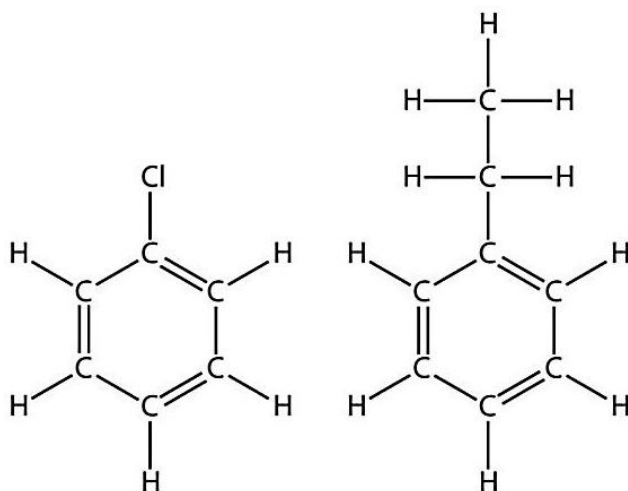


Figure 32. Structural formulas of chlorobenzene and ethylbenzene

If there are two or more substituents on a benzene molecule (figure 33), the relative positions must be numbered, just like an aliphatic chain of C atoms is numbered. The substituent that is first alphabetically is assigned position 1, and the ring is numbered in a circle to give the other substituents the lowest possible number(s).

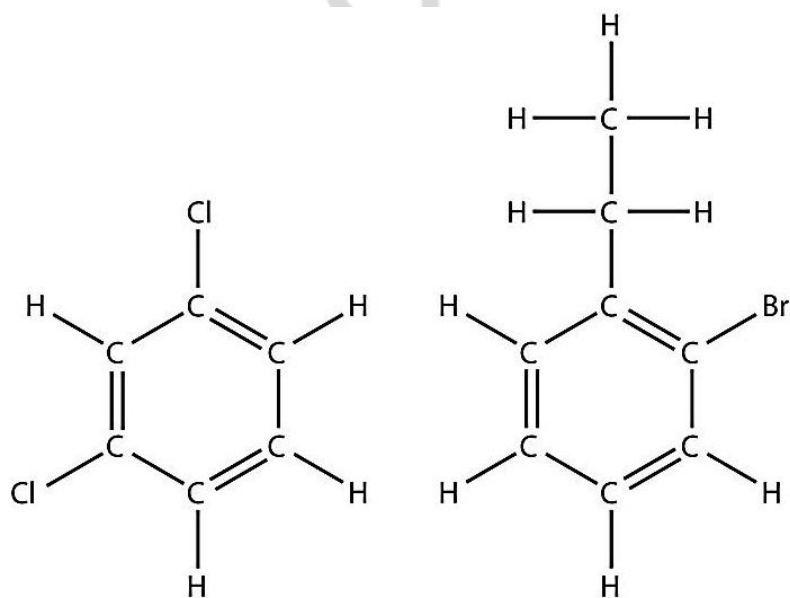


Figure 33. Structural formulas of 1,3-dichlorobenzene and 1-bromo-2-ethylbenzene

If a benzene ring is treated as a substituent, it is given the name *phenyl*-. The following molecule is 3-phenylpentane where the H atoms have been omitted for clarity (figure 34).

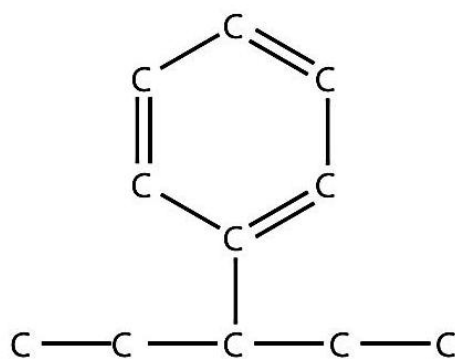


Figure 34. Carbon backbone of 3-phenylpentane (hydrogen atoms are not shown)

For identical substituents such prefixes as *ortho*-, *meta*- and *para*- are used. A compound that consists from benzene ring and two methyl substituents is called xylene. As one can see in figure 35 there are three isomers of xylene: *ortho*-, *meta*-, and *para*-xylene.

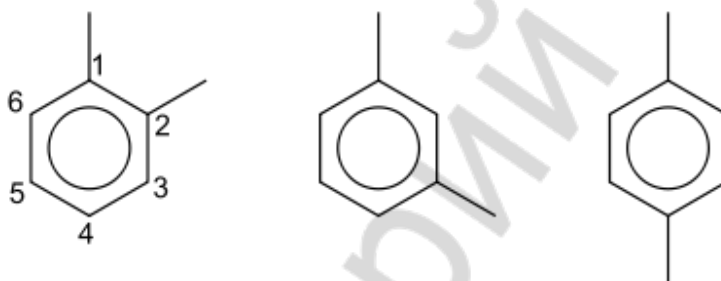
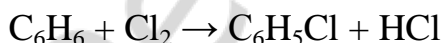


Figure 35. Schemes of 1,2-dimethylbenzene (*ortho*-xylene), 1,3-dimethylbenzene (*meta*-xylene), 1,4-dimethylbenzene (*para*-xylene)

Toluene (toluol) is a compound that consists from benzene ring and a single methyl substituent. Obviously, toluene has no isomers.

## CHEMICAL PROPERTIES OF ARENES

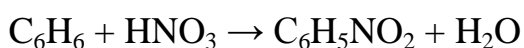
Aromatic hydrocarbons are prone to substitution reactions, in which one substituent on the arene ring (hydrogen) is replaced by another substituent (just like in case with alkanes).



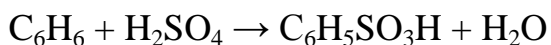
This reaction requires a catalyst like  $\text{FeCl}_3$ , while in water or  $\text{CCl}_4$  solution benzene does not react with halogens.

The mechanism of such substitution in arenes is different from the mechanism of substitution in alkanes. A special name for such reaction is the “electrophilic substitution”. Since the benzene ring is enriched by electrons (that make a  $\pi$ -system),

particles that are “seeking” for electrons (electrophiles) are attracted to it. Both cations and atoms with partial positive charge can play that role. In general, in the first step, a cation or a partially positively charged atom gains two electrons from benzene ring and forms a covalent dative bond with it. The intermediate of the reaction contains partially broken  $\pi$ -system, and the hydrogen atom that is still bound to the carbon atom that has been attacked by electrophile. The second step includes the addition of the proton of that hydrogen to the anion (if there was an electrophilic cation) or to the electronegative atom of the same molecule (if there was a molecule with electrophilic atom). As a result, the  $\pi$ -ring is reconstructed with the remaining pair of electrons. The main cause of this mechanism of a process is the stability of  $\pi$ -ring.

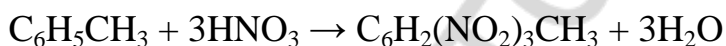


This reaction (nitration) requires the presence of concentrated sulfuric acid.



Concentrated sulfuric acid itself can also react with benzene. The higher its concentration, the faster the rate of this reaction.

Toluene (methylbenzene) is more reactive than benzene. Three hydrogen atoms can be replaced in the reactions with halogens (in  $\text{CCl}_4$ , and not in water), nitric and sulfuric acids.



Resulting compound (2,4,6-trinitrotoluene known as “TNT”) is an explosive material (figure 36).

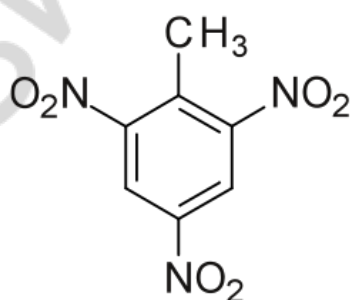
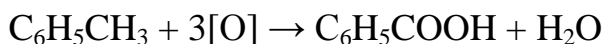


Figure 36. Structural formula of 2,4,6-trinitrotoluene

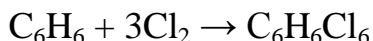
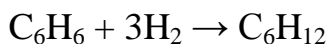
In the reaction between toluene and potassium permanganate in the presence of sulfuric acid methyl group will be the target, and not hydrogen atoms from the ring. As a result of oxidation, benzoic acid will be formed.



In organic chemistry they usually ignore inorganic substances. So, the same process can be written like this.



In special conditions (at high temperature under the influence of light) arenes are able to participate in addition reactions (just like alkenes and alkynes).

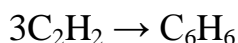


## PRODUCTION OF ARENES

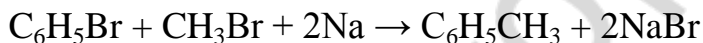
Benzene can be produced either from hexane or from cyclohexane in the dehydrogenation reaction.



It also can be produced from acetylene in trimerization reaction.



Substituents can be introduced into the aromatic ring in reactions between subsequent halides and active metals.



## TEST FOR CLASSWORK

- Which reactant can be used to distinguish unsaturated hydrocarbons from saturated ones?
  - Tollen's reagent
  - Fehling's solution
  - bromine water
  - silver nitrate
- Choose the common formula for alkenes and cyclic alkanes:
  - $\text{C}_n\text{H}_{2n-2}$
  - $\text{C}_n\text{H}_{2n}$
  - $\text{C}_n\text{H}_{2n+2}$
  - $\text{C}_n\text{H}_{2n-6}$
- Are there cis- and trans- isomers for 1-butene and 2-butene, respectively?
  - yes / no
  - no / yes
  - yes / yes
  - no / no
- Choose the product of acetylene trimerization:
  - vinyl acetylene
  - benzene
  - methane
  - toluene

5. Choose the most abundant product of propene reaction with HCl:
  - a) 1-chloropropane
  - b) 2-chloropropane
  - c) propyne
  - d) propane
6. Describe the type of chemical reaction between  $C_2H_4$  and  $Br_2$ :
  - a) addition
  - b) substitution
  - c) decomposition
  - d) composition
7. Choose the formula of polyvinylchloride:
  - a)  $[-CHCl=CH_2-]_n$
  - b)  $[-CH_2-CH_2-]_n$
  - c)  $[-CHCl-CH_2-]_n$
  - d)  $[-CHCl=CHCl-]_n$
8. Calculate the sum of all coefficients in the redox reaction:  $C_5H_{10} + O_2 \rightarrow CO_2 + H_2O$ 
  - a) 17
  - b) 20
  - c) 37
  - d) 48
9. Choose the hybridization state of outer shell electron orbitals in carbon atoms from benzene:
  - a) sp
  - b)  $sp^2$
  - c)  $sp^3$
  - d) no hybridization
10. What type of compound is produced in alkene hydration reaction?
  - a) alkane
  - b) diene
  - c) aldehyde
  - d) alcohol

#### TEST FOR HOMEWORK

1. Choose formulas of benzene homologs (arenes)?
  - a)  $C_6H_6$
  - b)  $C_8H_{10}$
  - c)  $C_8H_{18}$
  - d)  $C_2H_2$
2. Choose the common formula for alkynes and dienes:
  - a)  $C_nH_{2n-2}$
  - b)  $C_nH_{2n}$
  - c)  $C_nH_{2n+2}$
  - d)  $C_nH_{2n-6}$
3. Are there cis- and trans- isomers for 2-pentene and 2-pentyne, respectively?
  - a) yes / no
  - b) no / yes
  - c) yes / yes
  - d) no / no
4. Choose the product of acetylene dimerization:
  - a) toluene
  - b) benzene
  - c) methane
  - d) vinyl acetylene
5. Choose the product of 2-propanol dehydration at temperature higher than  $170^\circ C$  in the presence of  $H_2SO_4$ :
  - a) propene
  - b) 1-butene
  - c) 2-propyne
  - d) propane



6. Describe the type of chemical reaction between  $C_2H_2$  and  $H_2O$ :
- a) addition                      c) composition  
b) redox reaction              d) one step reaction
7. Choose the formula of polyethylene:
- a)  $[-CHCl=CH_2-]_n$       c)  $[-CHCl-CH_2-]_n$   
b)  $[-CH_2-CH_2-]_n$         d)  $[-CHCl=CHCl-]_n$
8. Calculate the sum of all coefficients in the redox reaction:  $C_4H_6 + O_2 \rightarrow CO_2 + H_2O$
- a) 13            b) 14            c) 27            d) 30
9. Choose correct statements about benzene molecule:
- a) it is prone to substitution reactions more than to addition reactions  
b) it is prone to addition reactions more than to substitution reactions  
c) three bonds between carbon atoms in the molecule are shorter than three other bonds  
d) lengths of all six bonds between carbon atoms are equal to each other
10. Choose the most abundant product of  $CH_2=CH-CH=CH_2 + H_2$  reaction?  
The molar ration between reactants is 1:1.
- a) 1-butene            b) 2-butene            c) butane            d) 1,2-butadiene

### EXERCISES FOR CLASSWORK

- 1. Write four reactions according to the following classic chain of chemical reactions and balance them:**

methane  $\rightarrow$  acetylene  $\rightarrow$  benzene  $\rightarrow$  cyclohexane  $\rightarrow$  cyclohexene

1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

- 2. Write four reactions according to the following classic chain of chemical reactions and balance them:**

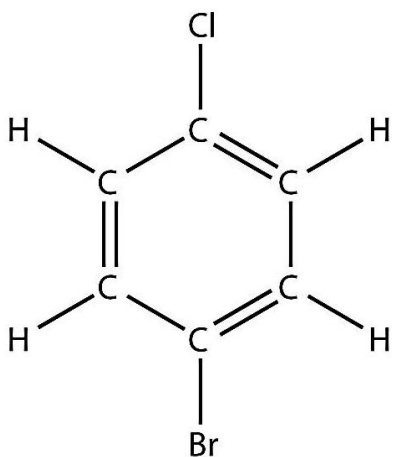
propane  $\rightarrow$  1-bromopropane  $\rightarrow$  hexane  $\rightarrow$  benzene  $\rightarrow$  styrene

1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

**Draw the structural formula for the last compound:**

**3. Draw structures of all isomers for trimethylbenzene and name them:**

**4. Name this molecule**



**5. Find the volume of hydrogen needed for complete saturation of 7 g of benzene.**

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6. Determine the mass of the organic product of the reaction between 15 g of toluene and the excess of bromine.

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7. Calculate the mass of benzene which can be produced from 44.8 L of acetylene. The yield of the reaction is equal to 40 %.

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8. Calculate the volume of oxygen which is required to burn down 34 L of benzene. The density of benzene is 0.89 g/ml.

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9. Calculate the volume of oxygen which is required to burn down a mixture of benzene and toluene. The mass of the mixture is equal to 10 kg. Mass percentage of toluene is 40 %.

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#### EXERCISES FOR HOMEWORK

1. Write four reactions according to the following classic chain of chemical reactions and balance them:

methane → acetylene → benzene → bromobenzene → ethylbenzene

1. 

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2. 

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3. 

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4. 

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2. Write four reactions according to the following classic chain of chemical reactions and balance them:

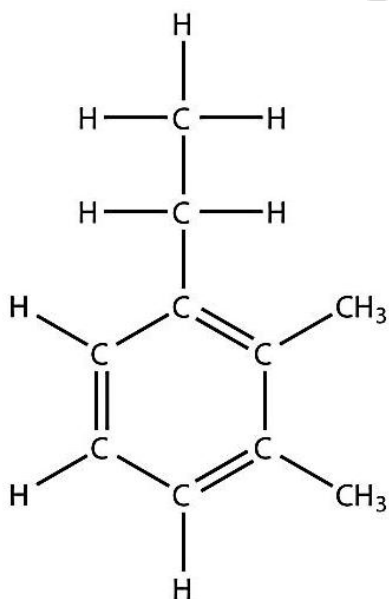
hexane  $\rightarrow$  benzene  $\rightarrow$  chlorobenzene  $\rightarrow$  toluene  $\rightarrow$  trinitrotoluene

1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

Draw the structural formula of the last compound:

3. Draw structures of all isomers for dichlorobenzene and name them:

4. Name this molecule



**5. Find the volume of chlorine gas (in normal conditions) needed for complete saturation of 9 g of benzene (up to hexachlorocyclohexane).**

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**6. 78 g of benzene reacted with bromine. The mass of bromobenzene is equal to 75 g. Determine the yield of the reaction.**

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**7. Calculate the mass of calcium carbide needed to make 100 g of benzene. The yield of the first step is 60 %, the yield of the second step is 75 %.**

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**8. Calculate the volume of air which is required to burn down 15 g of benzene.**

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**9. Calculate the volume of air which is required to burn down a mixture of xylene and toluene. The mass of the mixture is equal to 7 kg. Mass percentage of xylene is 25 %.**

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## LESSON 6. ALCOHOLS AND PHENOLS

### STRUCTURE AND NOMENCLATURE OF ALCOHOLS AND PHENOLS

An alcohol is an organic compound in which the hydroxyl functional group (-OH) is bound to an aliphatic carbon atom.

Simple acyclic alcohols have the general formula of  $C_nH_{2n+1}OH$ . In common speech the word alcohol refers specifically to ethanol ( $C_2H_5OH$ ).

Hydroxyl group can be linked to aromatic ring. The simplest compound formed by aromatic ring and hydroxyl group (phenol) has a formula of  $C_6H_5OH$ . It is important to highlight that phenol is not classified as an alcohol. In contrast, if -OH group is attached to any carbon atom that is not included in aromatic ring, but the molecule itself contains an aromatic ring, the compound is classified as an aromatic alcohol.

Hydroxyl group of alcohols cannot form the hydroxide ion; rather than being present as a negatively charged species, in organic chemistry it is a covalently bonded functional group.

Alcohols have a common naming system and a more formal system. The common system is similar to that of alkyl halides: name the alkyl group attached to the -OH group, ending with the suffix *-yl*, and add the word *alcohol* as a second word. So  $CH_3-OH$  is methyl alcohol;  $CH_3-CH_2-OH$  is ethyl alcohol, and  $CH_3-CH_2-CH_2-OH$  is propyl alcohol.

The formal system of naming uses the name of the hydrocarbon containing the -OH group and having the correct number of C atoms, dropping the final *-e* of the name and appending the suffix *-ol*. Thus  $CH_3-OH$  is methanol and  $CH_3-CH_2-OH$  is ethanol. For larger alcohol molecules, we use a number to indicate the position of the -OH group on the longest carbon chain, similar to the number needed for alkenes and alkynes. Again, the carbon chain is numbered to give the -OH group the lowest number, no matter how large the other numbers are. So,  $CH_3-CH_2-CH_2-OH$  is 1-propanol, while  $CH_3-CHOH-CH_3$  is 2-propanol.

If a carbon atom is connected to just one other carbon atom, it is called “primary” carbon atom; if it is connected to two other carbon atoms it is “secondary” carbon atom; if it is connected to three other carbon atoms, it is “tertiary” carbon atom; if it is connected to four other carbons, it is “quaternary” carbon atom.

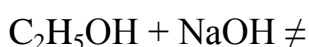
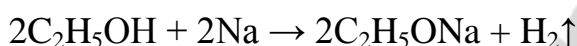
So, if –OH group is connected to primary carbon atom, the alcohol is primary; if –OH group is connected to secondary carbon atom, the alcohol is secondary; if –OH group is connected to tertiary carbon atom, the alcohol is tertiary.

Another acceptable way of naming an alcohol — especially a more complicated molecule — is to name the –OH group as the hydroxyl substituent and give it a numerical position like an alkyl group or a halogen atom. Thus 2-propanol would be called 2-hydroxypropane by this convention.

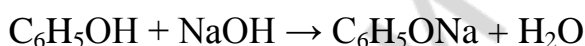
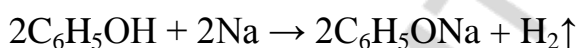
Small alcohols are highly soluble in H<sub>2</sub>O because these molecules can engage in hydrogen bonding with H<sub>2</sub>O molecules. For larger molecules, however, the polar –OH group is overwhelmed by the nonpolar alkyl part of the molecule. While methanol is soluble in H<sub>2</sub>O in all proportions, only about 2.6 g of pentanol will dissolve in 100 g of H<sub>2</sub>O. Larger alcohols have an even lower solubility in H<sub>2</sub>O.

## CHEMICAL PROPERTIES OF ALCOHOLS AND PHENOLS

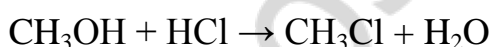
Acyclic alcohols can react with active metals, but cannot react with alkali.



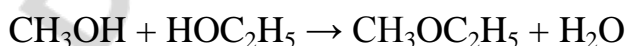
However, phenol is able to react with both active metals and alkali, since it shows acidic properties (even though they are very weak).



Alcohols are able to react with hydrogen chloride, bromide and iodide and form alkyl halides.



Two molecules of alcohol can react with each other and form ethers. This process requires the presence of sulfuric acid (as the provider of H<sup>+</sup> cations that catalyze the whole process and as the substance binding water and causing the shift towards products) and the temperature below 140 °C.

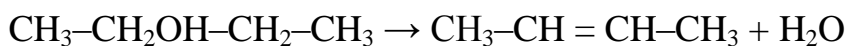


Alcohols participate in elimination reactions: the removal of the functional group (including –OH group) and an H atom from an adjacent carbon. That reaction also requires sulfuric acid, but the temperature for this process should be higher than

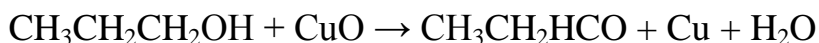
that for ether formation ( $t^\circ > 140^\circ\text{C}$ ). At the higher temperature ( $t > 170^\circ\text{C}$ ) there will be just alkene as a product.



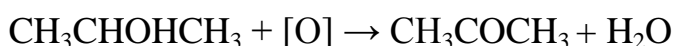
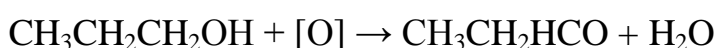
Notice that hydrogen atom in the dehydration process will be taken from the less hydrogenated carbon atom at a higher frequency.



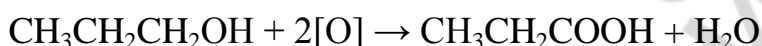
Oxidation of alcohols will produce aldehydes or ketones, if we use relatively mild oxidizer like copper (II) oxide.



Schematically we can show it like this.



If we use stronger oxidizer, alcohol will turn to carboxylic acid.

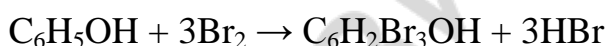


There is a specific reaction in which 1,3-butadiene can be produced from ethanol.



Polyatomic alcohols (those which contain two and more  $-\text{OH}$  groups) react with copper (II) hydroxide. The color of the solution becomes deep blue.

Phenol is more reactive compound than benzene because of the influence of  $-\text{OH}$  group on the aromatic ring. Just like toluene it is able to react with three moles of  $\text{Br}_2$ .

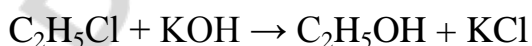


## PRODUCTION OF ALCOHOLS

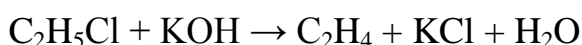
Alcohols can be produced in hydration reactions.



**Water solution of alkali** can react with alkyl halides and produce alcohols.



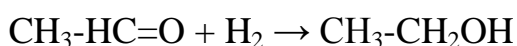
Pay attention to the fact that alkyl halides will produce alkenes (and not alcohols) with **alcohol solution of alkali**.



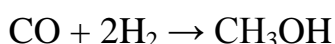


If the last reaction is known as elimination, the first one is known as nucleophilic substitution. Negatively charged ions (anions) and electronegative atoms from molecules are nucleophiles that are seeking for nuclei: in this case for nuclei of carbon atoms to make dative bonds with them. During nucleophilic substitution one nucleophile is substituted by another nucleophile that is attracted by the partially positively charged carbon atom.

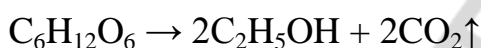
Alcohols can also be produced by the way of hydrogenation of aldehydes (primary alcohol will be formed) or ketones (secondary alcohol will be formed). The mechanism of this process is known as nucleophilic addition. We used to write this reaction in a simplified manner (see below), but the agent that initially attacks partially positively charged carbon from aldehyde or ketone group is thought to be a nucleophile (hydride anion). That is why special catalysts are necessary to perform this reaction with gaseous hydrogen. Alternatively, such reducing agents as sodium tetraborate ( $\text{NaBH}_4$ ) should be used instead of  $\text{H}_2$  itself.



Methanol can be produced from carbon monoxide and hydrogen gas.



Ethanol is produced by certain species of bacteria and fungi by the way of *glucose fermentation*.



#### EXERCISES FOR CLASSWORK

- 1. Write four reactions according to the following classic chain of chemical reactions and balance them:**

glucose  $\rightarrow$  ethanol  $\rightarrow$  1,3-butadiene  $\rightarrow$  2-butene  $\rightarrow$  2,3-dibromobutane

1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

- 2. Write four reactions according to the following classic chain of chemical reactions and balance them:**

ethane  $\rightarrow$  chloroethane  $\rightarrow$  ethanol  $\rightarrow$  diethyl ether  $\rightarrow$  carbon dioxide

1. \_\_\_\_\_
2. \_\_\_\_\_

3. \_\_\_\_\_

4. \_\_\_\_\_

**Draw the structural formula of the third compound:**

**3. Draw structures of all isomers for butanol and name them:**

**4. Calculate the mass of methanol which has been burnt down. The volume of carbon dioxide produced is equal to 56 L.**

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

**5. What is the mass of carbon dioxide formed in the reaction between 15 ml of ethanol (density is 0.8 g/ml) and the excess of oxygen?**

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

**6. What is the mass of diethyl ether formed from 12 g of ethanol?**

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\_\_\_\_\_  
\_\_\_\_\_

7. Calculate the volume of 96 % ethanol which can be produced from 100 L of ethylene. The density of 96 % ethanol is equal to 0.8 g/ml.

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8. A mixture of ethanol and propanol has a mass of 16.6 g. That mixture reacted with sodium and produced 3.36 L of hydrogen gas. Determine the mass percentage of ethanol in the mixture.

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#### EXERCISES FOR HOMEWORK

1. Write four reactions according to the following classic chain of chemical reactions and balance them:

methane → chloromethane → ethane → bromoethane → ethanol

1. \_\_\_\_\_

2. \_\_\_\_\_

3. \_\_\_\_\_

4. \_\_\_\_\_

2. Write four reactions according to the following classic chain of chemical reactions and balance them:

chloroethane → ethene → ethanol → 1,3-butadiene → 2-butene

1. \_\_\_\_\_

2. \_\_\_\_\_

3. \_\_\_\_\_

4. \_\_\_\_\_

**Draw the structural formula of the fourth compound:**

**3. Draw structures of all isomers for pentanol and name them:**

**4. Calculate the mass of 1,2-ethanediol (ethylene glycol) which has been burned down. The volume of carbon dioxide produced is equal to 26 L.**

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**5. What is the mass of carbon dioxide formed in the reaction between 15 ml of glycerol (density is 1.3 g/ml) and the excess of oxygen?**

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**6. What is the mass of polybutadiene that can be produced from 1 L of ethanol (density is 0.8 g/ml). The yield of the process is 40 %.**

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**7. 6 g of Br<sub>2</sub> reacted with 23.5 g of phenol solution. Calculate the mass percentage of phenol in the solution.**

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**8. Determine the formula of acyclic alcohol with a mass of 13.8 g that reacted with sodium and produced hydrogen gas which is sufficient to hydrogenate 3.36 L of propylene completely.**

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## LESSON 7. ALDEHYDES AND KETONES

### STRUCTURE AND NOMENCLATURE OF ALDEHYDES AND KETONES

The name “aldehyde” is originated from the “alcohol dehydrogenate”.

An **aldehyde** is an organic compound containing a formyl group. This functional group, with the structure  $R-HC=O$ , consists of a carbonyl center (a carbon double bonded to oxygen) bonded to hydrogen and an R group, which is any generic alkyl or side chain. Aldehydes differ from ketones: the carbonyl group is placed at the end of a carbon skeleton rather than between two carbon atoms. In other words, if one bond of the carbonyl group is made to an H atom, then the molecule is classified as an aldehyde.

When naming aldehydes, the main chain of C atoms must include the carbon in the carbonyl group, which is numbered as position 1 in the carbon chain. The parent name of the hydrocarbon is used, but the suffix *-al* is appended. (Do not confuse *-al* with *-ol*, which is the suffix used for alcohols.)

Methanal has a common name with which you may be familiar: formaldehyde (figure 37). The main thing to note about aldehydes is that the carbonyl group is at the *end* of a carbon chain.

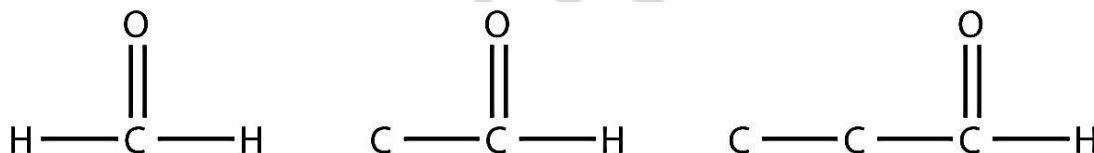


Figure 37. Carbon backbones of methanal, ethanal and propanal, hydrogen atoms are not shown

A carbonyl group in the middle of a carbon chain implies that both remaining bonds of the carbonyl group are made to C atoms. This type of molecule is called a **ketone**. Despite the fact that aldehydes and ketones have the same carbonyl group, they have different chemical and physical properties and are properly grouped as two different types of compounds. The smallest ketone has three C atoms in it (figure 38). When naming a ketone, we take the name of the parent hydrocarbon and change the suffix to *-one*:

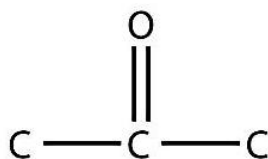


Figure 38. Carbon backbone of propanone (acetone), hydrogen atoms are not shown

The common name for propanone is acetone. With larger ketones, we must use a number to indicate the position of the carbonyl group, much like a number is used with alkenes and alkynes (figure 39):

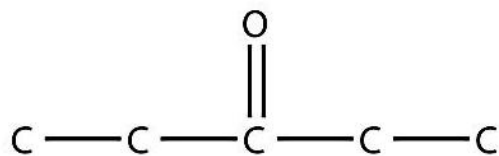


Figure 39. Carbon backbone of 3-pentanone, hydrogen atoms are not shown

There is another way to name ketones: name the alkyl groups that are attached to the carbonyl group and add the word *ketone* to the name (figures 40, 41). So propanone can also be called dimethyl ketone, while 2-butanone is called methyl ethyl ketone.

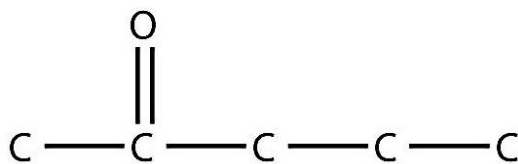


Figure 40. Carbon backbone of 2-pentanone (methyl propyl ketone), hydrogen atoms are not shown

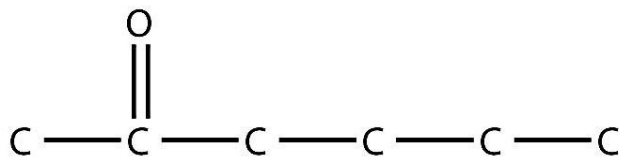
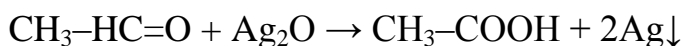


Figure 41. Carbon backbone of 2-hexanone (methyl butyl ketone), hydrogen atoms are not shown

## CHEMICAL PROPERTIES OF ALDEHYDES AND KETONES

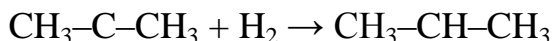
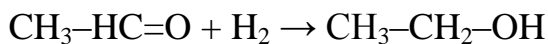
Aldehydes, unlike ketones, react with the solution of silver oxide in ammonia. In this *silver mirror* test, an aldehyde is treated with Tollens' reagent, which is prepared by adding a drop of sodium hydroxide solution into silver nitrate solution to give a precipitate of silver (I) oxide, and then adding just enough dilute ammonia solution to redissolve the precipitate in aqueous ammonia to produce  $[\text{Ag}(\text{NH}_3)_2]^+$  complex. This reagent will convert aldehydes to carboxylic acids without attacking carbon-oxygen double-bonds. The name *silver mirror test* arises because this reaction will produce a precipitate of silver which presence can be used to test for the presence of an aldehyde.



Another oxidation reaction involves Fehling's reagent ( $\text{Cu}(\text{OH})_2$ ) as a test. The  $\text{Cu}^{2+}$  complex ions are reduced to a red brick colored  $\text{Cu}_2\text{O}$  precipitate.

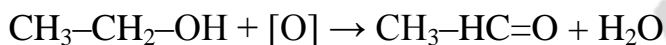


Both aldehydes and ketones can react with hydrogen (they can participate in addition reactions).

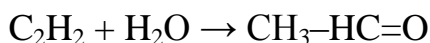


## PRODUCTION OF ALDEHYDES AND KETONES

Aldehydes and ketones may be produced from respective alcohols in oxidation reactions.



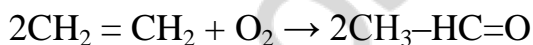
Acetaldehyde can be produced from acetylene and water.



The same reaction with longer alkynes will produce mostly ketones, because hydrogen atom will be attracted to the more hydrogenated carbon atom.



Acetaldehyde can also be produced from ethylene in the reaction with oxygen gas in special conditions.



### EXERCISES FOR CLASSWORK

**1. Write four reactions according to the following classic chain of chemical reactions and balance them:**

calcium carbide  $\rightarrow$  acetylene  $\rightarrow$  acetaldehyde  $\rightarrow$  ethanol  $\rightarrow$  ethene

1. \_\_\_\_\_

2. \_\_\_\_\_

3. \_\_\_\_\_

4. \_\_\_\_\_



**Draw the structural formula of the intermediate product of the second reaction:**

**2. Write four reactions according to the following classic chain of chemical reactions and balance them:**

propane  $\rightarrow$  1-chloropropane  $\rightarrow$  propanol  $\rightarrow$  propanal  $\rightarrow$  propionic acid

1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

**3. Draw structures of all isomers for pentanal and name them:**

**4. Calculate the mass of silver produced in the silver mirror test with 4 ml of 0.02 M solution of propanal.**

- \_\_\_\_\_
- \_\_\_\_\_
- \_\_\_\_\_
- \_\_\_\_\_

**5. The mass of an alcohol formed by the way of hydrogenation of a corresponding aldehyde is 3.45 % higher than the mass of that aldehyde. Find the formula of an aldehyde.**

- \_\_\_\_\_
- \_\_\_\_\_
- \_\_\_\_\_
- \_\_\_\_\_

6. What is the mass of acetaldehyde that can be produced from 5 L of acetylene (in normal conditions) if the yield of the process is 66 %?

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7. Determine the mass of acetaldehyde which can be produced from 900 kg of impure calcium carbide. The mass percentage of impurities is equal to 10 %. The yield of acetylene in the reaction between water and calcium carbide is equal to 95 %, the yield of acetaldehyde in the reaction between acetylene and water is equal to 75 %.

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#### EXERCISES FOR HOMEWORK

1. Write four reactions according to the following classic chain of chemical reactions and balance them:

methane → chloromethane → methanol → methanal → formic acid

1. \_\_\_\_\_

2. \_\_\_\_\_

3. \_\_\_\_\_

4. \_\_\_\_\_

2. Write four reactions according to the following classic chain of chemical reactions and balance them:

butanone → 2-butanol → 2-butene → butane → ethane

1. \_\_\_\_\_

2. \_\_\_\_\_

3. \_\_\_\_\_

4. \_\_\_\_\_

**Draw structural formulas of the most abundant and the less abundant products of the second reaction:**

**3. Draw structures of all isomers for hexanone and name them:**

**4. Calculate the mass of silver produced in the silver mirror test with 200 g of a solution containing 4 % of ethanal and 3 % of butanal by mass.**

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**5. The mass of an alcohol formed by the way of hydrogenation of a corresponding aldehyde is 4.45 % higher than the mass of that aldehyde. Find the formula of an aldehyde.**

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6. 1.74 g of a mixture of acetaldehyde and pentanal reacted with Tollens' reactant and produced 6.48 g of silver. Determine the mass percentage of acetaldehyde in the mixture.

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7. 200 g of the solution of propanal and propanone produced 3 g of silver in the silver mirror test. The total mass percentage of organic substances (propanal and propanone) in the initial solution was equal to 15 %. Find the mass percentage of propanone in the initial solution.

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## LESSON 8. CARBOXYLIC ACIDS

### STRUCTURE OF CARBOXYLIC ACIDS

The combination of a carbonyl functional group and an –OH group makes the carboxyl group (figure 42).

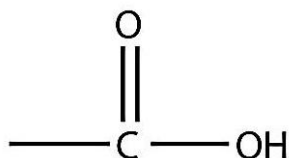


Figure 42. Scheme of the carboxyl group

Molecules with a carboxyl group are called *carboxylic acids*. As with aldehydes, the functional group in carboxylic acids is at the end of a carbon chain. Also as with aldehydes, the C atom in the functional group is counted as one of the C atoms that defines the parent hydrocarbon name. To name carboxylic acids, the parent name of the hydrocarbon is used, but the suffix *-oic* and a word *acid* are added (figure 43).

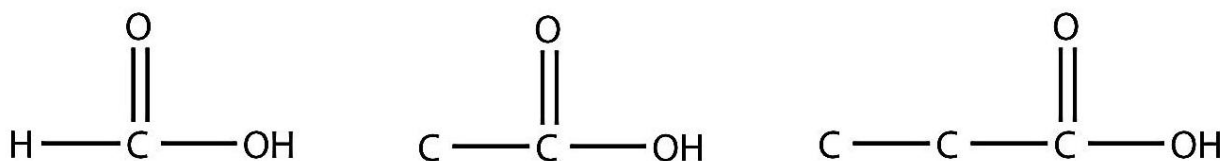


Figure 43. Structural formula of methanoic (formic) acid, carbon backbones of ethanoic (acetic) and propanoic acids

Methanoic acid and ethanoic acid are also called *formic acid* and *acetic acid*, respectively.

All carboxylic acids are weak acids. A 1M solution of formic acid is only about 1.3 % dissociated into H<sup>+</sup> ions and formate ions, while a similar solution of acetic acid is ionized by about only 0.4 %. However, trichloroacetic acid is about 45 % dissociated in aqueous solution. But no carboxylic acid approaches the 100 % dissociation amount required by the definition of a strong acid.

### CHEMICAL PROPERTIES OF CARBOXYLIC ACIDS

Carboxylic acids react with bases. The H atom in the carboxyl group comes off as the H<sup>+</sup> ion (figure 44), leaving a carboxylate anion:

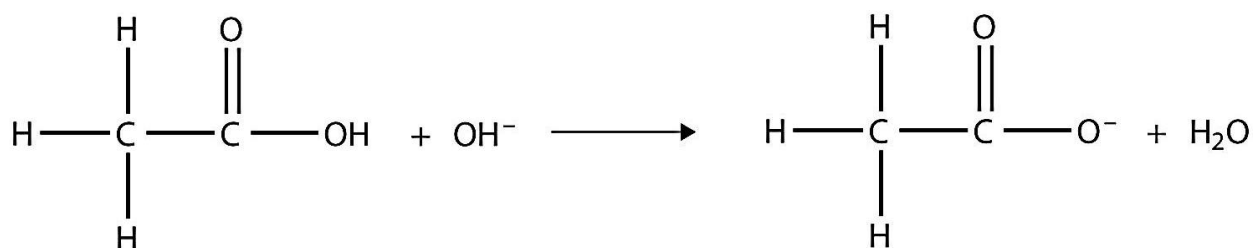


Figure 44. Ionic reaction between acetic acid and alkali

Carboxylate ions are named from the acid name: the *-oic acid* is replaced with *-oate* to name the ion. The carboxylate ion (figure 45), which has the condensed structural formula  $\text{CH}_3\text{COO}^-$  (R is the methyl group in that particular ion), is the ethanoate ion, but it is commonly called the acetate ion.

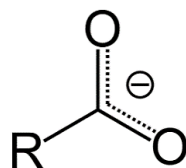
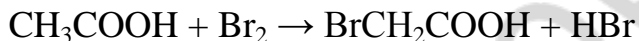


Figure 45. Scheme of carboxylic acid ion

Of course, carboxylic acids are able to form salts in reactions with pure metals, metal oxides and other salts (in certain conditions), just like inorganic acids do.

Hydrocarbon tails of carboxylic acids may react with halogens.



Carboxylic acids are able to form acid anhydrides. Below is an example of acetic anhydride composed of two acetic acid molecules connected via oxygen atom (figure 46).

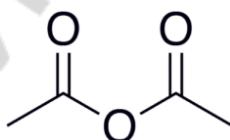


Figure 46. Scheme of carboxylic acid anhydride

One may consider that formic acid has both carboxyl and carbonyl functional groups (figure 47).

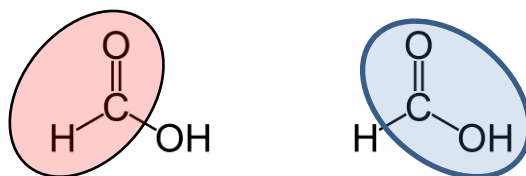
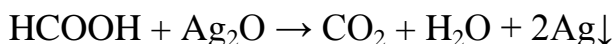


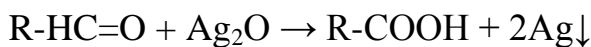
Figure 47. Carboxyl and carbonyl functional groups of the formic acid

For this reason, formic acid is able to react with Tollens' reactant.

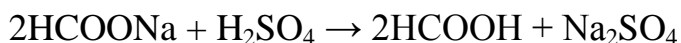
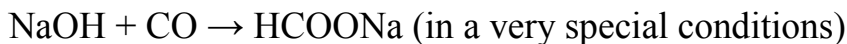


## PRODUCTION OF CARBOXYLIC ACIDS

Carboxylic acids can be produced by the way of oxidation of aldehydes, for example, in the silver mirror reaction.



There is a specific way to produce formic acid.



Acetic acid can be produced from butane.



### EXERCISES FOR CLASSWORK

- 1. Write four reactions according to the following classic chain of chemical reactions and balance them:**

chloromethane  $\rightarrow$  methanol  $\rightarrow$  methanal  $\rightarrow$  formic acid  $\rightarrow$  methyl formiate

1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

**Write the same reaction as the first one but in the alcoholic solution and with chloroethane instead of chloromethane:**

\_\_\_\_\_

- 2. Write four reactions according to the following classic chain of chemical reactions and balance them:**

propionic acid  $\rightarrow$  ethyl propionate  $\rightarrow$  sodium propionate  $\rightarrow$  ethane  $\rightarrow$  ethene

1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

**Write the same reaction as the second one in acidic medium:**

\_\_\_\_\_

**3. Draw the structural formula of oxalic acid:**

**4. What is the mass of acetic anhydride which has to be dissolved in 500 g of 95 % acetic acid solution to produce a 100% acetic acid?**

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**5. Calculate the volume of carbon dioxide produced in the reaction between 20 g of 9 % acetic acid solution and 5 g of sodium bicarbonate.**

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**6. Find the mass of acetic acid anhydride needed to prepare 300 g of acetic acid solution with the mass percentage of 5 %.**

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**7. The volume of hydrogen released in the reaction between 10 g of a saturated monoprotic carboxylic acid and potassium is equal to 1.273 L. Find the formula of that acid.**

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8. Determine the formula of an organic acid containing a single carboxyl group. 28.8 g of that acid can be completely neutralized by 101.7 ml of KOH solution with density equal to 1.18 g/ml and mass percentage equal to 22.4 %.

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#### EXERCISES FOR HOMEWORK

1. Write four reactions according to the following classic chain of chemical reactions and balance them:

ethanal  $\rightarrow$  ethanol  $\rightarrow$  acetaldehyde  $\rightarrow$  acetic acid  $\rightarrow$  acetic acid anhydrate

1. \_\_\_\_\_  
2. \_\_\_\_\_  
3. \_\_\_\_\_  
4. \_\_\_\_\_

Write the third reaction with another oxidizer:

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2. Write four reactions according to the following classic chain of chemical reactions and balance them:

butane  $\rightarrow$  1-butyne  $\rightarrow$  butanone  $\rightarrow$  2-butanol  $\rightarrow$  2-bromobutane

1. \_\_\_\_\_  
2. \_\_\_\_\_  
3. \_\_\_\_\_  
4. \_\_\_\_\_

Write the second reaction in which its minor product is formed:

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3. Draw the structural formula of butanoic acid:

**4. What is the mass of acetic anhydride which has to be dissolved in 300 g of 9 % acetic acid solution to produce a 100% acetic acid?**

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**5. Calculate the volume of carbon dioxide produced in the reaction between 30 g of 9 % acetic acid solution and 15 g of potassium carbonate.**

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**6. Find the mass of acetic acid anhydride needed to prepare 250 g of acetic acid solution with the mass percentage of 15 %.**

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**7. The volume of hydrogen released in the reaction between 8 g of a saturated monoprotic carboxylic acid and sodium is equal to 1.211 L. Find the formula of that acid.**

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**8. 0.75 g of 40 % formaldehyde reacted with Tollens' reactant and produced 0.224 L of CO<sub>2</sub>. Determine the mass of silver produced in that process.**

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## LESSON 9. ESTERS AND FATS

### ESTERS

Carboxylic acids can react with alcohols. When combined under the proper conditions (in the presence of sulfuric acid that works as a producer of a catalyst —  $H^+$  cations — and a substance that catches produced water molecules), a water molecule will be removed, and the remaining pieces will combine to form a new functional group — the ester functional group (figure 48). Note how the acid molecule contributes one alkyl side (represented by R), while the alcohol contributes the other side (represented by R').

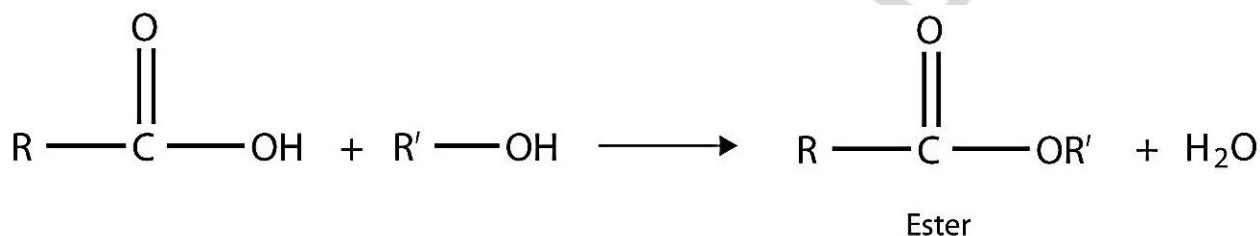


Figure 48. Scheme of ester formation reaction

Esters are named using the alkyl group name from the alcohol plus the carboxylate name from the acid. The compound shown below is called methyl propanoate (figure 49).

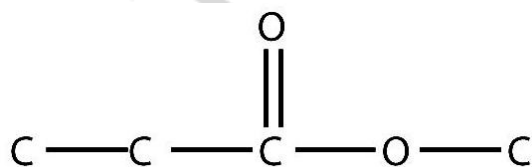
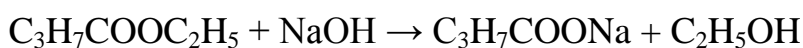


Figure 49. Carbon backbone of methyl propanoate, hydrogen atoms are not shown

Esters are very interesting compounds, in part because many have pleasant odors and flavors. Many esters occur naturally and contribute to the odor of flowers and the taste of fruits. Other esters are synthesized industrially and are added to food products to improve their smell or taste; it is likely that if you eat a product whose ingredients include artificial flavorings, those flavorings are esters.

Ester can be hydrolyzed back into carboxylic acid salt and alcohol in the presence of alkali.



Notice that ester is the product of the reaction between an alcohol and a carboxylic acid, while ether is the product of the reaction between two alcohols. Carboxylic acid anhydride is the product of the reaction between two carboxylic acids.

## FATS

Fats are esters of triatomic alcohol glycerol and fatty acids. In other words, fats are triglycerides: triesters of glycerol and any of several fatty acids (figure 50). Fatty acids are carboxylic acids with long nonbranched aliphatic tails.

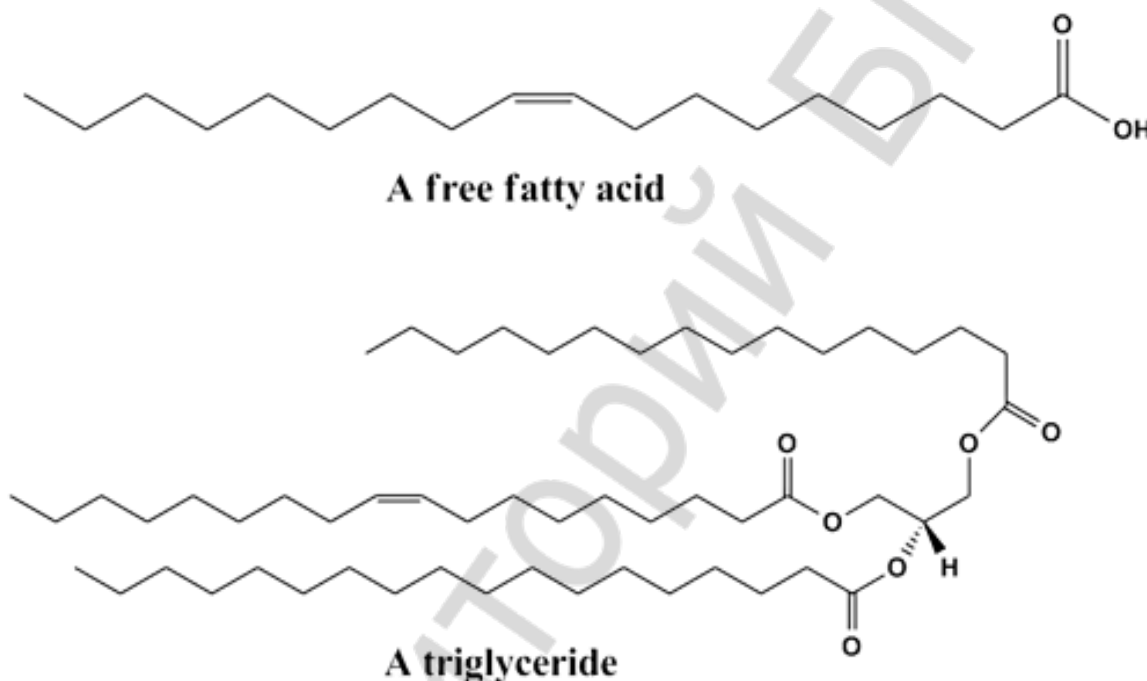


Figure 50. Carbon backbone of a free fatty acid and a triglyceride

There are several examples of fatty acids that are especially important.

*Palmitic acid:*  $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$

*Stearic acid:*  $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$

*Oleic acid:*  $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

*Linoleic acid:*  $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

*Linolenic acid:*  $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

*Arachidonic acid:*

$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_3\text{COOH}$

Note that oleic, linolenic and arachidonic acids have unsaturated hydrocarbon tails, while palmitic and stearic acids are saturated. So, fats can be classified into saturated fats and unsaturated fats.

Fat is one of the possible variants of a lipid. In other words, the term “lipid” is much wider than the term “fat”. Fats form cellular membranes (both outer membrane and membranes of intracellular organelles) together with other lipids. There are two layers of fats (and other lipids) in a membrane (figure 51). Glycerol is a relatively hydrophilic part of a fat molecule. That is why the “heads” of fats are in contact with intra- and intercellular liquid, while hydrophobic “tails” are situated inside the membrane.

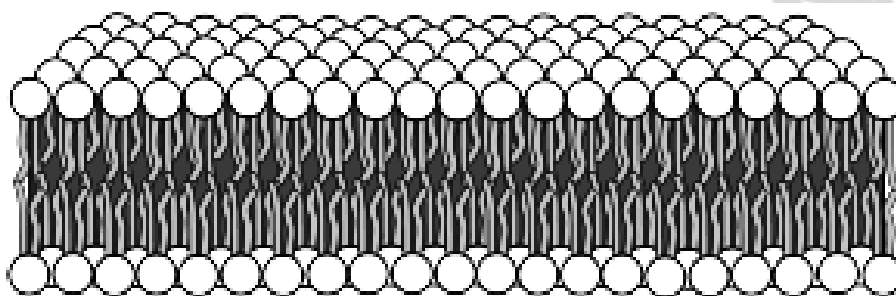


Figure 51. Cellular membrane structure

Fats are used in the production of soap. Saponification is the organic chemical reaction known since ancient times. Natural soaps are sodium or potassium salts of fatty acids, originally made by boiling lard or other animal fat together with lye (potassium hydroxide) made from potash (salts of potassium). Hydrolysis of the fats and oils occurs, yielding glycerol and crude soap (figure 52).

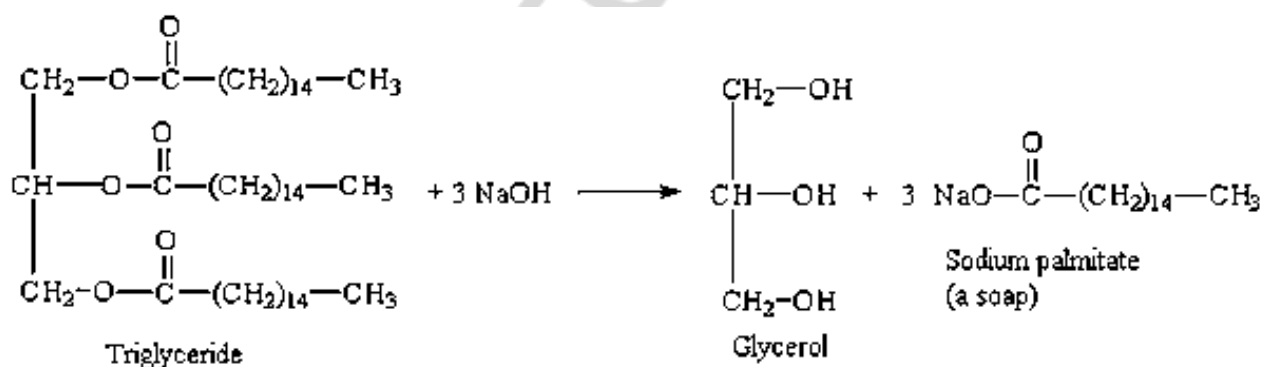


Figure 52. Reaction of glyceride tripalmitate saponification

Margarine is made of hydrogenated plant oils. Those oils contain triglycerides of unsaturated fatty acids. Hydrogenation makes a solid (at 4 °C) substance from liquid oils (figure 53).

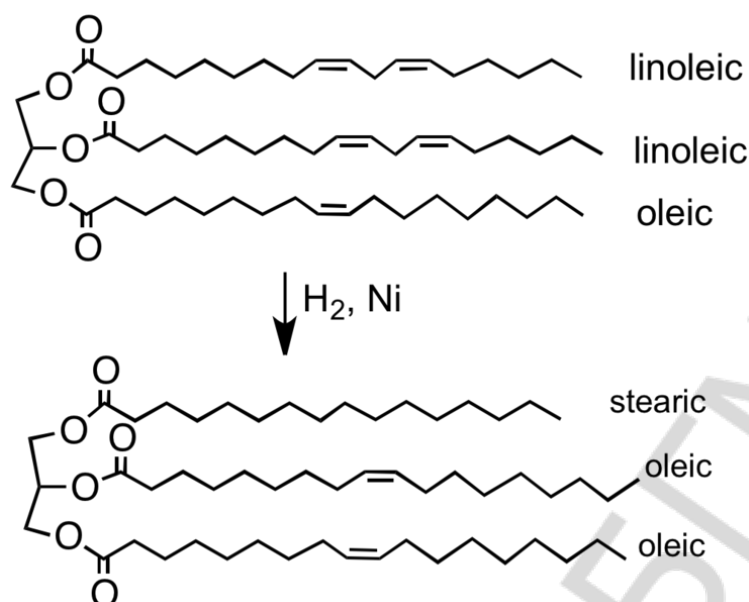


Figure 53. Reaction of unsaturated triglyceride partial hydrogenation

### TEST FOR CLASSWORK

- Esters may be described as products of the reaction between:
  - alcohols and aldehydes
  - carboxylic acids and aldehydes
  - carboxylic acids and alcohols
  - alcohols and alkanes
- Choose the common formula for monoatomic saturated acyclic alcohols:
 

a) $C_nH_{2n-1}OH$	c) $C_nH_{2n+2}OH$
b) $C_nH_{2n}OH$	d) $C_nH_{2n+1}OH$
- Ethers are isomers of:
 

a) esters	c) alcohols
b) aldehydes	d) carboxylic acids
- Choose the product of 1-propanol dehydration reaction at the temperature lower than 140 °C in the presence of H<sub>2</sub>SO<sub>4</sub>:
 

a) propanal	c) dipropyl ether
b) propene	d) ethyl acetate
- Acetic acid reacts with:
 

a) K	b) KOH	c) KCl	d) Cl <sub>2</sub>
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- Fat can be described as:
 

a) ether	b) ester	c) aldehyde	d) carboxylic acid
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7. Silver mirror test (reaction with  $\text{Ag}_2\text{O}$ ) can be used to approve the presence of:
  - a) aldehyde
  - b) ketone
  - c) glucose
  - d) fructose
8. Calculate the sum of all coefficients in the reaction between formic acid aldehyde ( $\text{H}_2\text{CO}$ ) and the excess of Tollen's reactant ( $\text{Ag}_2\text{O}$ ):
  - a) 9
  - b) 5
  - c) 10
  - d) 4
9. How many isomers can you suggest for butanol molecule?
  - a) 2
  - b) 4
  - c) 5
  - d) 7
10. Which products may be formed in the process of ethanol oxidation (consider different oxidizers and conditions)?
  - a)  $\text{CO}_2$
  - b)  $\text{CH}_3\text{CHO}$
  - c)  $\text{CH}_3\text{COOH}$
  - d)  $\text{C}_2\text{H}_6$

### TEST FOR HOMEWORK

1. Ethers may be described as products of the reaction between:
  - a) alcohols
  - b) carboxylic acids and alcohols
  - c) carboxylic acids
  - d) alkenes
2. Choose the common formula for monoprotic saturated acyclic carboxylic acids:
  - a)  $\text{C}_n\text{H}_{2n+1}\text{COOH}$
  - b)  $\text{C}_n\text{H}_{2n+2}\text{O}_2$
  - c)  $\text{C}_n\text{H}_{2n+2}\text{COOH}$
  - d)  $\text{C}_n\text{H}_{2n-1}\text{COOH}$
3. Esters are isomers of:
  - a) esters
  - b) aldehydes
  - c) alcohols
  - d) carboxylic acids
4. Which substances react with both phenol and ethanol?
  - a)  $\text{NaOH}$
  - b)  $\text{Na}$
  - c)  $\text{HCl}$
  - d)  $\text{H}_2$
5. Choose the final products of glucose alcoholic fermentation:
  - a)  $\text{H}_2\text{O}$
  - b)  $\text{CO}_2$
  - c)  $\text{C}_2\text{H}_5\text{OH}$
  - d)  $\text{CH}_3\text{COOH}$
6. Methylacetate is:
  - a) ether
  - b) ester
  - c) salt
  - d) carboxylic acid
7. Reaction with Fehling's solution (usually written as  $\text{Cu}(\text{OH})_2$ ) can be used to approve the presence of:
  - a) aldehyde
  - b) glycerol
  - c) glucose
  - d) fructose

8. Calculate the sum of all coefficients in the reaction between acetaldehyde ( $\text{CH}_3\text{CHO}$ ) and the excess of Fehling's solution ( $\text{Cu}(\text{OH})_2$ ):  
a) 6      b) 7      c) 8      d) 9
9. How many isomers can you suggest for butanal molecule?  
a) 2      b) 3      c) 4      d) 5
10. Choose the product of propanal reduction by hydrogen:  
a) propane      b) propene      c) propyne      d) propanol

#### EXERCISES FOR CLASSWORK

1. Write four reactions according to the following classic chain of chemical reactions and balance them:

ethanol  $\rightarrow$  diethyl ether  $\rightarrow$  ethanol  $\rightarrow$  ethyl propionate  $\rightarrow$  sodium propionate

1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

Write the first reaction at higher temperature (higher than  $170\text{ }^\circ\text{C}$ ):

2. Draw a structure of a fat molecule made from two residues of palmitic acid and one residue of stearic acid:

Write the reaction of saponification (with sodium hydroxide) for this fat:



**3. Find the mass of sodium stearate that can be obtained in the reaction of saponification of 500 g of the fat from the previous exercise.**

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**4. Determine the mass of a soap which can be produced from 2 tons of glyceride trilinolate in the reaction with KOH. The yield is equal to 85 %.**

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**5. What is the mass of an ester produced in the reaction between 5 g of acetic acid and 6 g of propanol?**

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**6. Ethyl butanoate has been hydrolyzed with the help of sodium hydroxide. Then sodium butanoate has been decarboxylized. The mass of propane is 4 g. Find the mass of ethyl butanoate used in this process. The yield of the first step is 85 %, the yield of the second step is 55 %.**

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**7. Determine the formula of an ester in case if 12 g of that ester can be hydrolyzed completely by 80 g of 10 % NaOH solution.**

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### EXERCISES FOR HOMEWORK

1. Write four reactions according to the following classic chain of chemical reactions and balance them:

1-bromopropane → 1-propanol → propanal → propionic acid → ethyl propanoate

1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

Write the third reaction with another oxidizer:

\_\_\_\_\_

2. Draw a structure of a fat molecule made from one residues of oleic acid, one residue of linolenic acid, and one residue of stearic acid:

Write the reaction of saponification (with potassium hydroxide) for this fat:

3. Find the mass of potassium oleate that can be obtained in the reaction of saponification of 300 g of the fat from the previous exercise.

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

4. Glyceride trioleate has been hydrolyzed. Oleic acid produced has been hydrogenated. The process required 13.44 L of hydrogen gas. Determine the mass of glyceride trioleate.

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5. What is the mass of an ester produced in the reaction between 7 g of propionic acid and 9 g of ethanol?

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6. Propyl propionate has been hydrolyzed with the help of potassium hydroxide. Find the yield of this process if the mass of propanol is 24 g, while the mass of an ester was 50 g.

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7. Calculate the mass of ethyl acetate which can be produced from 30 g of acetic acid and 66 g of ethanol. The yield is equal to 85 %.

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## LESSON 10. CARBOHYDRATES

### STRUCTURE OF CARBOHYDRATES

A *carbohydrate* is a compound that has the general formula of  $C_n(H_2O)_n$ . Many carbohydrates are relatively small molecules, such as glucose (figure 54).

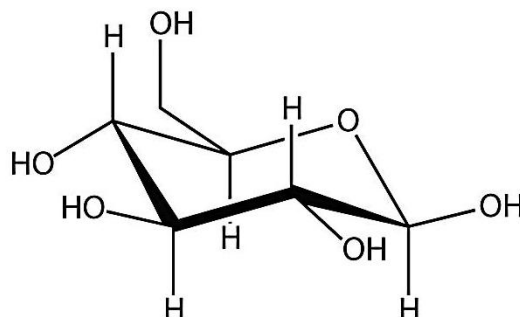


Figure 54. Structural formula of cyclic form of glucose

Glucose is a monosaccharide with formula  $C_6H_{12}O_6$  or  $H-(C=O)-(CHOH)_5-H$ , whose five hydroxyl ( $-OH$ ) groups are arranged in a specific way along its six-carbon backbone. In its fleeting open-chain form, the glucose molecule has an open (as opposed to cyclic) and unbranched backbone of six carbon atoms, C-1 through C-6; where C-1 is a part of an aldehyde group ( $-HC=O$ ), and each of the other five carbons has one hydroxyl group  $-OH$ . The remaining bonds of the backbone carbons are filled by hydrogen atoms. Therefore, glucose is a hexose (consisting of six carbon atoms) and an aldose (aldehyde group possessing), or an aldohexose (figure 55).

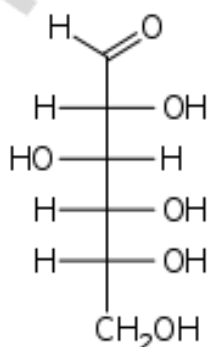


Figure 55. Structural formula of linear form of glucose

Each of the four carbons C-2 through C-5 is a stereocenter, meaning that its four bonds are connected with four different substituents (carbon C-2, for example, connects to  $-(C=O)H$ ,  $-OH$ ,  $-H$ , and  $-(CHOH)_4H$ ). In D-glucose, these four parts must be in a specific three-dimensional arrangement. The hydroxyls on C-2, C-4, and C-5 must be on the right side, while that on C-3 must be on the left side.

The cyclic form of glucose arises from the open-chain form by the way of reaction between the aldehyde group  $\text{-HC=O}$  at C-1 atom and the hydroxyl group  $\text{-OH}$  at C-4 or C-5 atom, yielding a hemiacetal group  $\text{-C(OH)H-O-}$  (the bond is formed between carbon of aldehyde group and oxygen of hydroxyl group).

The reaction between C-1 and C-5 atoms creates a molecule with a six-membered ring, called pyranose, after the cyclic ether "pyran", the simplest molecule with the same carbon-oxygen ring. The reaction between C-1 and C-4 atoms creates a molecule with a five-membered ring, called furanose, after the cyclic ether "furan". In either case, each carbon in the ring has one hydrogen and one hydroxyl attached, except for the last carbon (C-4 or C-5) where the hydroxyl is replaced by the remainder of the open molecule (which is  $\text{-(CH(CH}_2\text{OH)OH)-H}$  or  $\text{-(CHOH)-H}$ , respectively).

The ring-closing reaction makes carbon C-1 chiral, since its four bonds lead to  $\text{-H}$ , to  $\text{-OH}$ , to carbon C-2, and to the ring oxygen. These four parts of the molecule may be arranged around C-1 in two distinct ways, designated by the prefixes " $\alpha$ -" and " $\beta$ -" (figure 56). The designation " $\alpha$ -" means that the hydroxyl group attached to C-1 and the  $\text{-CH}_2\text{OH}$  group at C-5 lies on opposite sides of the ring's plane (a *trans* arrangement), while " $\beta$ -" means that they are on the same side of the plane (a *cis* arrangement).

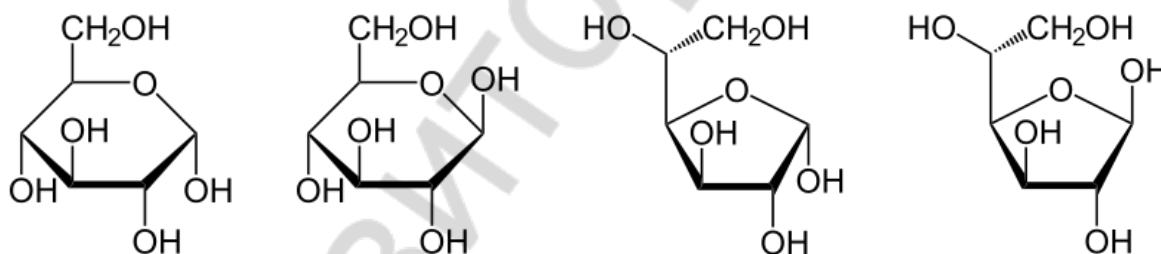


Figure 56. Structural formulas of  $\alpha$ -D-glucopyranose,  $\beta$ -D-glucopyranose,  $\alpha$ -D-glucofuranose, and  $\beta$ -D-glucofuranose

In aqueous solution, however, more than 99 % of glucose molecules, at any given time, exist as pyranose. The open-chain form is limited to about 0.25 % and furanose exists in negligible amounts.

Fructose is a 6-carbon polyhydroxyketone. It is an isomer of glucose. Both glucose and fructose have the same molecular formula ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) but they differ structurally. In water solution fructose exists as an equilibrium mixture of 70 % fructopyranose and about 22 % fructofuranose, as well as small amounts of three other forms, including the acyclic structure (figure 57).

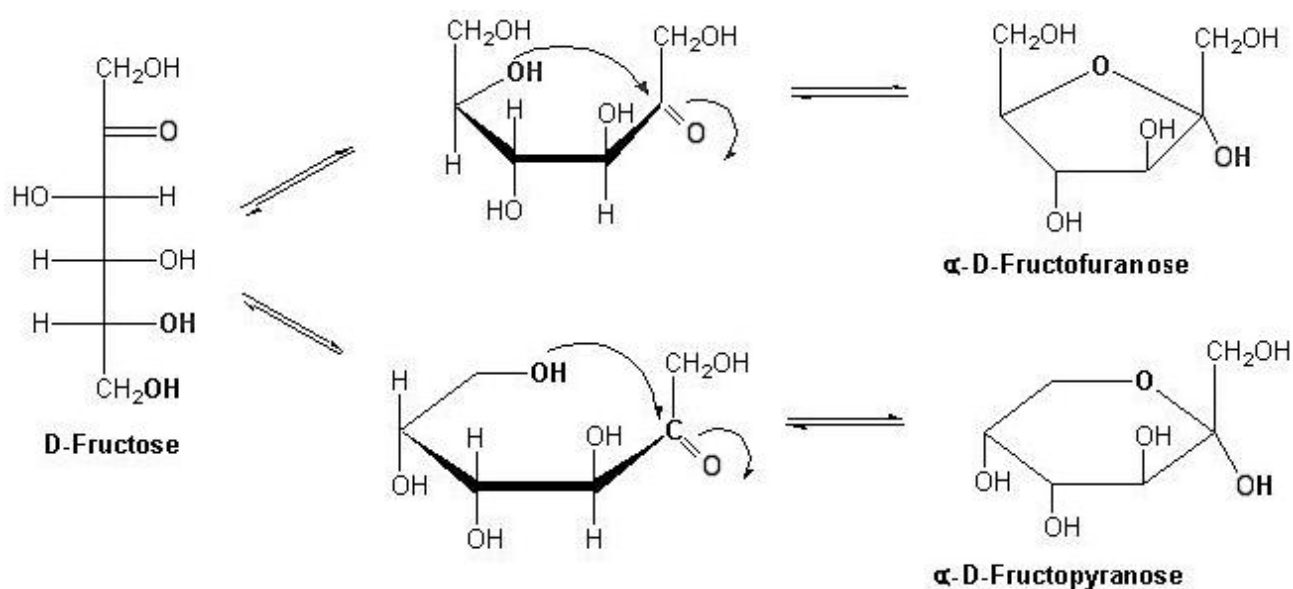


Figure 57. Isomeric forms of fructose

**Sucrose** is the organic compound commonly known as **table sugar** and sometimes called **saccharose**. A white, odorless, crystalline powder with a sweet taste, it is best known for its nutritional role. The molecule is a disaccharide composed of the monosaccharaides glucose and fructose with the molecular formula  $C_{12}H_{22}O_{11}$  (figure 58) and the 1,2-glycosidic bond. The word was formed in the mid-19th century from Latin *sucrum* = “sugar” and the chemical suffix *-ose*.

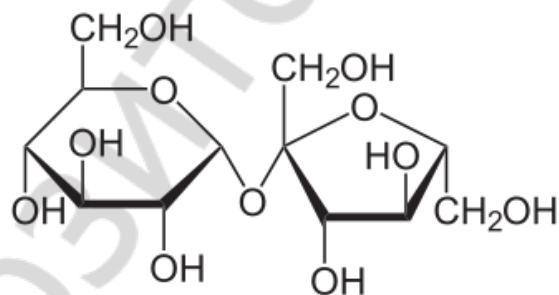


Figure 58. Structural formula of sucrose

Linking hundreds of glucose molecules together makes a relatively common material known as *starch*. Pure starch is a white, tasteless and odorless powder that is insoluble in cold water or alcohol. It consists of two types of molecules: the linear amylose (figure 59), and the branched amylopectin (figure 60). Depending on the plant, starch generally contains from 20 to 25 % of amylose and from 75 to 80 % of amylopectin by weight. Glycogen, the glucose store of animals, is a more branched version of amylopectin.

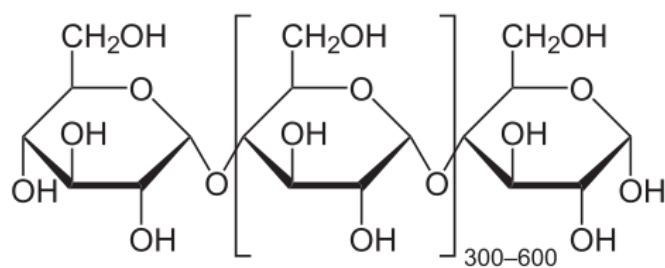


Figure 59. Schematic representation of amylose

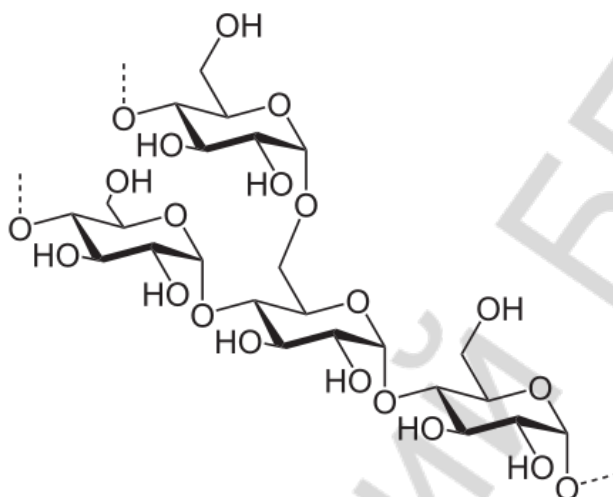


Figure 60. Schematic representation of amylopectin

The enzyme starch synthase adds the ADP-glucose via a 1,4-alpha glycosidic bond to a growing chain of glucose residues, liberating ADP and creating amylose. Starch branching enzyme introduces 1,6-alpha glycosidic bonds between these chains, creating the branched amylopectin. The starch debranching enzyme isoamylase removes some of these branches. Several isoforms of these enzymes exist, leading to a highly complex synthesis process which may be represented by the simple equation given below.



Glycogen and amylopectin have the same structure, but the former has about one branch point per ten 1,4-alpha bonds, compared to about one branch point per thirty 1,4-alpha bonds in amylopectin.

**Cellulose** is an organic compound with the formula  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , a polysaccharide consisting of a linear chain of several hundred to over ten thousand  $\beta(1\rightarrow4)$  linked D-glucose units (figure 61). Cellulose is an important structural component of the primary cell wall of green plants and many forms of algae. Some species of bacteria secrete it to form biofilms ("pili" which help them to adhere to different substrates).

Some animals (such as humans) cannot digest cellulose; those animals that can digest cellulose typically rely on symbiotic bacteria in the digestive tract for the actual digestion. Animals do not have the proper enzymes to break apart the glucose units in cellulose, so it passes through the digestive tract and is considered *dietary fiber*.

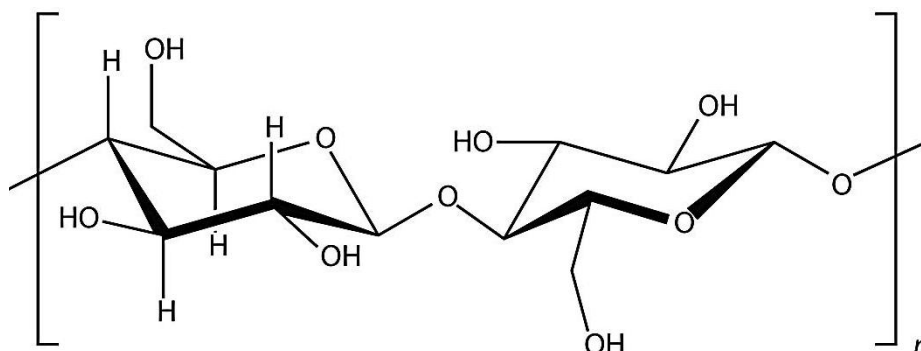


Figure 61. Schematic representation of cellulose

## RIBOSE AND DEOXYRIBOSE AS PARTS OF NUCLEIC ACIDS

**Deoxyribonucleic acid (DNA)** and **ribonucleic acid (RNA)** are polymers, composed of long, three-part chains consisting of phosphate groups, carbohydrates with 5 carbon atoms (ribose or deoxyribose), and N-containing rings referred to as bases. Each combination of the three parts is called a nucleotide. DNA and RNA are essentially polymers of nucleotides that have rather complicated but intriguing structures. DNA is the fundamental material of chromosomes and is directly responsible for heredity, while RNA is an essential substance in protein synthesis.

Here is an example of nucleoside (building block of RNA). **Adenosine (ADO)** is a purine nucleoside comprising a molecule of adenine attached to a ribose sugar molecule (ribofuranose) moiety via a  $\beta$ -N<sub>9</sub>-glycosidic bond (figure 62).

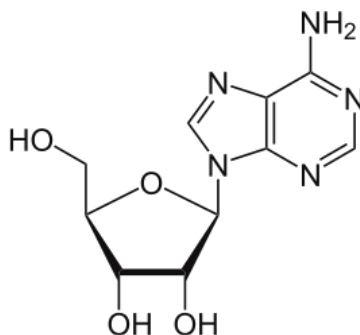


Figure 62. Structure of adenosine

**Deoxyadenosine** is a deoxyribonucleoside which is one of the four building blocks of DNA (figure 63). It is a derivative of the nucleoside adenosine, differing



from the latter by the replacement of a hydroxyl group ( $-OH$ ) by hydrogen ( $-H$ ) at the 2' position of its ribose sugar moiety.

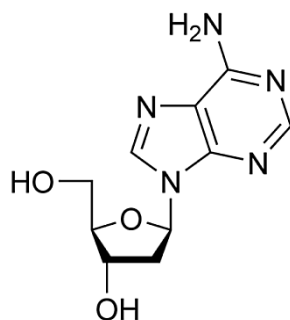


Figure 63. Structure of deoxyadenosine

DNA consists of two nonbranched strands. Nucleotides in each strand are connected together by phosphodiester bonds. A **phosphodiester bond** is a group of strong covalent bonds between a phosphate group and two 5-carbon ring carbohydrates (pentoses) over two ester bonds. Phosphodiester bonds are essential to all known forms of life, as they make up the backbone of each helical strand of DNA. In DNA and RNA, the phosphodiester bond (figure 64) is the linkage between the 3' carbon atom of one sugar molecule and the 5' carbon atom of another; the sugar molecules being deoxyribose in DNA and ribose in RNA.

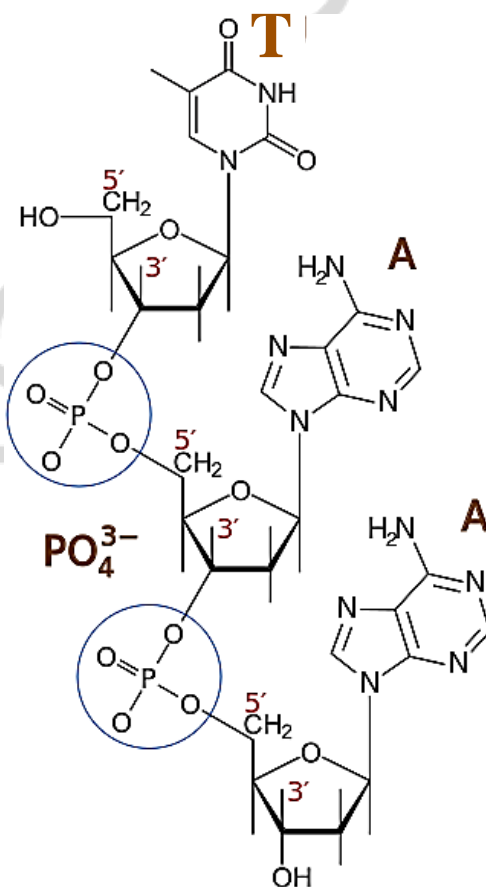


Figure 64. Scheme of the single strand of DNA

Two strands of DNA are connected together by hydrogen bonds formed between bases (figure 65). Adenine forms two hydrogen bonds with thymine, while guanine forms three hydrogen bonds with cytosine. Those bonds are strong enough to keep the genetic information (it is “written” in the sequence of nucleotides). However, those hydrogen bonds are weak enough to let two strands of DNA be separated from each other during the replication process in which a single DNA molecule forms two identical daughter molecules (figure 66).

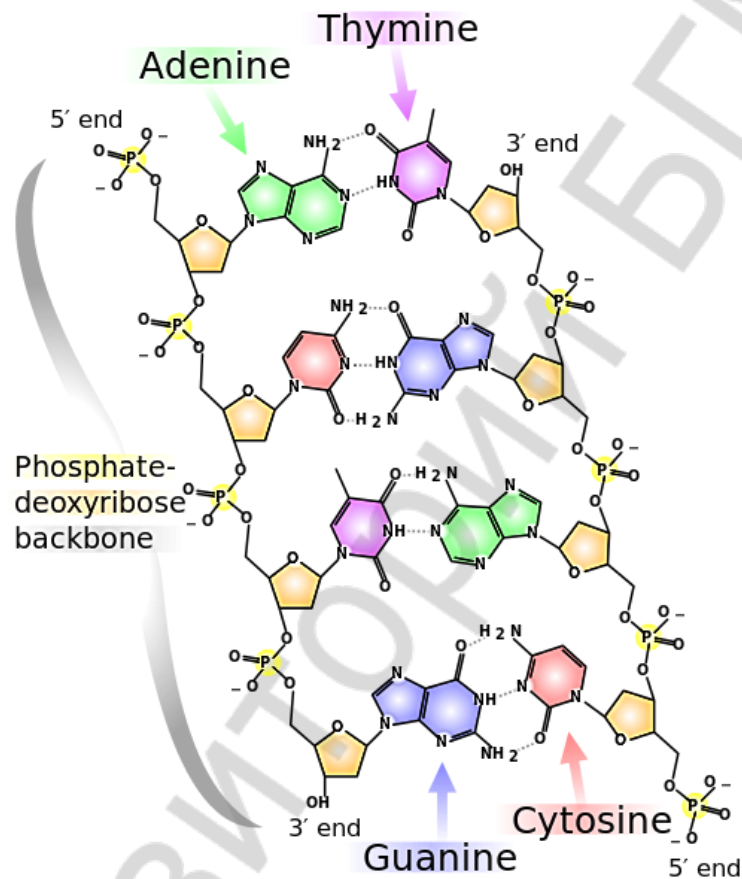


Figure 65. Scheme of the two strands of DNA connected together

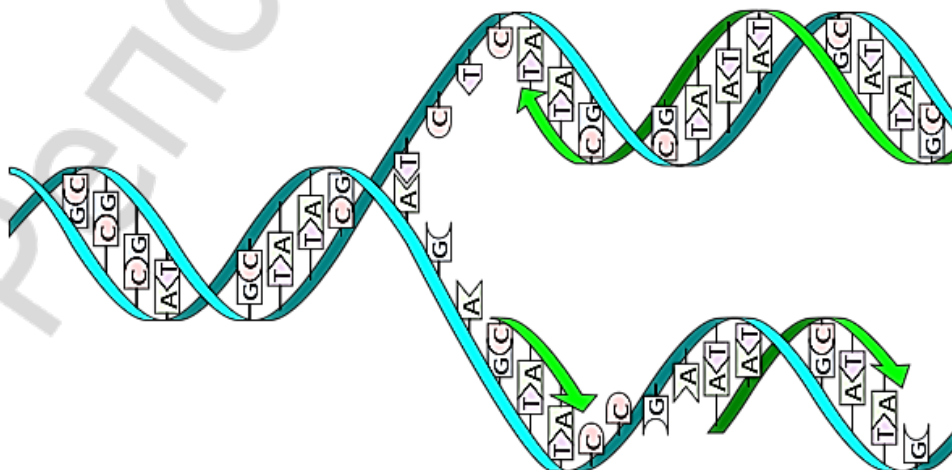
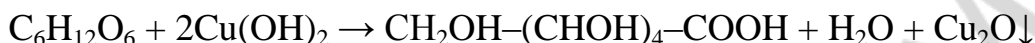


Figure 66. Scheme of DNA replication

## CHEMICAL PROPERTIES OF CARBOHYDRATES

Since glucose has an aldehyde group in its linear form, it is able to react with Tollens' reactant and Fehling's reactant, unlike fructose (fructose has a keto group in its linear form).

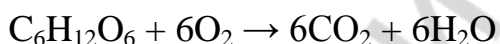


Glucose can react with hydrogen gas and form a six-atom alcohol (sorbitol).



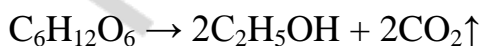
Since glucose (as well as other hydrocarbons) has several hydroxyl ( $-\text{OH}$ ) groups, it can react with  $\text{Cu}(\text{OH})_2$ . Those  $-\text{OH}$  groups are also able to form esters with carboxyl acids.

Glucose is a ubiquitous fuel in living organisms. Use of glucose may be by either aerobic respiration, anaerobic respiration, or fermentation. Glucose is the human body's key source of energy, through aerobic respiration, providing approximately 3.75 kilocalories of food energy per gram. Breakdown of carbohydrates (e. g. starch) yields mono- and disaccharides, most of which is glucose. Through glycolysis and later in the reactions of the citric acid cycle, glucose is oxidized to  $\text{CO}_2$  and water, yielding energy sources, mostly in the form of ATP. The common reaction for all those steps of glucose aerobic metabolism is written below.



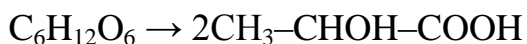
An opposite reaction to the one written above is called photosynthesis. Due to that process proceeding in plants under the influence of visible light carbon dioxide is converted to glucose, and oxygen is released in the air.

**Alcoholic Fermentation**, also referred to as **ethanol fermentation**, is a biological process in which sugars such as glucose, fructose, and sucrose are converted into cellular energy and thereby produce ethanol and carbon dioxide as metabolic waste products. Because yeasts perform this conversion in the absence of oxygen, alcoholic fermentation is considered an anaerobic process.



**Lactic acid fermentation** is a biological process by which glucose, fructose, and sucrose are converted into cellular energy and the metabolite lactate (lactic acid). It is an anaerobic fermentation reaction that occurs in some bacteria. Anaerobic

glycolysis in animal cells, such as muscle cells, can be described by the same reaction.



### EXERCISES FOR CLASSWORK

- 1. Write four reactions according to the following classic chain of chemical reactions and balance them:**

glucose  $\rightarrow$  ethanol  $\rightarrow$  ethene  $\rightarrow$  1,2-dichloroethane  $\rightarrow$  ethylene glycol

1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

**Write the process of lactic acid and not alcoholic fermentation (the first reaction):**

\_\_\_\_\_

- 2. Write four reactions according to the following classic chain of chemical reactions and balance them:**

starch  $\rightarrow$  glucose  $\rightarrow$  sucrose  $\rightarrow$  fructose  $\rightarrow$  sorbitol

1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

**Which substance from this chain shows a positive silver mirror test? Write the corresponding reaction:**

\_\_\_\_\_

- 3. Draw the structural formula of ribose:**

**4. Calculate the mass of glucose produced from 20 g of sucrose in the hydrolysis reaction.**

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**5. Find the mass of starch needed to make 200 g of ethanol in the alcoholic fermentation process if the yield is 75 %.**

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**6. What mass of silver will be formed in the silver mirror test with 15 g of glucose?**

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**7. What is the volume of carbon dioxide produced in the process of alcoholic fermentation of 38 g of glucose. The yield of the reaction is equal to 60 %.**

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**8. Determine the number of monomers ( $C_6H_{10}O_5$ ) in the polymeric molecule of cotton fiber with molecular mass equal to 1 750 000.**

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## EXERCISES FOR HOMEWORK

1. Write four reactions according to the following classic chain of chemical reactions and balance them:

glucose  $\rightarrow$  ethanol  $\rightarrow$  ethanal  $\rightarrow$  acetic acid  $\rightarrow$  sodium acetate

1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

Write the last reaction with another reactant:

\_\_\_\_\_

2. Write four reactions according to the following classic chain of chemical reactions and balance them:

sucrose  $\rightarrow$  glucose  $\rightarrow$  ethanol  $\rightarrow$  diethyl ether  $\rightarrow$  carbon dioxide

1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

Draw the structural formula of an isomer of the fourth substance which can react with metallic sodium:

3. Draw the structural formula of deoxyribose:

**4. Calculate the mass of glucose produced from 300 g of starch in the hydrolysis reaction.**

---

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**5. Find the mass of grape needed to make 300 g of ethanol in the alcoholic fermentation process if the yield is 75 %, the mass percentage of starch in grape is 19 %.**

---

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**6. What mass of silver will be formed in the silver mirror test with 20 g of the mixture of glucose and sucrose, if the mass percentage of sucrose is 40 %?**

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**7. One ton of potatoes contain 20 % of the starch. 100 liters of 96 % ethanol have been produced from that mass of potatoes after the alcoholic fermentation. The density of 96 % ethanol is equal to 0.8 g/ml. Determine the yield of the reaction.**

---

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**8. Determine the number of monomers ( $C_6H_{10}O_5$ ) in the cellulose molecule with molecular mass equal to 97200000.**

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## LESSON 11. AMINES AND PROTEINS

### AMINES

An amine is an organic derivative of ammonia (NH<sub>3</sub>). In amines, one or more of the H atoms in NH<sub>3</sub> is substituted with an organic group. A *primary* amine has one H atom substituted with an R group (figure 67).



Figure 67. Structural formula of methylamine

A *secondary* amine has two H atoms substituted with R groups (figure 68).

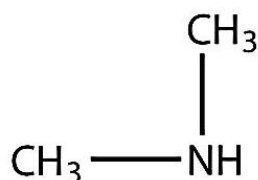


Figure 68. Structural formula of dimethylamine

A *tertiary* amine has all three H atoms substituted with R group (figure 69).

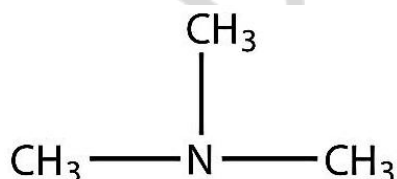


Figure 69. Structural formula of trimethylamine

Naming simple amines is straightforward: name the R groups as substituents and then add the suffix *-amine*, using numerical suffixes on the substituent names if necessary. Below is a structure of diethylamine (figure 70).

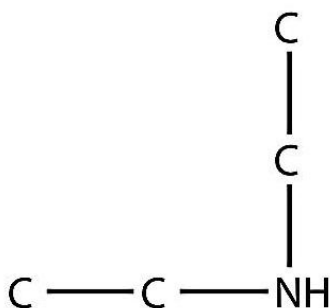


Figure 70. Structural formula of diethylamine (hydrogen atoms connected to carbon atoms are not shown)



The amine represented below has a methyl group, an ethyl group, and a propyl group. Listing the names in alphabetical order, this amine is ethylmethylpropylamine (figure 71).

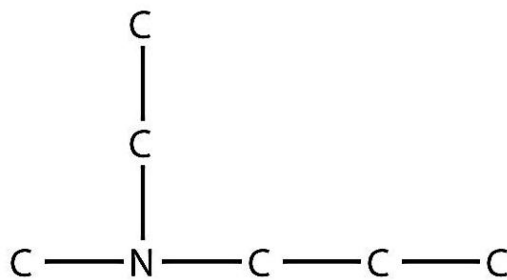


Figure 71. Structural formula of ethylmethylpropylamine (hydrogen atoms connected to carbon atoms are not shown)

As with  $\text{NH}_3$ , the N atom in amines can accept a proton onto the lone electron pair on the N atom (figure 72). That is, amines act as bases (i. e., proton acceptors):

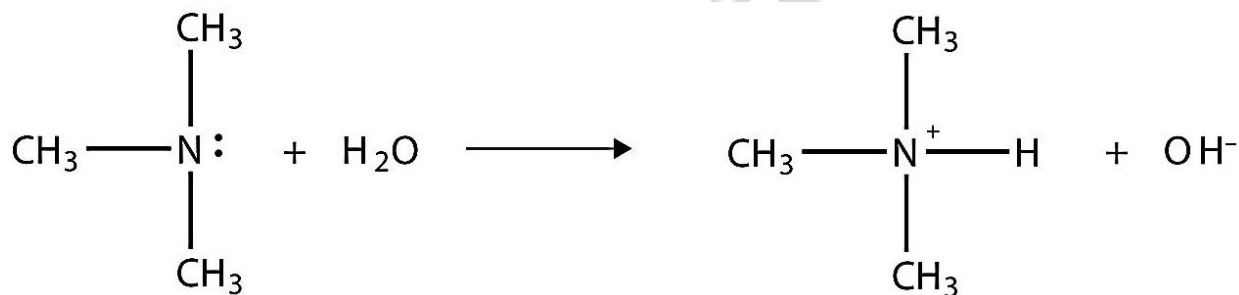
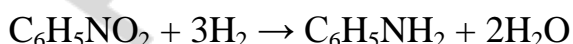
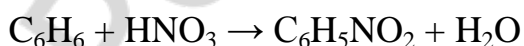
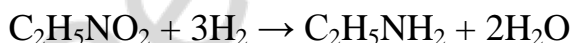
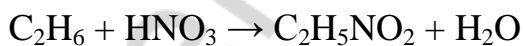


Figure 72. Reaction of trimethylamine and water

The amine becomes an ion similar to the ammonium ( $\text{NH}_4^+$ ) ion. Remember that all amines are weak bases, as well as ammonium hydroxide. The longer the alkyl radical of an amine, the stronger it is as a base. In contrast, the longer the chain of carboxyl acid, the weaker acid it is.

To produce an amine one may first perform reaction between alkane (or arene) and nitric acid. Then resulting nitroalkane (or nitroarene) should be reduced by hydrogen.



Amino group can be attached to the benzene ring as a substituent. Resulting compound is called aniline (figure 73).

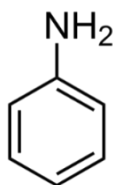
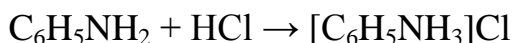
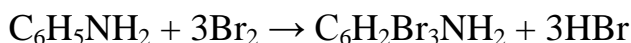


Figure 73. Structural formula of aniline

Aniline is a weaker base than aliphatic amines. However, it still can react with acids.



Reaction of aniline with bromine results in 2,4,6-tribromoaniline formation.



## AMIDES

An *amide functional group* is a combination of an amine group and a carbonyl group (figure 74).

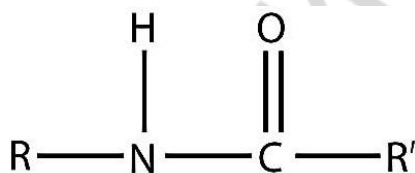


Figure 74. Scheme of amide functional group

Amides are actually formed by bringing together an amine containing molecule and a carboxylic acid containing molecule. A molecule of  $\text{H}_2\text{O}$  is lost in that process (figure 75).

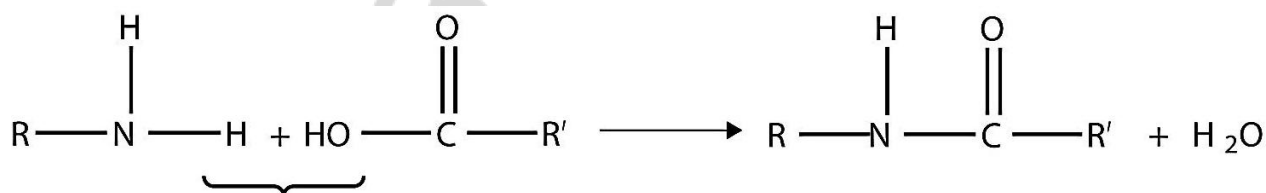


Figure 75. Scheme of amide bond formation

The bond between the N of the amine group and the C of the carbonyl group is called an amide bond. Amide bonds are particularly important in biological molecules called **proteins**, which are composed of strings of amino acids — molecules that have an amine group and a carboxylic acid group in them. The amine group on one amino acid reacts with the carboxylic acid group of another amino acid, making a chain held together by amide bonds.

For example, amide may be formed by the combination of ethylamine and butanoic acid (figure 76).

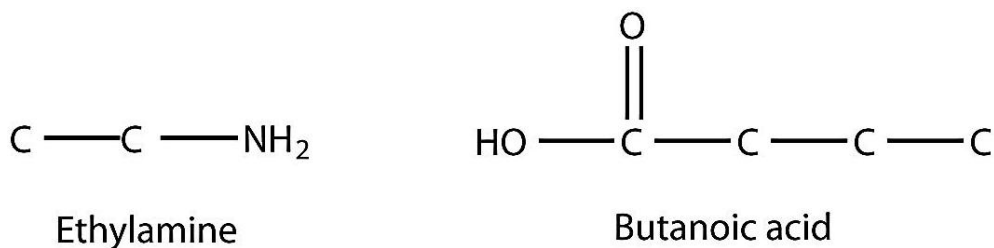


Figure 76. Ethylamine and butanoic acid, hydrogen atoms are not shown

When they come together to make an amide, an H<sub>2</sub>O molecule is lost, and the N of the amine group bonds to the C of the carboxyl group. The resulting molecule is shown in figure 77.

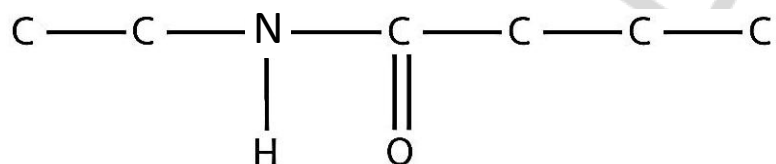


Figure 77. The product of the reaction between ethylamine and butanoic acid, hydrogen atoms are not shown

## PROTEINS

Amide bonds between amino acids are called *peptide bonds*.

Proteins are polymers of amino acids, which are monomers that have an amine functional group and a carboxylic acid functional group. These two groups react to make a condensation polymer, forming an amide (peptide) bond (figure 78).

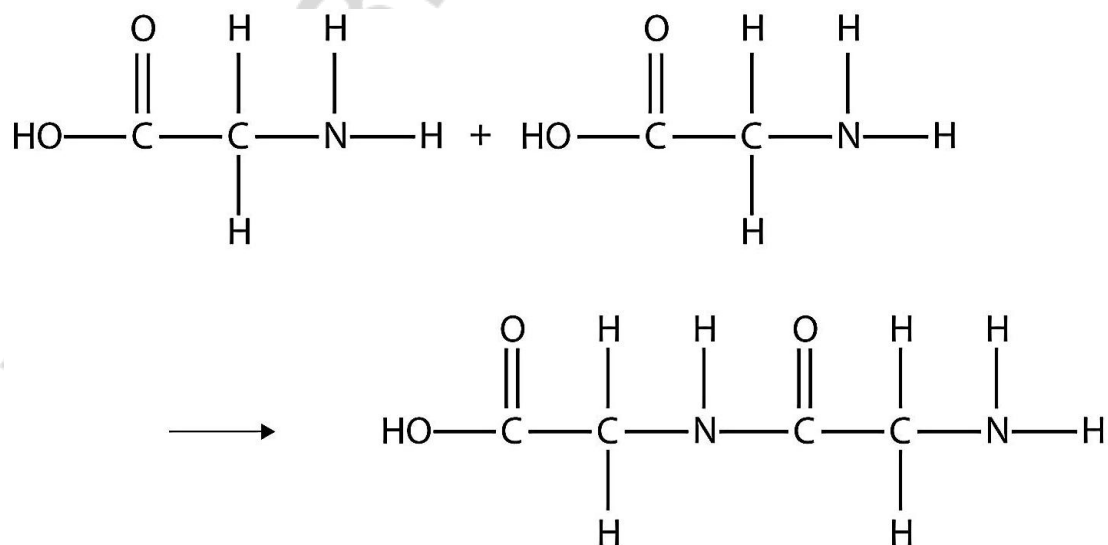


Figure 78. Formation of glycyl glycine

The reaction between two molecules of glycine is represented above.

In the water solution amino acids exist as zwitterions. Carboxyl groups become deprotonated, while amino groups become protonated (figure 79).

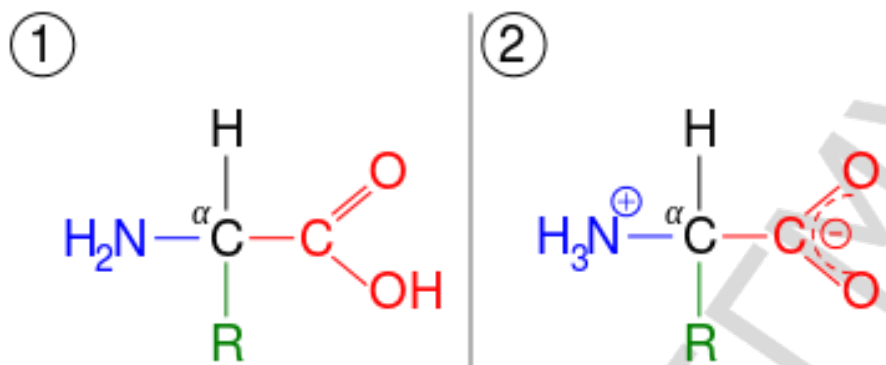


Figure 79. Zwitterion formation

Proteins are formed when hundreds or even thousands of amino acids form amide bonds to make polymers. Actually, this process is called polycondensation, since water molecules are released during the formation of a polymer. In the same way, polysaccharides are also produced in the process of polycondensation. In contrast, rubber is produced by the way of polymerization: in this process there are no subproducts. Proteins play a crucial role in living organisms. Structures of the “bricks” of proteins are given below (figure 80).

There are 20 proteinogenic amino acids in the universal genetic code. Selenocysteine is considered as 21th proteinogenic amino acid. That selenium containing analogue of cysteine can be encoded by certain species of microorganisms.

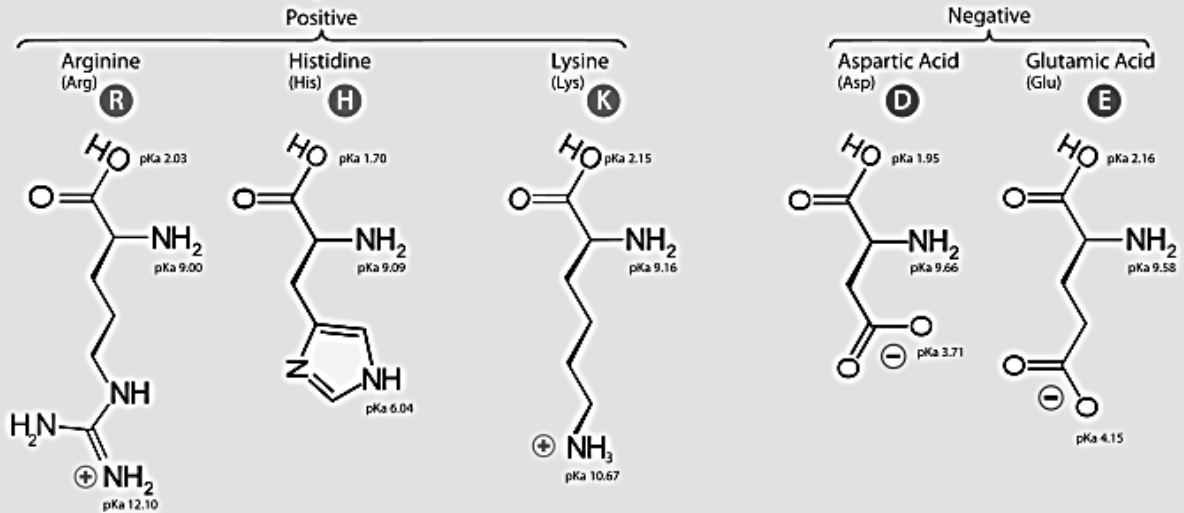
Notice that asparagine and glutamine contain amide groups in their side chains, while aspartic and glutamic acids contain additional carboxyl groups. Lysine has additional amino group, while arginine has a guanidine group that is also positively charged. Serine, threonine and tyrosine contain hydroxyl groups. Phenylalanine and tyrosine possess aromatic benzene rings. Tryptophan and histidine are also aromatic amino acids, while they have heterocycles. Proline has a cyclic, but saturated side chain. Methionine and cysteine contain sulfur atoms in their side chains.

Leucine, isoleucine and valine have aliphatic branched side chains. Glycine is a unique amino acid that has no side chain at all.

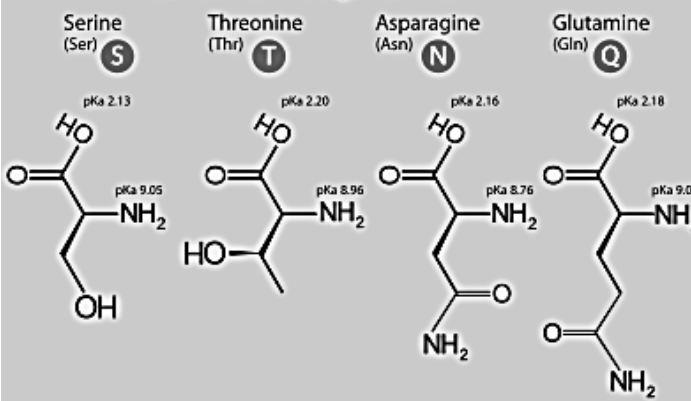
Twenty-One Amino Acids

⊕ Positive ⊖ Negative  
 • Side chain charge at physiological pH 7.4

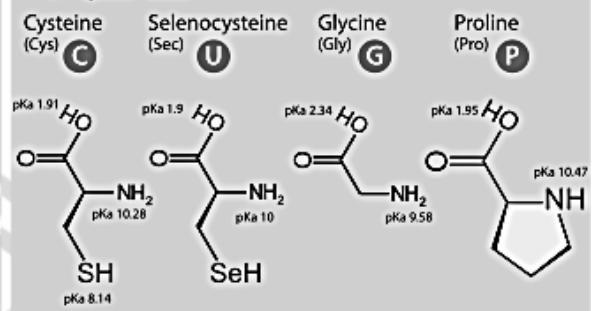
A. Amino Acids with Electrically Charged Side Chains



B. Amino Acids with Polar Uncharged Side Chains



C. Special Cases



D. Amino Acids with Hydrophobic Side Chain

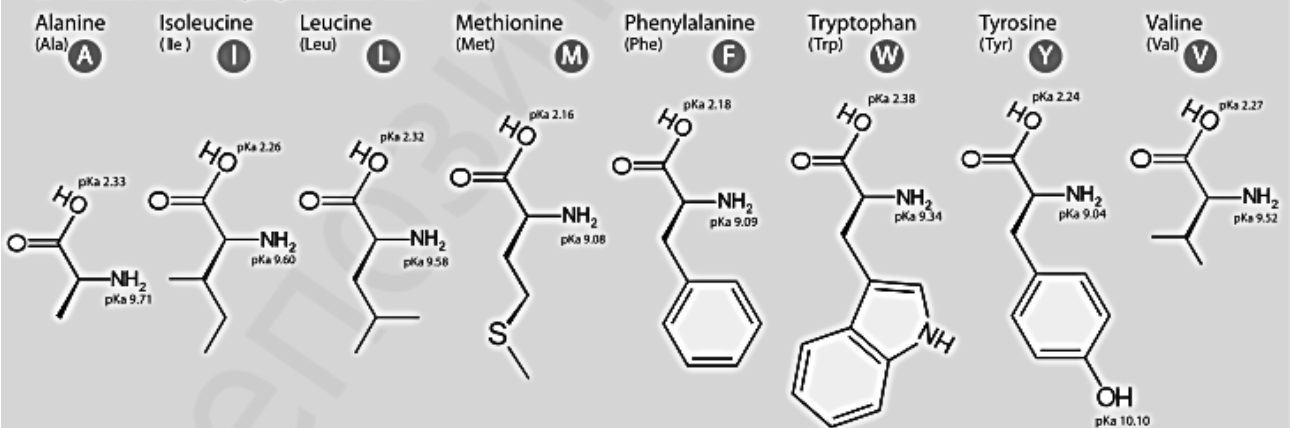
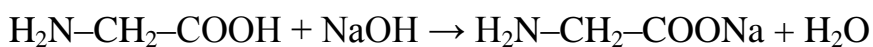
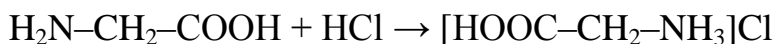


Figure 80. Proteinogenic amino acids

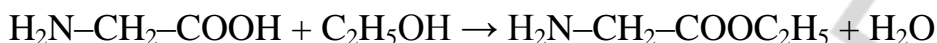
## CHEMICAL PROPERTIES AND PRODUCTION OF AMINO ACIDS

Amino acids can react with both acids and alkali.



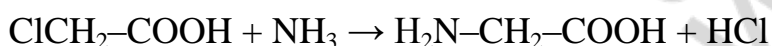
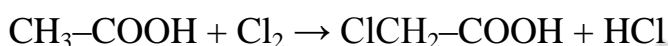
Amino groups become protonated if pH is low. Carboxyl groups become deprotonated if pH is high.

Carboxyl groups of amino acids are able to form esters with alcohols.

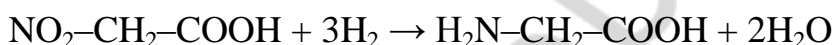
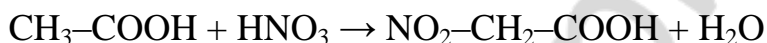


One of the ways to synthesize amino acid is as follows.

Carboxylic acid should react with halogen. Then the product of that reaction should react with ammonia.



Another way is to perform a nitration of a carboxylic acid. Then the product of that reaction should be reduced: nitro group should be converted into amino group.



### TEST FOR CLASSWORK

1. What is the difference between polymerization and polycondensation?
  - a) there are no subproducts of polycondensation
  - b) there are no subproducts of polymerization
  - c) polymerization and polycondensation are synonyms
  - d) synthesis of a polysaccharide is polycondensation, synthesis of polyethylene is polymerization
2. Nucleotide is a monomer of:
  - a) RNA
  - b) protein
  - c) glycogen
  - d) DNA
3. What is the difference between cellulose and starch?
  - a) in starch molecules of glucose are connected by  $\alpha(1\rightarrow4)$  and  $\alpha(1\rightarrow6)$  bonds, while in cellulose they are connected by  $\beta(1\rightarrow4)$  bonds
  - b) cellulose is unbranched, while starch is branched
  - c) starch is unbranched, while cellulose is branched

d) in starch molecules of glucose are connected by  $\alpha(1\rightarrow4)$  bonds, while in cellulose they are connected by  $\beta(1\rightarrow4)$  and  $\beta(1\rightarrow6)$  bonds

4. Choose the pathway to synthesize alanine from  $\text{CH}_3\text{COOH}$ :

- a)  $+\text{Cl}_2 / +\text{NH}_3$                       c)  $+\text{Br}_2 / +\text{NH}_3$   
b)  $+\text{NH}_3 / +\text{H}_2\text{O}$                       d)  $+\text{H}_2 / +\text{N}_2$

5. Amino acids in proteins are connected with each other by:

- a) ionic bonds                              c) peptide bonds  
b) covalent bonds                        d) hydrogen bonds

6. Choose the products of glycine combustion:

- a)  $\text{CO}_2$     b)  $\text{H}_2\text{O}$     c)  $\text{N}_2$     d)  $\text{H}_2$

7. How many atoms are connected to the nitrogen atom of serine in the state of zwitterion?

- a) 1            b) 2            c) 3            d) 4

8. Two strands of DNA are connected together by:

- a) covalent bonds                        c) peptide bonds  
b) ionic bonds                             d) hydrogen bonds

9. DNA molecule is made from the following chemical elements:

- a) C, N, O, P, H                        c) C, N, O, H  
b) C, N, O, S, H                        d) C, N, O, P, S, H

10. Human proteins are made from the following chemical elements (ignore posttranslational modifications):

- a) C, N, O, H                            c) C, N, O, S, H  
b) C, N, O, P, H                        d) C, N, O, P, S, H

#### TEST FOR HOMEWORK

1. Choose amino acids with hydrophilic side chains:

- a) alanine    b) aspartic acid    c) glutamic acid    d) glycine

2. Glucose is a monomer of:

- a) starch            b) cellulose            c) glycogen            d) DNA

3. What is the difference between DNA and RNA?

a) nucleotides of DNA contain deoxyribose, while nucleotides of RNA contain ribose

- b) uracil is normally included in RNA, but not in DNA  
 c) RNA is more stable than DNA  
 d) in all forms of life, except some types of viruses, DNA and not RNA is used for the storage of genetic information
4. Choose the pathway to synthesize ethyl amine from  $C_2H_6$ :  
 a)  $+ Cl_2 / + NH_3$                       c)  $+ Br_2 / + NH_3$   
 b)  $+ HNO_3 / + H_2$                       d)  $+ HNO_3 / + O_2$
5. Nucleotides in a single strand of DNA or RNA are connected with each other by:  
 a) ionic bonds                              c) phosphodiester bonds  
 b) hydrogen bonds                      d) covalent bonds
6. Choose the products of methylamine chloride reaction with alkali:  
 a)  $CO_2$     b)  $H_2O$     c)  $N_2$     d)  $CH_3NH_2$
7. How many atoms are connected to the carbon atom of carboxylic group?  
 a) 1            b) 2            c) 3            d) 4
8. Amino acids can react with:  
 a) alkalis            b) acids            c) oxygen            d) nitrogen
9. Glycogen is made from the following chemical elements:  
 a) C, N, O, P                              c) C, H, O  
 b) C, N, O, S                              d) C, N, O, P, S
10. Human proteins are made from the following chemical elements (consider the possibility of posttranslational modifications):  
 a) C, N, O, H                              c) C, N, O, S, H  
 b) C, N, O, P, H                            d) C, N, O, P, S, H

#### EXERCISES FOR CLASSWORK

- 1. Write four reactions according to the following classic chain of chemical reactions and balance them:**

calcium carbide  $\rightarrow$  acetylene  $\rightarrow$  benzene  $\rightarrow$  nitrobenzene  $\rightarrow$  aniline

1. \_\_\_\_\_  
 2. \_\_\_\_\_  
 3. \_\_\_\_\_  
 4. \_\_\_\_\_



**Write the second reaction with another product:**

**2. Write four reactions according to the following classic chain of chemical reactions and balance them:**

butane → ethane → nitroethane → ethylamine → ethylamine chloride

1. \_\_\_\_\_

2. \_\_\_\_\_

3. \_\_\_\_\_

4. \_\_\_\_\_

**Write the backward process for the fourth reaction:**

**3. Draw the structural formula of glycyl serine:**

**4. Determine the mass of hydrochloric acid required for the reaction with 20 g of glycine.**

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

**5. Find the simplest formula of an organic substance. Complete combustion of 1.384 g of that substance resulted in the production of 1 L of carbon dioxide, 0.5 L of nitrogen and 2 g of water.**

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\_\_\_\_\_

6. Calculate the volume of methylamine (in normal conditions) produced in the reaction between 10 g of methylamine chloride and the excess of potassium hydroxide.

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7. Calculate the mass of glycyl alanine formed from 4 g of glycine.

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8. 7.8 g of nitrobenzene reacted with hydrogen. As a result, 5.5 g of aniline have been produced. Determine the yield of the reaction.

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#### EXERCISES FOR HOMEWORK

1. Write four reactions according to the following classic chain of chemical reactions and balance them:

ethane → chloroethane → ethylamine → ethylamine chloride → ethylamine

1. \_\_\_\_\_

2. \_\_\_\_\_

3. \_\_\_\_\_

4. \_\_\_\_\_

Write the first reaction with another halogen:

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2. Write four reactions according to the following classic chain of chemical reactions and balance them:

methanol  $\rightarrow$  chloromethane  $\rightarrow$  ethane  $\rightarrow$  nitroethane  $\rightarrow$  nitrogen

1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

Write the second reaction if the product is propane:

\_\_\_\_\_

3. Draw the structural formula of alanyl aspartate:

4. Determine the mass of sodium hydroxide required for the reaction with 20 g of glycine.

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

5. The products of the combustion of 20 g of organic substance are 23.172 L of carbon dioxide and 18.621 g of water. Determine the simplest formula of that compound.

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

**6. Calculate the volume of propylamine (density is 0.72 g/ml) produced in the reaction between 20 g of propylamine chloride and the excess of sodium hydroxide.**

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**7. Calculate the mass of alanyl valine formed from 3 g of alanine.**

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**8. The yield of the solid phase peptide synthesis is 99.5 % for each peptide bond formation. Determine the yield of the synthesis of a peptide 30 amino acids in length.**

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## LESSON 12. CONTROL WORK ON ORGANIC CHEMISTRY

### SAMPLE TASKS FROM THE CONTROL WORK

1. What volume is occupied by 68 g of ethylene in normal conditions?

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2. Determine the volume of oxygen gas which is needed to burn down a mixture composed of 7 liters of ethane and 25 liters of propane.

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3. Nitrobenzene (8.8 g) reacted with hydrogen gas. As a result, 2.5 g of aniline have been produced. Determine the yield of the reaction.

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4. Determine the volume of acetylene which can be produced from 1 kg of calcium carbide containing 35 % of impurities.

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5. What is the volume carbon dioxide (CO<sub>2</sub>) produced in the process of alcoholic fermentation of 38 g of glucose. The yield of the reaction is equal to 60 %.

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6. Acetaldehyde reacted with Tollens' reagent and produced 6.48 g of silver. Determine the mass of acetaldehyde.

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7. The products of the combustion of 10 g of organic substance are 7.304 L of carbon dioxide and 7.826 g of water. Determine the simplest formula of that compound.

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8. Find the mass of alanine produced after the complete hydrolysis of 25 g of alanyl glutamate.

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## SAMPLE CHAINS OF CHEMICAL REACTIONS FROM THE CONTROL WORK

- 1. Write four reactions according to the following classic chain of chemical reactions and balance them:**

ethane → ethene → bromoethane → ethanol → chloroethane

1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

- 2. Write four reactions according to the following classic chain of chemical reactions and balance them:**

methanol → chloromethane → propane → bromopropane → propene

1. \_\_\_\_\_
2. \_\_\_\_\_
3. \_\_\_\_\_
4. \_\_\_\_\_

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