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БЕЛОРУССКИЙ ГОСУДАРСТВЕННЫЙ МЕДИЦИНСКИЙ УНИВЕРСИТЕТ
КАФЕДРА ОБЩЕЙ ХИМИИ

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**ВВЕДЕНИЕ
В ОРГАНИЧЕСКУЮ ХИМИЮ**

**INTRODUCTION
TO THE ORGANIC CHEMISTRY**

Учебно-методическое пособие



Минск БГМУ 2015

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PREFACE

The book provides an introduction into the Organic Chemistry. It is necessary for foreign students who are going to pass the entrance Chemistry exam into the Belorussian State Medical University in English.

The material from this book is enough for answering questions and solving tasks on the organic chemistry from the entrance exam. This book is a good background for students who are studying the “Bioorganic Chemistry” and “Biochemistry” subjects on the first course.

Authors are looking forward to receive any feedback from readers and colleagues regarding style and content of the book.

LESSON 1

1.1. STRUCTURE OF ALKANES

The simplest organic compounds are those composed of only two elements: hydrogen (H) and carbon (C). These compounds are called hydrocarbons. 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 a ring of C atoms; these hydrocarbons are called cycloalkanes.

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:

The methane molecule is three dimensional, with the H atoms in the positions of the four corners of a tetrahedron (figure 1.1). Each carbon atom exists in a state of sp^3 hybridization in alkanes.

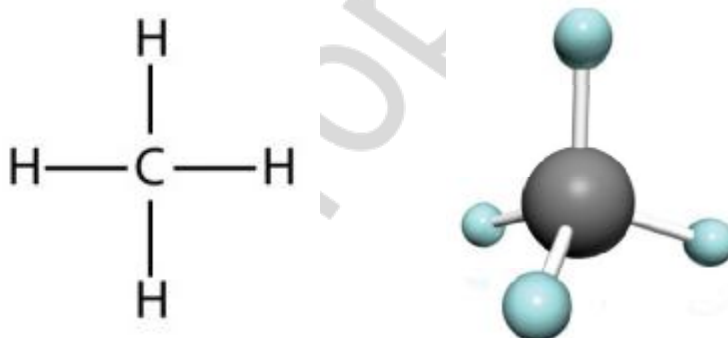


Figure 1.1. 2D and 3D structures of methane

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 1.2).

Propane (C_3H_8) has a backbone of three C atoms surrounded by H atoms (figure 1.3).

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_3CH_3 , while for propane it is $\text{CH}_3\text{CH}_2\text{CH}_3$.

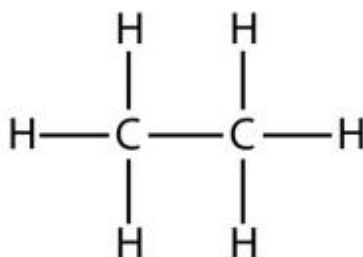


Figure 1.2. Structural formula of ethane

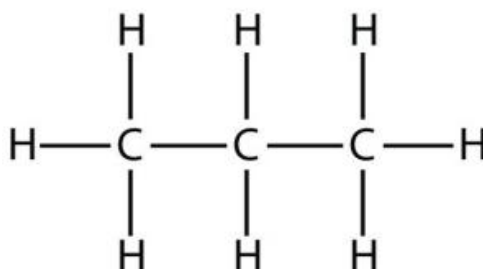


Figure 1.3. Structural formula of propane

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 $\text{C}_n\text{H}_{2n+2}$, 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 1.1.

Table 1.1

First ten alkanes and their characteristics

Molecular Formula	Condensed Structural Formula	Name	State of matter in normal conditions
CH_4	CH_4	methane	gas
C_2H_6	CH_3CH_3	ethane	gas
C_3H_8	$\text{CH}_3\text{CH}_2\text{CH}_3$	propane	gas
C_4H_{10}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	butane	gas
C_5H_{12}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	pentane	liquid
C_6H_{14}	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	hexane	liquid
C_7H_{16}	$\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	heptane	liquid
C_8H_{18}	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	octane	liquid
C_9H_{20}	$\text{CH}_3(\text{CH}_2)_7\text{CH}_3$	nonane	liquid
$\text{C}_{10}\text{H}_{22}$	$\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	decane	liquid

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.

1.2. 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 1.4 the longest chain of carbons has six C atoms. Therefore, it will be named as a **hexane**.

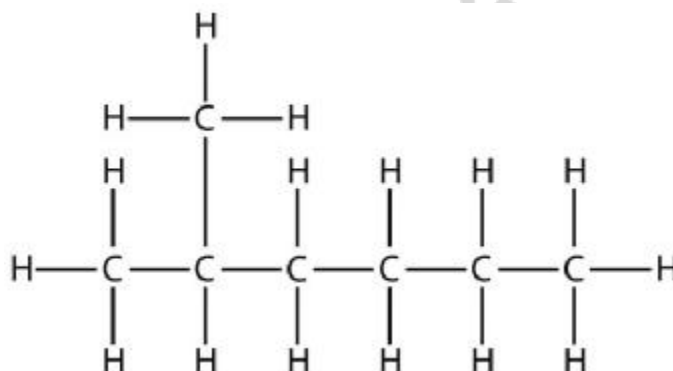


Figure 1.4. Structural formula of 2-methylhexane

However, in the molecule from figure 1.5 the longest chain of C atoms is not six, but seven, as shown by arrows. So this molecule will be named as a **heptane**.

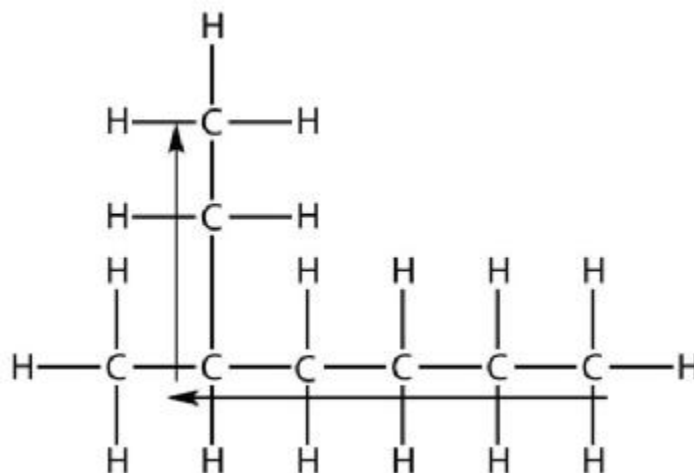


Figure 1.5. Structural formula of 3-methylheptane

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 2.1); however, rather than having the ending *-ane*, the substituent name has the ending *-yl*.

Table 2.1

Alkyl substituent names

Substituent Formula	Number of C Atoms	Name of Substituent
CH ₃	1	<i>methyl-</i>
CH ₃ CH ₂	2	<i>ethyl-</i>
CH ₃ CH ₂ CH ₂	3	<i>propyl-</i>
CH ₃ CH ₂ CH ₂ CH ₂	4	<i>butyl-</i>
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂	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 1.6 the longest chain is five C atoms long, so it is a pentane.

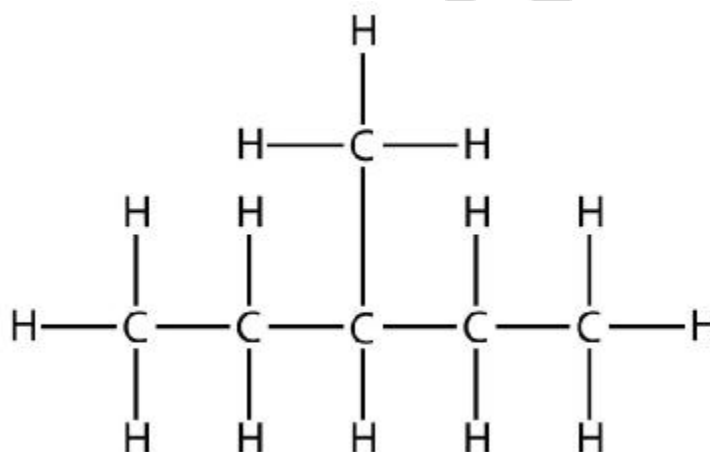


Figure 1.6. Structural formula of 3-methylpentane

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.

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.

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 1.7, there are several ways to reproduce its structure (both in 2D and 3D pictures).

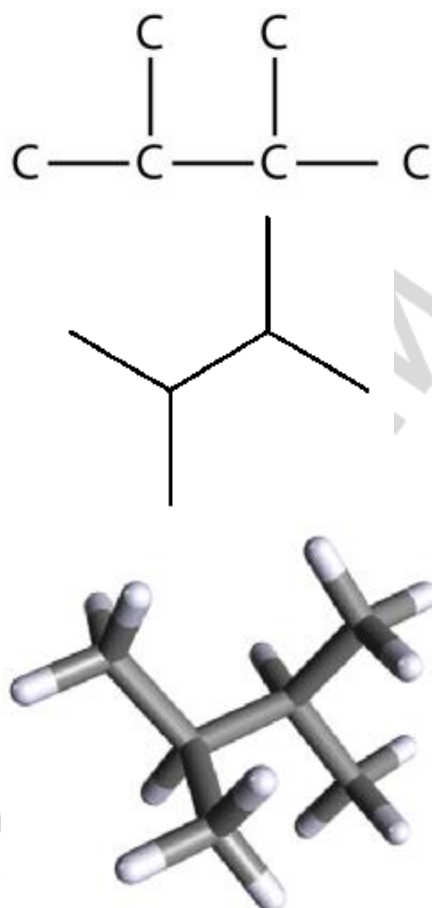


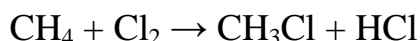
Figure 1.7. Three ways to represent the structure of 2,3-dimethylbutane

One of the simplest ways of structural formula reproduction is called representation by “smiles”: CC(C)C(C)C.

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*.

1.3. 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 sometimes used 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.

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 CH_3Cl 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 1.8 is 2-bromobutane, while the molecule from figure 1.9 is 2,3-dichloropentane.

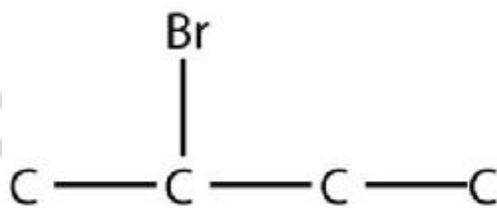


Figure 1.8. Structural formula of 2-bromobutane (hydrogen atoms are not shown)

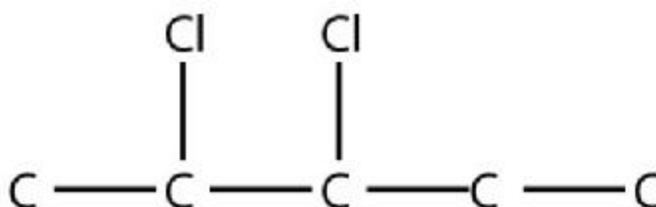
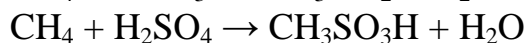
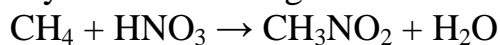


Figure 1.9. Structural formula of 2,3-dichloropentane (hydrogen atoms are not shown)

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

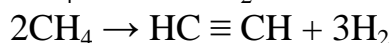
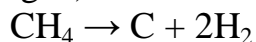
Alkanes react with diluted nitric and concentrated sulfuric and nitric acids in a way similar to halogens.



The products are nitromethane and sulfomethane. We can simplify those reactions and say that $-\text{OH}$ group of nitric acid (or sulfuric acid) interacts with hydrogen from an alkane and forms water, while the remaining part of HNO_3 molecule ($-\text{NO}_2$ group) combines with the carbon atom (the remaining part of sulfuric acid molecule is $-\text{SO}_3\text{H}$ group).

Reactions of alkanes with halogens and acids are substitution reactions.

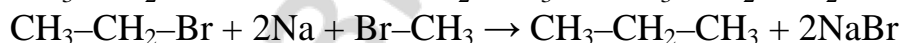
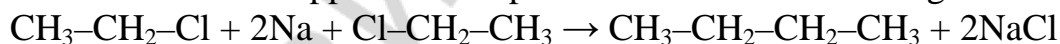
Alkanes can be decomposed at high temperatures without access of oxygen. That decomposition may be complete (breaking into hydrogen and soot), or incomplete (when unsaturated hydrocarbons are formed along with hydrogen).



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 alkyl 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:

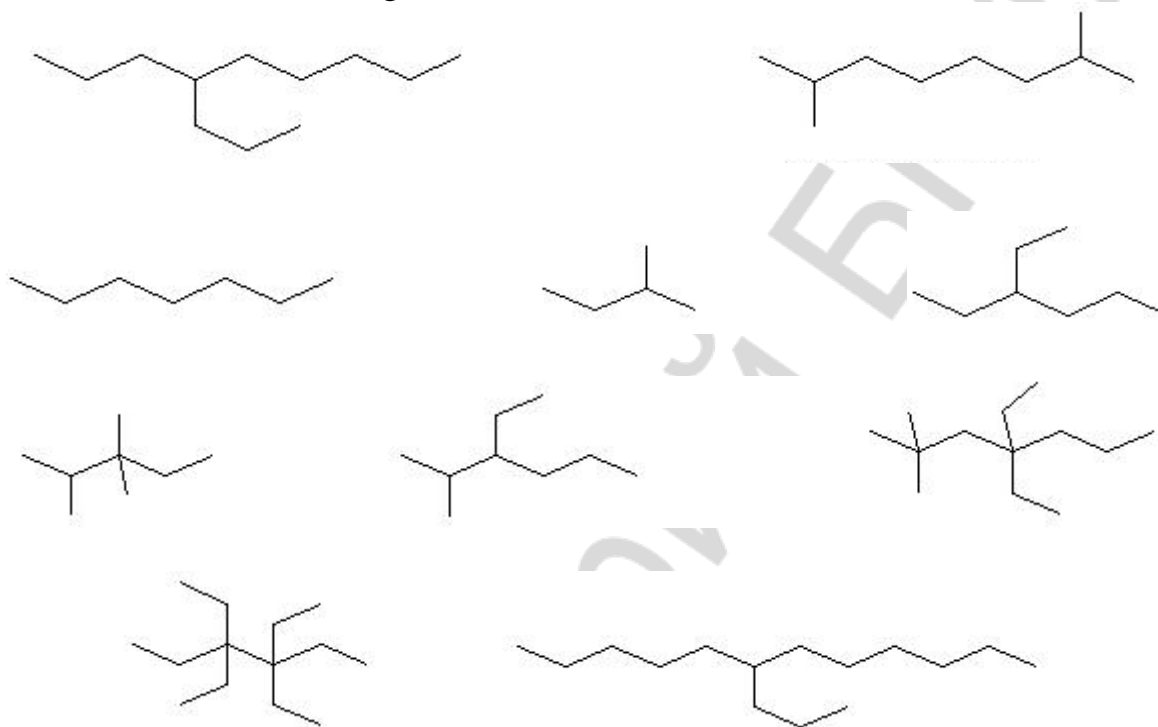


Exercises

1. Draw the carbon backbone for each molecule.

1. 3,4-diethyloctane
2. 2,2-dimethyl-4-propylnonane
3. 5-butyl-2,2-dimethyldecane
4. 4-propyl-3-ethyl-2-methyloctane
5. 4-isopropylheptane

2. Name the following alkanes



3. Determine the volume of air which is needed to burn down a mixture composed of 3 liters of ethane and 20 liters of propane.

4. A mixture of propane and butane has a volume of 6 liters. 37.2 liters of oxygen gas been used to burn down that mixture of gases. Determine the volume percentage of that mixture.

5. An alkane (4.3 g) has been burned down. The volume of carbon dioxide produced is equal to 6.72 liters, the mass of water is equal to 6.3 g. Determine the formula of that compound.

LESSON 2

2.1. STRUCTURE AND NOMENCLATURE OF ALKENES

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

Alkenes have a double bond (C=C). Because they have less than the maximum number of possible H atoms, 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 2.1) and is also known by its common name ethylene.

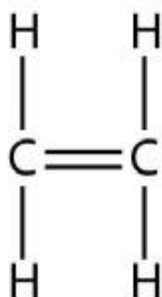


Figure 2.1. Structural formula of ethene (ethylene)

The next alkene (propene) has three C atoms with a C=C double bond between two of the C atoms (figure 2.2). It is also known as propylene.

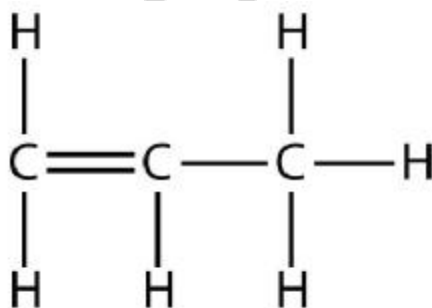


Figure 2.2. Structural formula of propene

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 2.3).

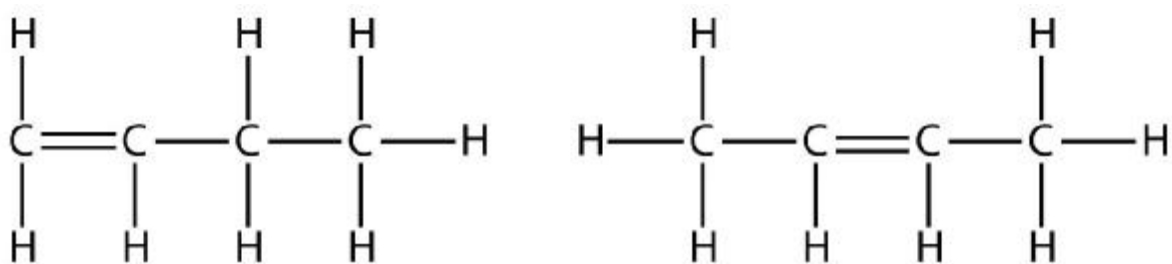


Figure 2.3. Structural formulas of two isomers of butene (1-butene and 2-butene)

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. 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 .

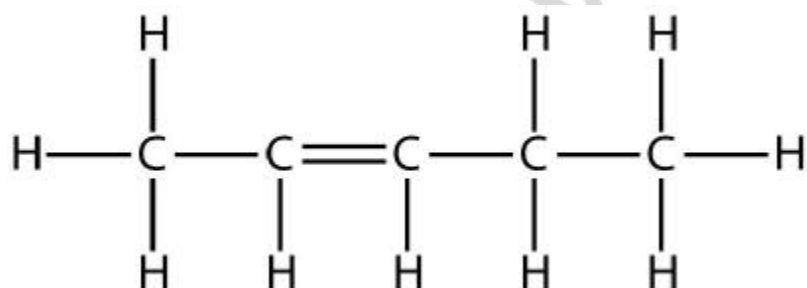


Figure 2.4. Structural formula of 2-pentene

With five C atoms, we will use the *pent-* stem, and with a $\text{C}=\text{C}$ 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.

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 2.5). 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-butane there are two hydrogen atoms connected to the first carbon atom which participates in the double bond formation. For these reason such molecule cannot have *cis-* and *trans-* isomers.

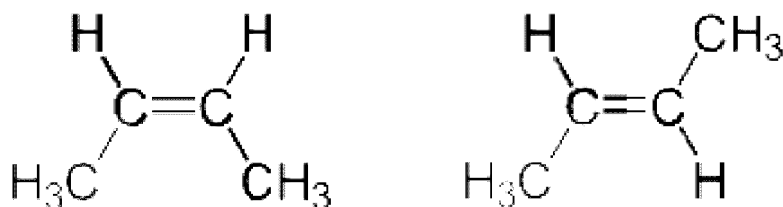


Figure 2.5. Structural formulas of 2-*cis*-butene and 2-*trans*-butene

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.

2.2. 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.

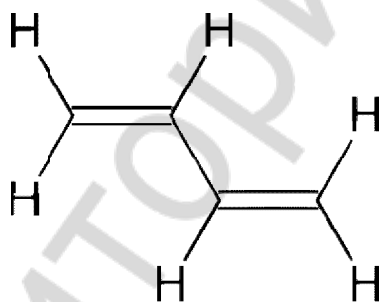


Figure 2.6. Structural formula of 1,3-butadiene

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.

2.3. 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, which is also known as acetylene:



Figure 2.7. Structural formula of ethyne (acetylene)

Propyne has the structure shown in figure 2.8.

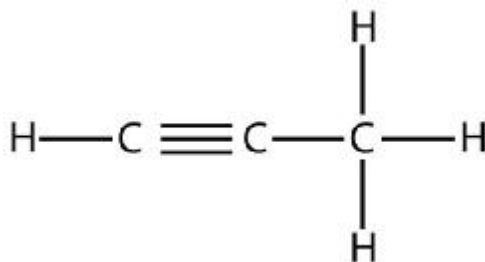


Figure 2.8. Structural formula of propyne

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

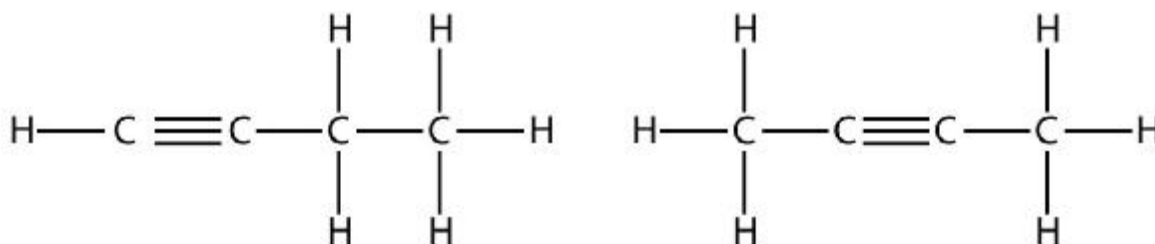


Figure 2.9. Structural formulas of two isomers of butyne (1-butyne and 2-butyne)

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 2.10 is 2,4-dimethyl-3-heptene (note the number and the hyphens that indicate the position of the double bond).

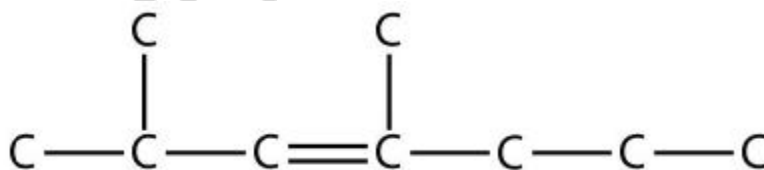


Figure 2.10. Carbon backbone of 2,4-dimethyl-3-heptene (hydrogen atoms are not shown)

The longest chain of the molecule from figure 2.11 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.

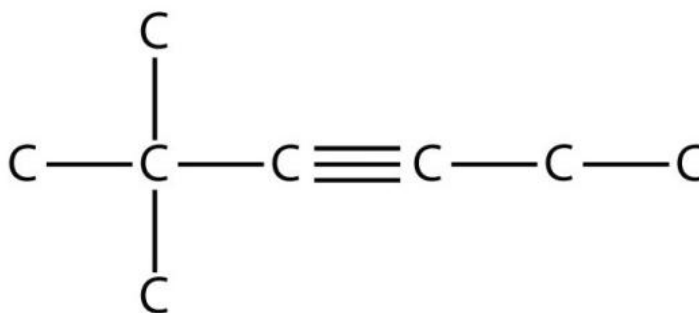


Figure 2.11. Carbon backbone of 2,2-dimethyl-3-hexyne (hydrogen atoms are not shown)

Electron orbitals of carbon atoms forming the triple bond are in the sp^1 hybridization state.

Exercises

- Name and draw the structural formula of each isomer of pentene.
- Name and draw the structural formula of each isomer of 1,3-pentadiene.
- Name and draw the structural formula of each isomer of hexyne.
- Draw the carbon backbone for each molecule.
 - 3-ethyl-4-methyl-3-heptene
 - 5,5-diethyl-1,3-octadiene
 - 3,4-diethyl-1-hexyne
- Are there cis- and trans- isomers for:
 - 2,3-dimethyl-2-butene
 - 1-butene
 - 2-methyl-2-butene
 - 2-hexene
 - 3,4-dimethyl-3-hexene
 - 3,4-dimethyl-2-hexene
 - 3,4-dimethyl-1-hexene
 - 3-ethyl-2-pentene
- How many isomers are there for the molecule with the C_8H_{14} formula?

LESSON 3

3.1. 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 3.1.

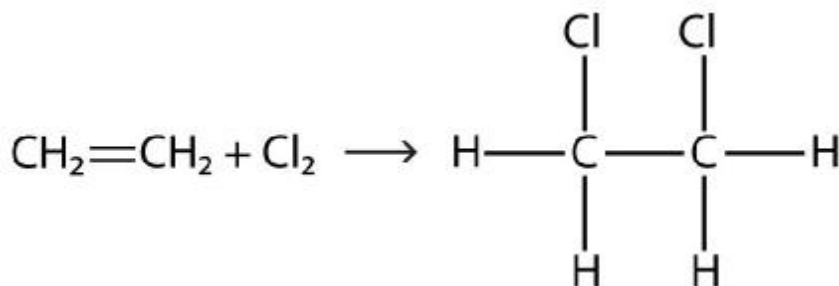
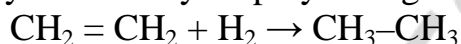


Figure 3.1. Reaction between ethene and chlorine

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

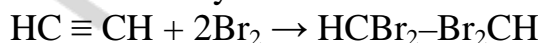
Hydrogen can also be added across a multiple bond; this reaction is called a hydrogenation reaction. In this case, however, the reaction conditions may not be mild; high pressures of H_2 gas may be necessary. A platinum or palladium catalyst is usually employed to get the reaction to proceed.



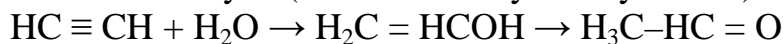
Hydrogen chloride, hydrogen bromide, hydrogen iodide and water can also participate in addition reactions with alkenes, dienes and alkynes. In those reactions a hydrogen atom from an inorganic compound more frequently goes to that carbon atom which already has a higher number of hydrogen atoms, while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



Reaction with bromine water (intense yellow mixture containing diatomic bromine — Br_2 — of 2.8 % dissolved in H_2O) 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.



Alkynes react with water in a special manner. 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.

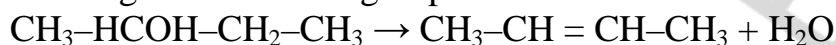


3.2. PRODUCTION OF ALKENES, DIENES AND ALKYNES

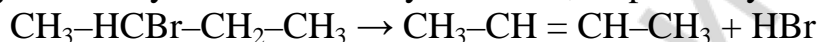
Double bond may be formed in a saturated hydrocarbon in the dehydrogenation reaction.



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.



In a similar way hydrogen chloride or hydrogen bromide may be taken away from alkyl chloride or alkyl bromide, respectively.



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).

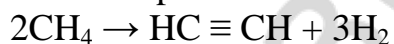


Acetylene can be produced in a very specific reaction between calcium carbide (an inorganic compound) and water.



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.



Exercises

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. Draw the structure of the product of the reaction of hydrogen with 1-butene.
4. Draw the structure of the product of the reaction of hydrogen with 2-pentene.
5. Determine the volume of acetylene which can be produced from 1 kg of calcium carbide containing 30 % of impurities.

6. What is the volume of vinyl chloride produced in the following 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 %.

7. A mixture of ethane and acetylene reacted with bromine water. The mass of bromine water solution became higher. The difference was equal to 1.3 g. 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?

8. 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 that mixture of gases.

LESSON 4

4.1. POLYMERIZATION OF ALKENES

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

For example, ethylene has a double bond.

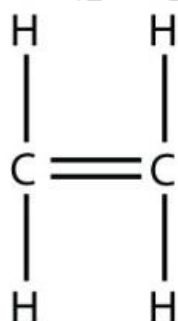


Figure 4.1. Structural formula of ethene (ethylene)

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

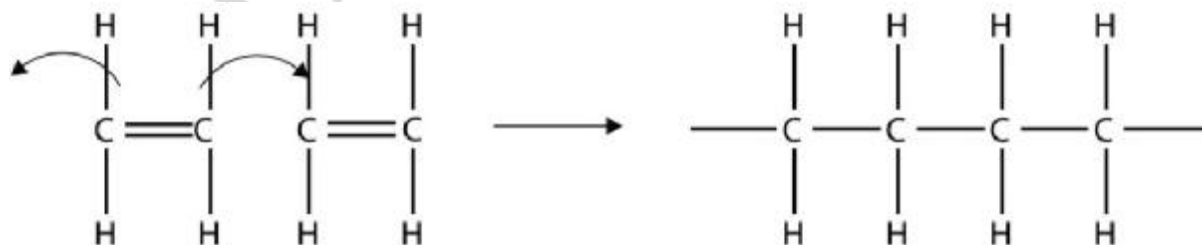


Figure 4.2. Polymerization of ethene

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.

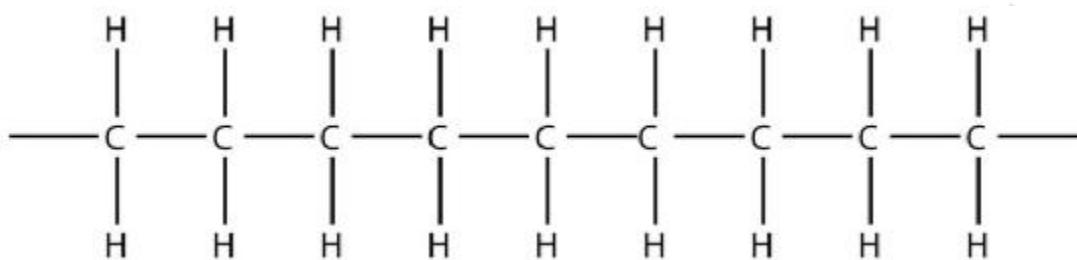


Figure 4.3. Structural formula of polyethylene fragment

This long, almost endless molecule is called a polymer (from the Greek word meaning “something made from many similar parts”). The original part — ethylene — is called a monomer (meaning “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.

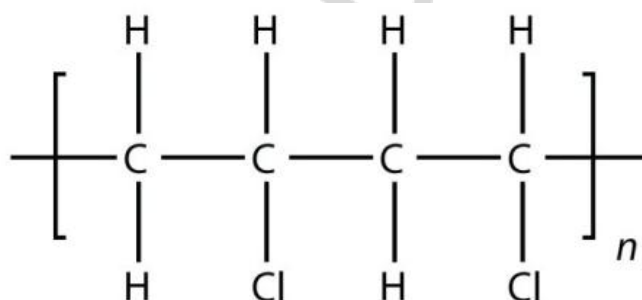


Figure 4.4. Structural formula of polyvinylchloride fragment

It is a product of ethylene chloride polymerization.

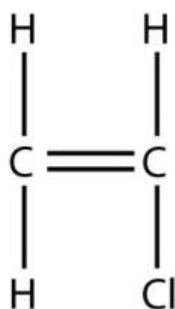


Figure 4.5. Structural formula of vinyl chloride

4.2. 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, 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, polybutadienes differ in terms of their branching and molecular weights.

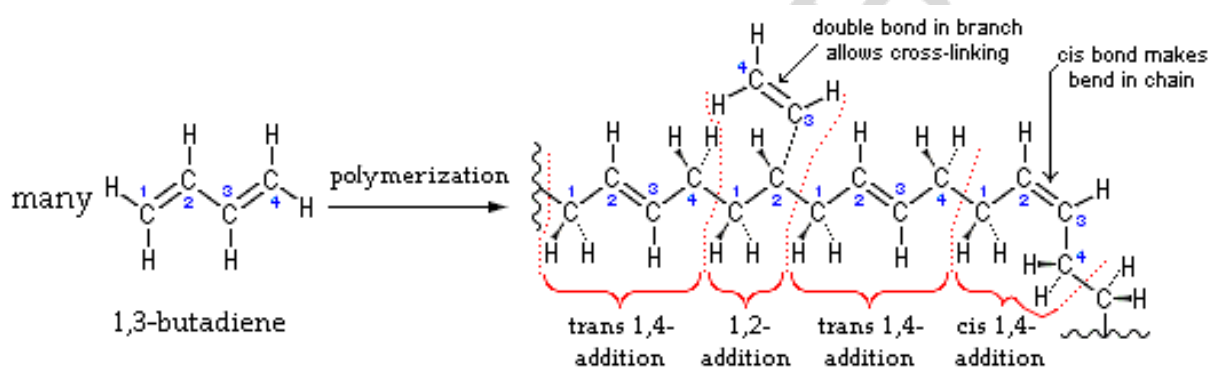


Figure 4.6. 1,3-butadiene polymerization

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

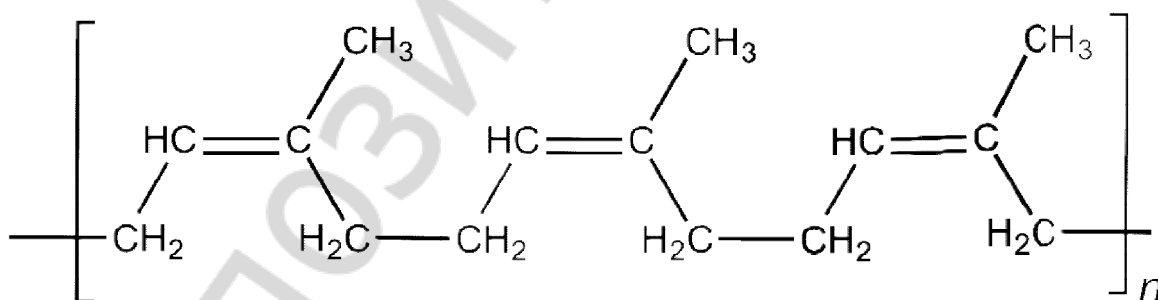
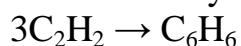


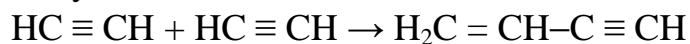
Figure 4.7. Structure of the cis-polyisoprene fragment

4.3. POLYMERIZATION OF ALKYNES

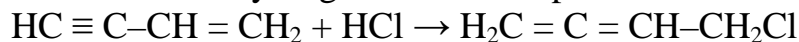
Acetylene polymerization may produce benzene molecules. This process requires three acetylene molecule and so it is called trimerization.



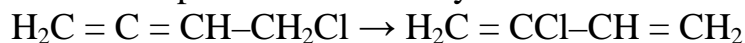
Acetylene molecules can also be dimerized. The product contains one single, one double and one triple bond. The name of that compound is vinylacetylene.



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

1. What is the number of monomers in the polyethylene pocket that has a mass of 10 g?
2. What is the number of monomers in the synthetic rubber made from 1,3-butadiene that has a mass of 100 g?
3. What is the number of monomers in the synthetic rubber made from chloroprene that has a mass of 200 g?
4. What is the number of monomers in the natural rubber made from isoprene that has a mass of 300 g?
5. Calculate the mass of acetylene that is needed to produce 1 kg of polyvinylchloride if the total yield is equal to 80 %. How many steps are required for this process?
6. Calculate the mass of ethanol required for synthesis of 5 kg of poly-1,3-butadiene. The total yield of the process equals to 70 %.

LESSON 5

5.1. 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. In modern chemistry the term *aromatic* denotes the presence of a six-membered ring 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.

Aromatic compounds contain the benzene unit. Benzene itself is composed of six C atoms in a ring, with alternating single and double bonds (figure 5.1).

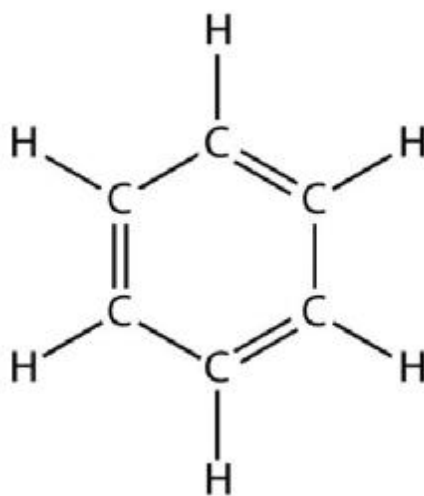


Figure 5.1. Structural formula of benzene with 3 double and 3 single bonds

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 structural formula for arenes is C_nH_{2n-6} .

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 5.2). 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 5.3).

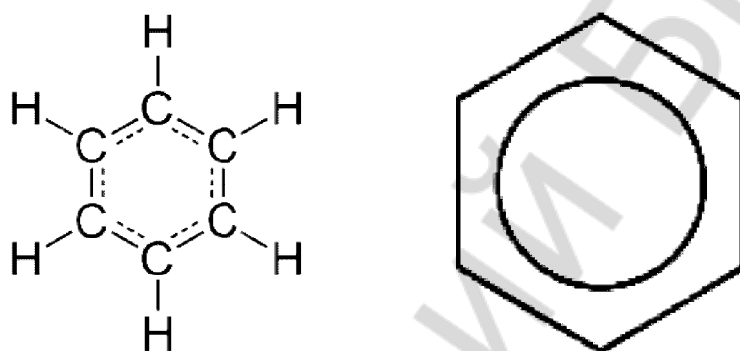


Figure 5.2. Structural formula of benzene with 1.5 bonds and aromatic ring

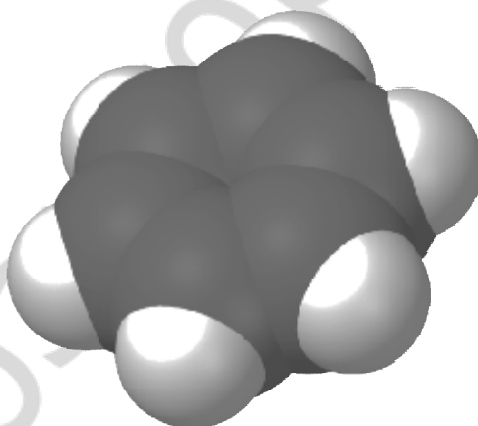


Figure 5.3. 3D structure of benzene

Indeed, the distance between two carbons connected by a single bond is equal to 0.154 nm. The distance between two carbons connected by 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 5.4.

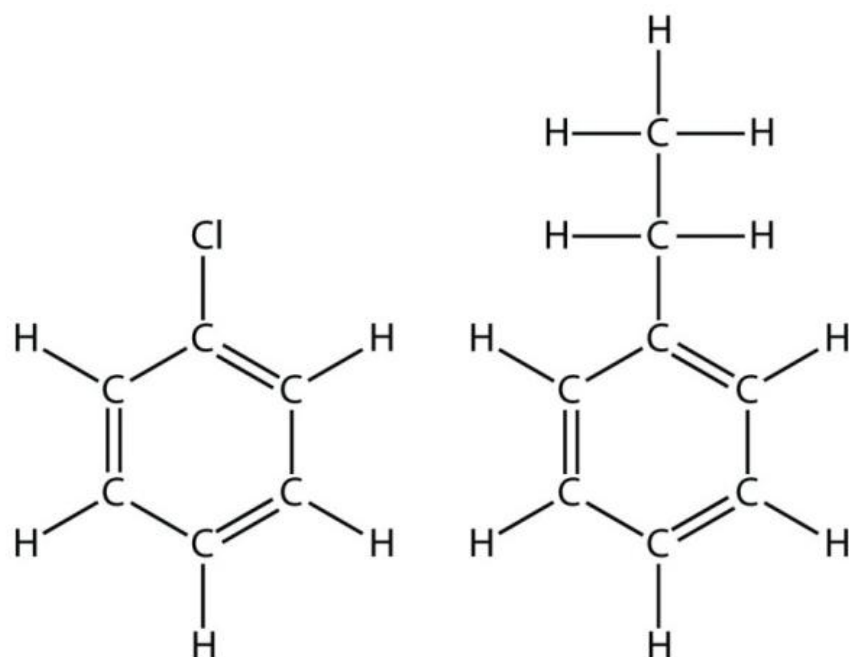


Figure 5.4. Structural formulas of chlorobenzene and ethylbenzene

If there are two or more substituents on a benzene molecule, 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).

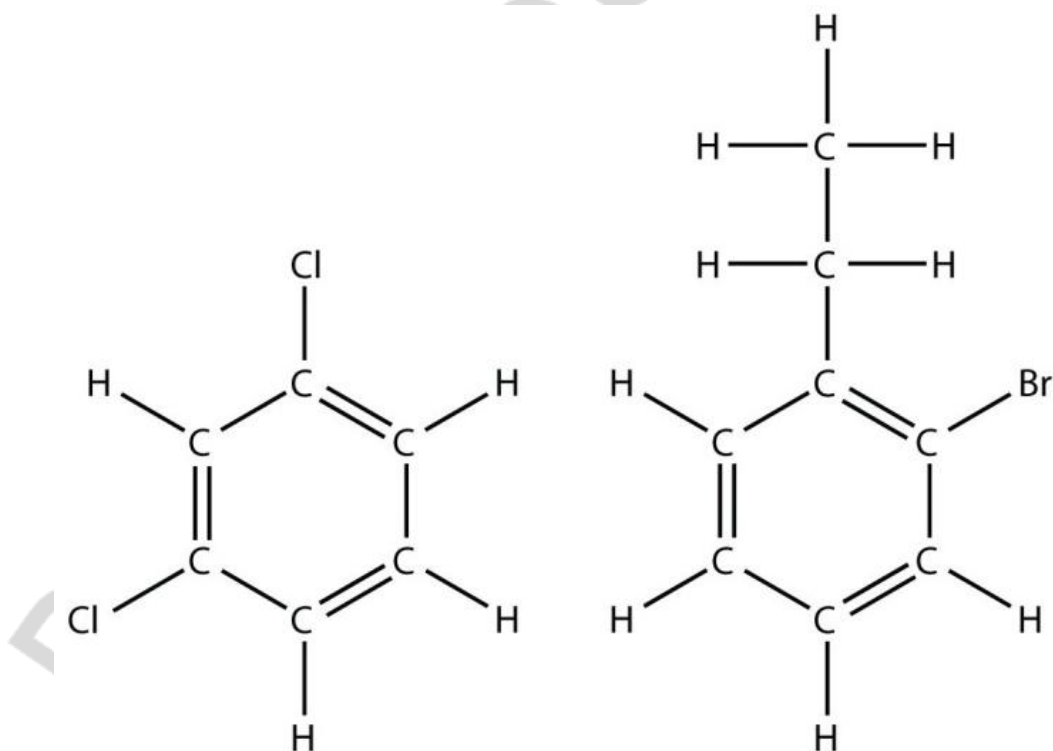


Figure 5.5. Structural formulas of 1,3-dichlorobenzene and 1-bromo-2-ethylbenzene

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 5.6).

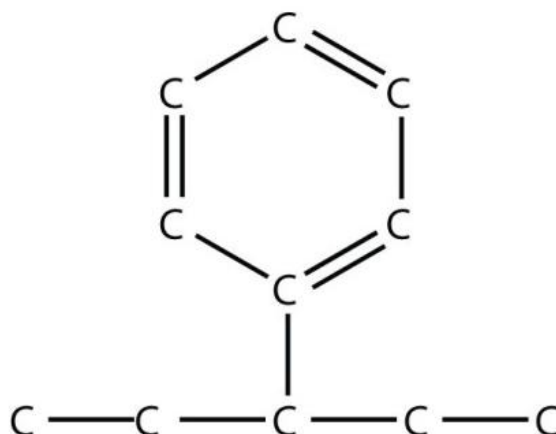


Figure 5.6. Carbon backbone of 3-phenylpentane (hydrogen atoms are not shown)

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 5.7 there are three isomers of xylene: *ortho*-, *meta*-, and *para*-xylene.

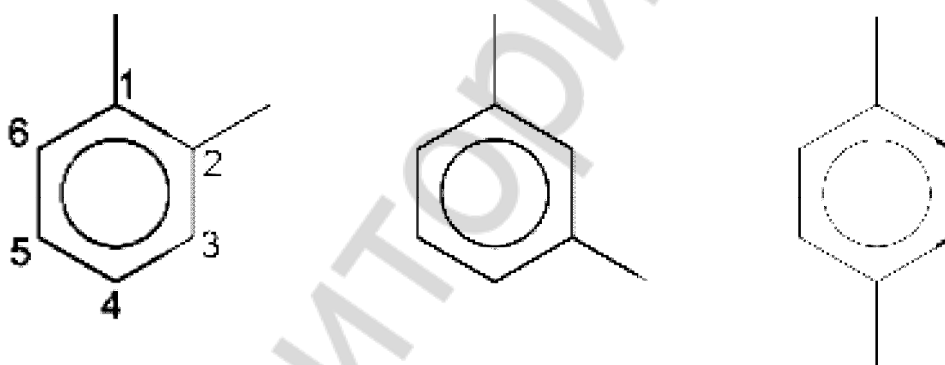
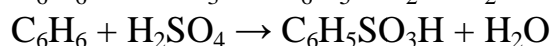
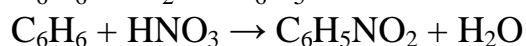
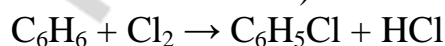


Figure 5.7. Schemes of 1,2-dimethylbenzene (*ortho*-xylene), 1,3-dimethylbenzene (*meta*-xylene), 1,4-dimethylbenzene (*para*-xylene)

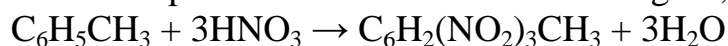
Toluene (toluol) is a compound that consists from benzene ring and a single methyl substituent. Obviously, toluene has no isomers.

5.2. 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).



Toluene (methylbenzene) is more reactive than benzene. Three hydrogen atoms can be replaced in the reactions with halogens, nitric and sulfuric acids.



Resulting compound (2,4,6-trinitrotoluene known as “TNT”) is an explosive material (figure 5.8).

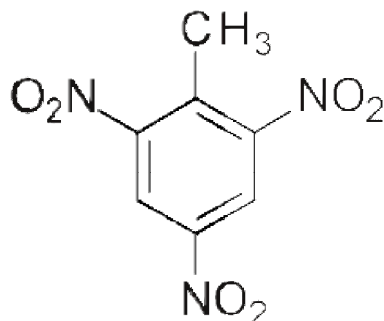
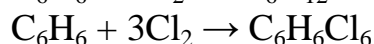
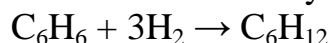


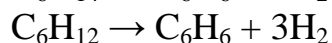
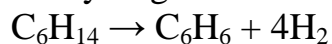
Figure 5.8. Structural formula of 2,4,6-trinitrotoluene

In special conditions arenes are able to participate in addition reactions (just like alkenes and alkynes).

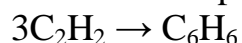


5.3. PRODUCTION OF ARENES

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.



Questions

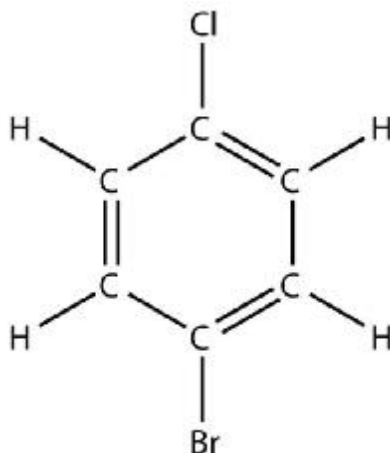
1. What does the term *aromatic* imply about an organic molecule?
2. What are the distances between two carbon atoms connected by single, double and aromatic bonds?

Exercises

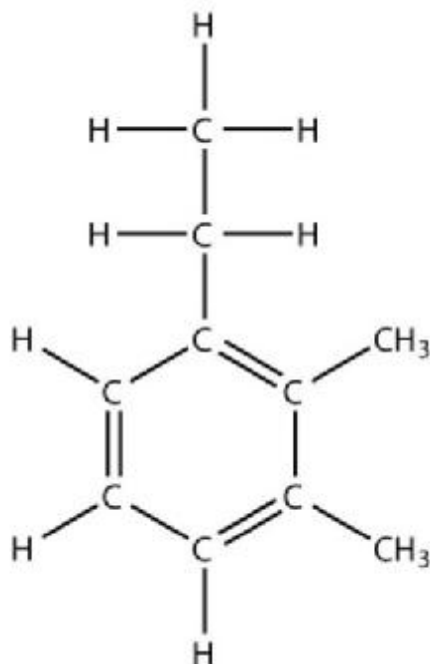
1. Calculate the mass of benzene which can be produced from 44.8 L of acetylene. The yield of the reaction is equal to 40 %.
2. 78 g of benzene reacted with bromine. The mass of bromobenzene is equal to 75 g. Determine the yield of the reaction.

3. Calculate the volume of oxygen which is required to burn down a mixture of benzene and toluene. The volume of the mixture is equal to 10 L. Volume percentage of toluene is 40 %.

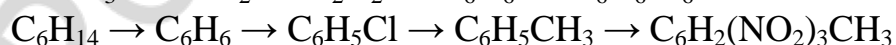
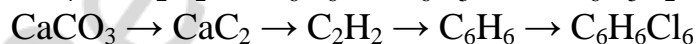
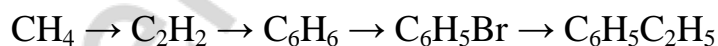
4. Name this molecule.



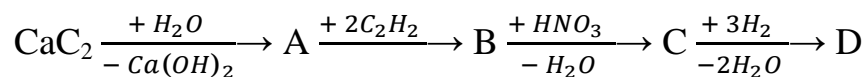
5. Name this molecule.



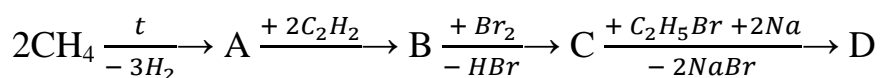
6. Classic chains of chemical reactions



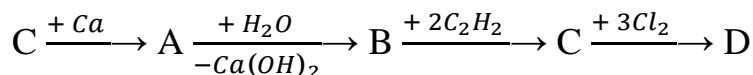
7. Calculate the sum of molecular masses for compounds A, B, C and D from the chain of chemical reactions.



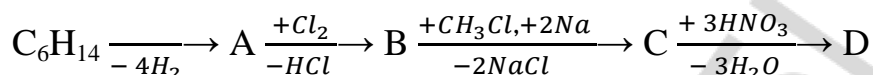
8. Calculate the sum of molecular masses for compounds A, B, C and D from the chain of chemical reactions.



9. Calculate the sum of molecular masses for compounds A, B, C and D from the chain of chemical reactions.



10. Calculate the sum of molecular masses for compounds A, B, C and D from the chain of chemical reactions.



LESSON 6

6.1. STRUCTURE AND NOMENCLATURE OF ALCOHOLS

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

Simple acyclic alcohols have the general formula of $\text{C}_n\text{H}_{2n+1}\text{OH}$. In common speech the word alcohol refers specifically to ethanol ($\text{C}_2\text{H}_5\text{OH}$).

Hydroxyl group can be linked to aromatic ring. The simplest compound formed by aromatic ring and hydroxyl group (phenol) has a formula of $\text{C}_6\text{H}_5\text{OH}$.

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_3OH is methyl alcohol; $\text{CH}_3\text{CH}_2\text{OH}$ is ethyl alcohol, and $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ is propyl alcohol.

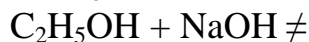
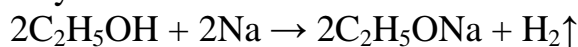
The formal system of naming uses the name of the hydrocarbon containing the OH group and having the correct number of C atoms, dropping the final *-e* of the name and appending the suffix *-ol*. Thus CH_3OH is methanol and $\text{CH}_3\text{CH}_2\text{OH}$ is ethanol. For larger alcohol molecules, we 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, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ is 1-propanol, while $\text{CH}_3\text{CHOHCH}_3$ is 2-propanol.

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.

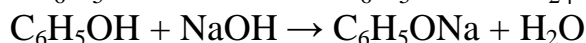
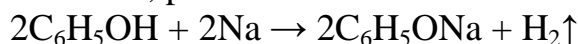
Small alcohols are highly soluble in H₂O because these molecules can engage in hydrogen bonding with H₂O molecules. For larger molecules, however, the polar OH group is overwhelmed by the nonpolar alkyl part of the molecule. While methanol is soluble in H₂O in all proportions, only about 2.6 g of pentanol will dissolve in 100 g of H₂O. Larger alcohols have an even lower solubility in H₂O.

6.2. CHEMICAL PROPERTIES OF ALCOHOLS

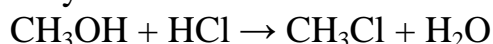
Acyclic alcohols can react with active metals, but cannot react with alkali.



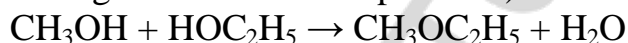
However, phenol is able to react with both active metals and alkali.



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 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 ($t^\circ > 140^\circ \text{C}$).



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.

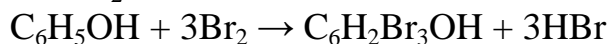


There is a specific reaction in which 1,3-butadiene can be produced from ethanol.



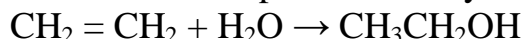
Polyatomic alcohols (those which contain two and more OH groups) react with copper (II) hydroxide. The color of the solution becomes blue.

Phenol is more reactive compound than benzene because of the influence of OH group on the aromatic ring. Just like toluene it is able to react with three moles of Br₂.

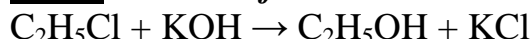


6.3. PRODUCTION OF ALCOHOLS

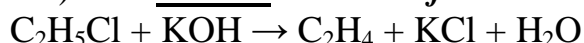
Alcohols can be produced in hydration reactions.



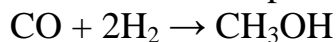
Water solution of alkali can react with alkyl halides and produce alcohols.



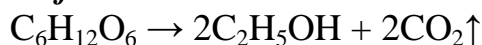
Pay attention to the fact that alkyl halides will produce alkenes (and not alcohols) with **alcohol solution of alkali**.



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

a. 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.

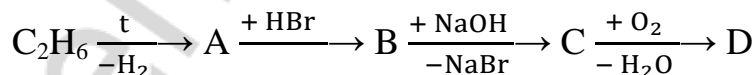
b. Calculate the mass of methanol which has been burned down. The volume of CO₂ produced is equal to 56 L.

c. 6 g of Br₂ reacted with 23.5 g of phenol solution. Calculate the mass percentage of phenol in the solution.

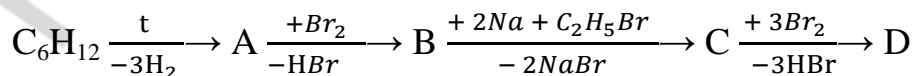
d. A mixture of ethanol and propanol has a mass of 16.6 g. That mixture reacted with sodium and produced 3.36 L of hydrogen gas. Determine the mass percentage of ethanol in the mixture.

e. Determine the formula of acyclic alcohol reacted with 13.8 g of sodium and produced hydrogen gas which is sufficient to hydrate 3.36 L of propylene.

f. Calculate the sum of molecular masses for compounds A, B, C and D from the chain of chemical reactions.



g. Calculate the sum of molecular masses for compounds B and D from the chain of chemical reactions.



LESSON 7

7.1. 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-CHO, 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 7.1). The main thing to note about aldehydes is that the carbonyl group is at the *end* of a carbon chain.

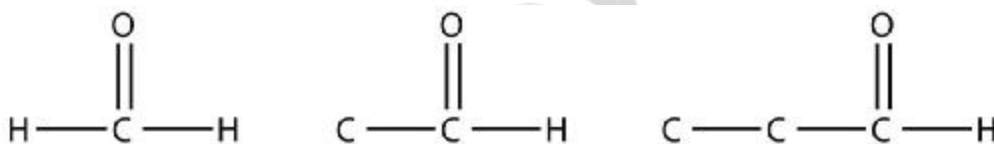


Figure 7.1. Carbon backbones of methanal, ethanal and propanal

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 7.2). When naming a ketone, we take the name of the parent hydrocarbon and change the suffix to *-one*:

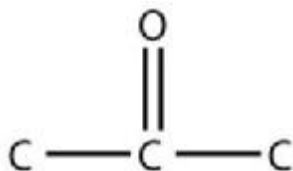


Figure 7.2. Carbon backbone of propanone (acetone), hydrogen atoms are not shown

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 7.3):

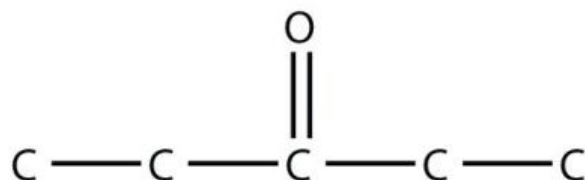


Figure 7.3. Carbon backbone of 3-pentanone, hydrogen atoms are not shown

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 7.4, 7.5). So propanone can also be called dimethyl ketone, while 2-butanone is called methyl ethyl ketone.

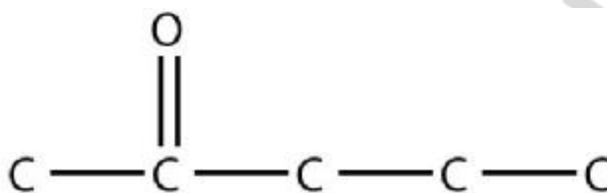


Figure 7.4. Carbon backbone of 2-pentanone (methyl propyl ketone), hydrogen atoms are not shown

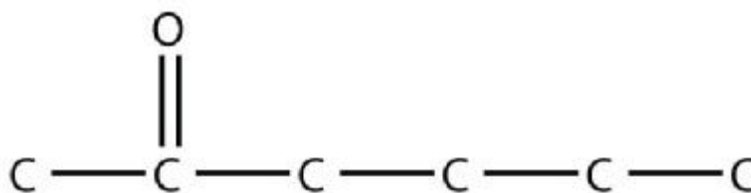
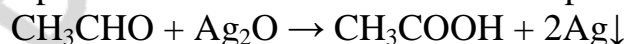


Figure 7.5. Carbon backbone of 2-hexanone (methyl butyl ketone), hydrogen atoms are not shown

7.2. CHEMICAL PROPERTIES OF ALDEHYDES AND KETONES

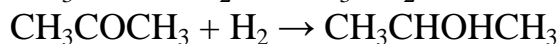
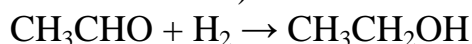
Aldehydes, unlike ketones, react with the solution of silver oxide in ammonia. In this *silver mirror* test, an aldehyde is treated with Tollens' reagent, which is prepared by adding a drop of sodium hydroxide solution into silver nitrate solution to give a precipitate of silver (I) oxide, and then adding 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-carbon 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 Cu^{2+} complex ions are reduced to a red brick colored Cu_2O precipitate.

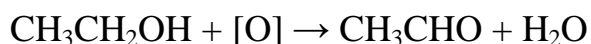


Both aldehydes and ketones can react with hydrogen (they can participate in addition reactions).

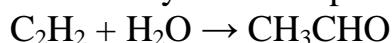


7.3. PRODUCTION OF ALDEHYDES AND KETONES

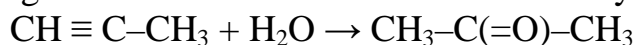
Aldehydes and ketones may be produced from respective alcohols in oxidation reactions.



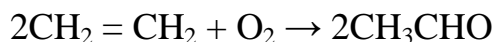
Acetaldehyde can be produced from acetylene and water.



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



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

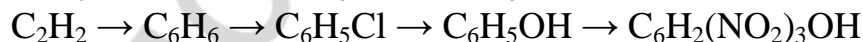
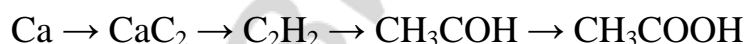


Exercises

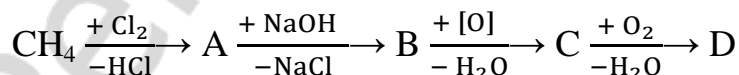
a. Determine the mass of acetaldehyde which can be produced from 900 kg of impure calcium carbide. The mass percentage of impurities is equal to 10 %. The yield of acetylene in the reaction between water and calcium carbide is equal to 95 %, the yield of acetaldehyde in the reaction between acetylene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

b. 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.

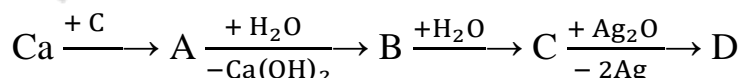
c. Chains of chemical reactions



d. Calculate the sum of molecular masses for compounds A, B, C and D from the chain of chemical reactions.



e. Calculate the sum of molecular masses for compounds A, B, C and D from the chain of chemical reactions.



LESSON 8

8.1. STRUCTURE OF CARBOXYLIC ACIDS

The combination of a carbonyl functional group and an OH group makes the carboxyl group (figure 8.1).

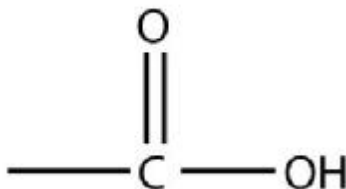


Figure 8.1. Scheme of the carboxyl group

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 8.2).

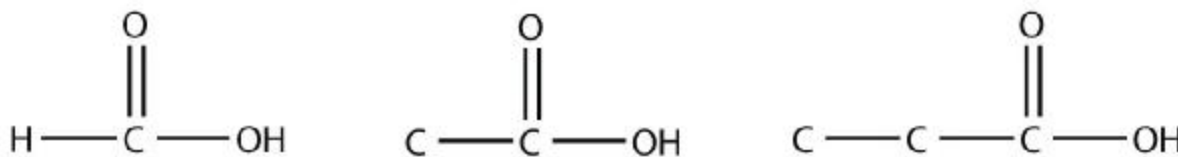


Figure 8.2. Structural formula of methanoic (formic) acid, carbon backbones of ethanoic (acetic) and propanoic acids

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^+ 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.

8.2. CHEMICAL PROPERTIES OF CARBOXYLIC ACIDS

Carboxylic acids react with bases. The H atom in the carboxyl group comes off as the H^+ ion, leaving a carboxylate anion:

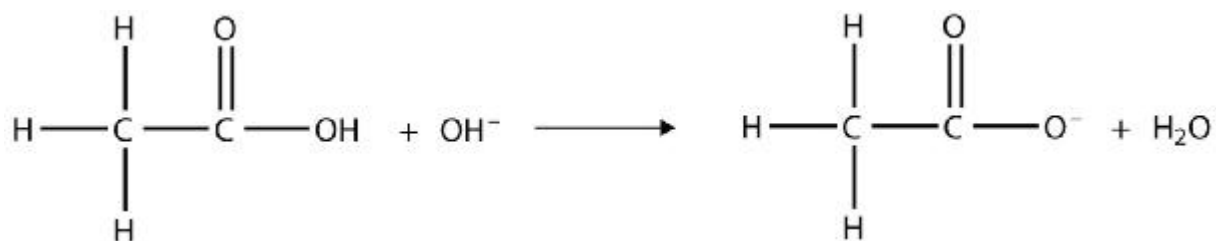


Figure 8.3. Ionic reaction between acetic acid and alkali

Carboxylate ions are named from the acid name: the *-oic acid* is replaced with *-oate* to name the ion. The carboxylate ion (figure 8.4), which has the condensed structural formula CH_3COO^- (R is the methyl group in that particular ion), is the ethanoate ion, but it is commonly called the acetate ion.

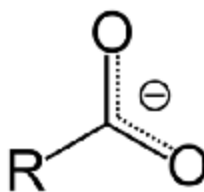
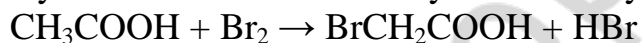


Figure 8.4. Scheme of carboxylic acid ion

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 compounds connected via oxygen atom (figure 8.5).

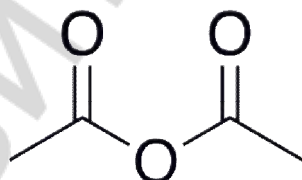


Figure 8.5. Scheme of carboxylic acid anhydride

One may consider that formic acid has both carboxyl and carbonyl functional groups (figure 8.6).

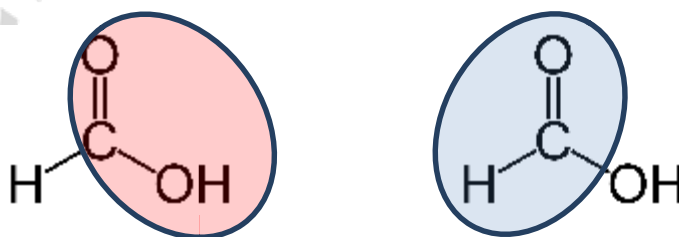
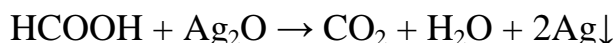


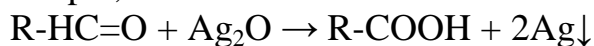
Figure 8.6. Carboxyl and carbonyl functional groups of the formic acid

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

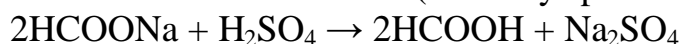
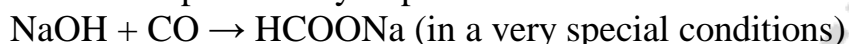


8.3. PRODUCTION OF CARBOXYLIC ACIDS

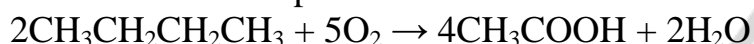
Carboxylic acids can be produced by the way of oxidation of aldehydes, for example, in the silver mirror reaction.



There is a specific way to produce formic acid.



Acetic acid can be produced from butane.



Exercises

a. Determine the formula of the 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 %.

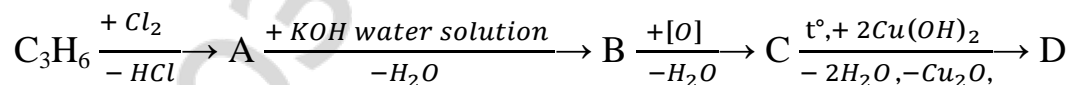
b. What is the mass of acetic anhydride which has to be dissolved in 500 g of 95 % acetic acid solution to produce a 100% acetic acid?

c. 0.75 g of 40 % formaldehyde reacted with Tollens' reactant and produced 0.224 L of CO_2 . Determine the mass of silver produced in that process.

d. Calculate the sum of molecular masses for compounds A, B, C and D from the chain of chemical reactions.



e. Calculate the sum of molecular masses for compounds A, B, C and D from the chain of chemical reactions.



LESSON 9

9.1. ESTERS

Carboxylic acids can react with alcohols. When combined under the proper conditions, a water molecule will be removed, and the remaining pieces will combine to form a new functional group — the ester functional group (figure 9.1). Note how the acid molecule contributes one alkyl side (represented by R), while the alcohol contributes the other side (represented by R').

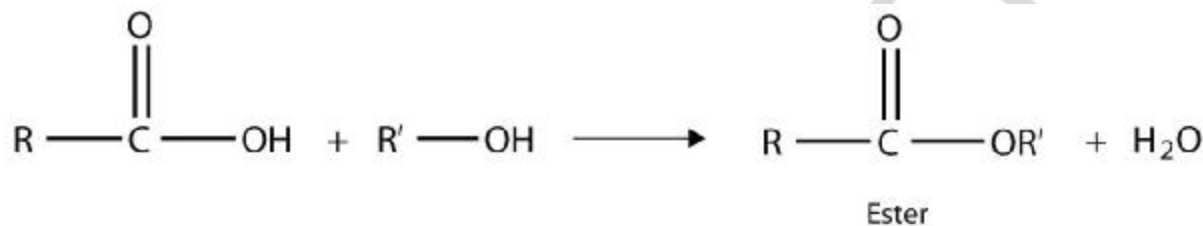


Figure 9.1. Scheme of ester formation reaction

Esters are named using the alkyl group name from the alcohol plus the carboxylate name from the acid. The compound drawn below is called methyl propanoate (figure 9.2).

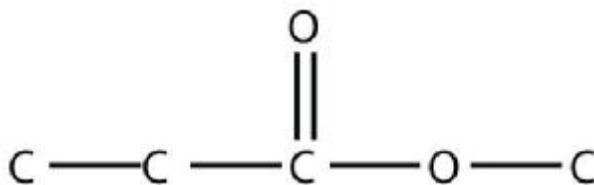
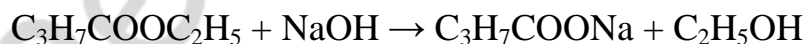


Figure 9.2. Carbon backbone of methyl propanoate, hydrogen atoms are not shown

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.



Questions

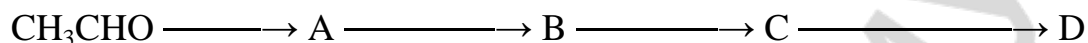
- What is the difference between ether and ester?
- What is the difference between ester and carboxylic acid anhydride?

Exercises

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

b. 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 %.

c. Calculate the molar mass for the organic compound D



d. Calculate the molar mass for the organic compound D containing potassium atom.



9.2. 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 9.3). Fatty acids are carboxylic acids with long nonbranched aliphatic tails.

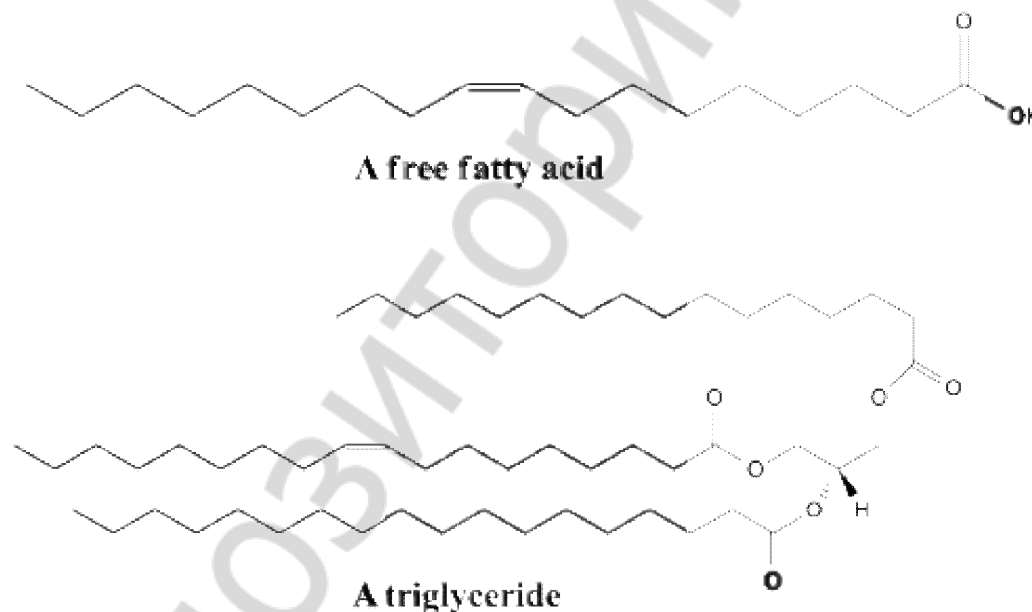


Figure 9.3. Carbon backbone of a free fatty acid and a triglyceride

There are several examples of fatty acids.

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

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

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

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

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 nonsaturated hydrocarbon tails. So, fats can be classified into saturated fats and unsaturated fats.

Fats form cellular membranes (both outer membrane and membranes of intracellular organelles). There are two layers of fats (and other lipids) in a membrane (figure 9.4). Glycerine is a relatively hydrophilic part of 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.

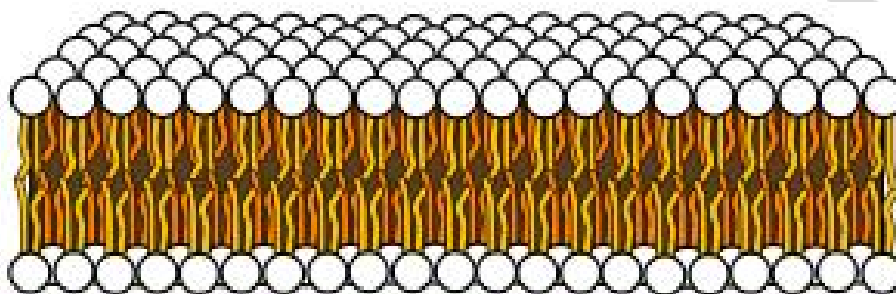


Figure 9.4. Cellular membrane structure

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 9.5).

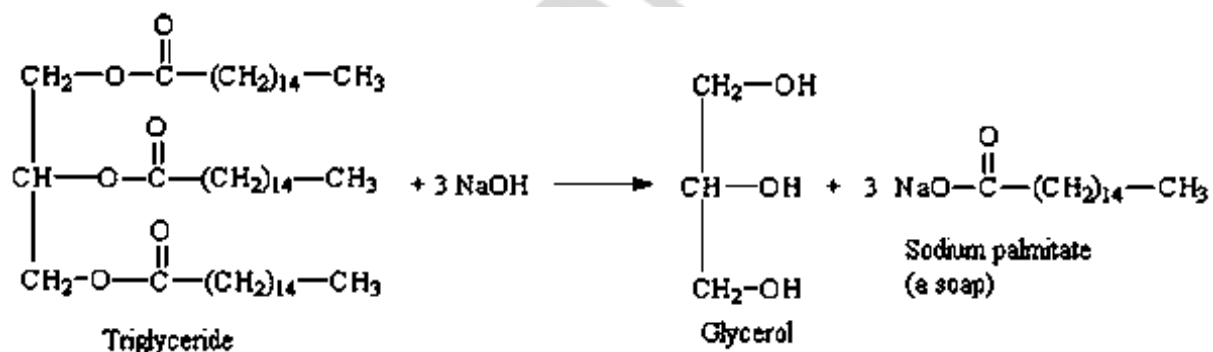


Figure 9.5. Reaction of glyceride tripalmitate saponification

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 9.6).

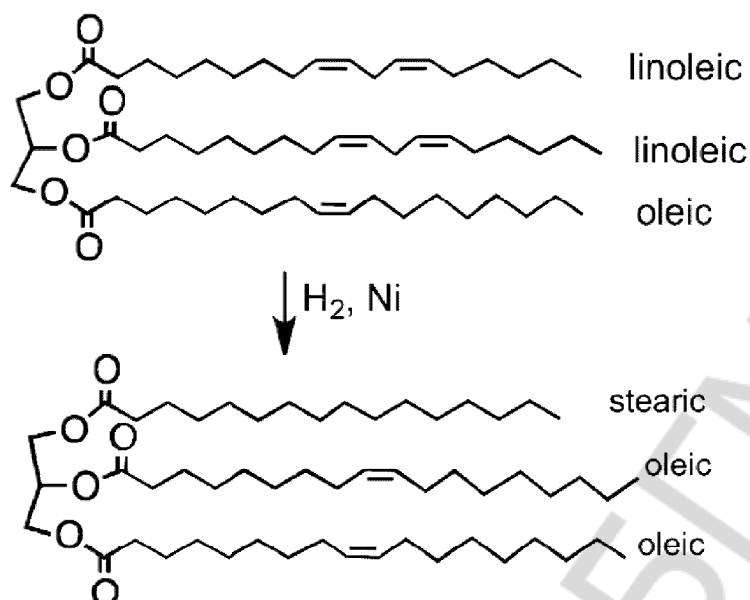


Figure 9.6. Reaction of unsaturated triglyceride partial hydrogenation

Exercises

- Determine the mass of soap which can be produced from 2 tons of glyceride tristearate in the reaction with NaOH. The yield is equal to 85 %.
- 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.

LESSON 10

10.1. 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 10.1).

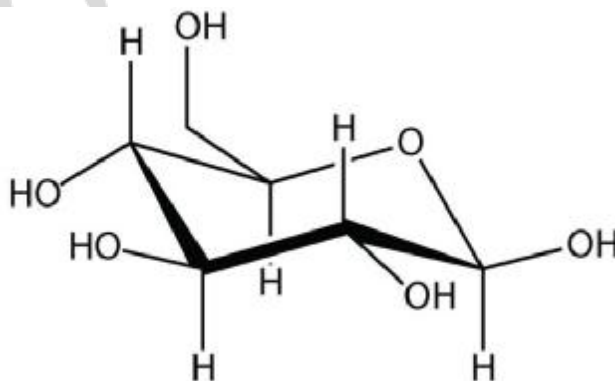


Figure 10.1. Structural formula of cyclic form of glucose

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 10.2).

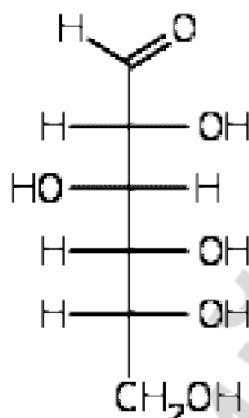


Figure 10.2. Structural formula of linear form of glucose

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 $-HC=O$ at C-1 atom and the hydroxyl group $-OH$ at C-4 or C-5 atom, yielding a hemiacetal group $-C(OH)H-O-$ (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 $-(CH(CH_2OH)OH)-H$ or $-(CHOH)-H$, respectively).

The ring-closing reaction makes carbon C-1 chiral, since its four bonds lead to $-H$, to $-OH$, 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 “ α -” and “ β -” (figure 10.3). The designation “ α -” 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 “ β -” means that they are on the same side of the plane (a *cis* arrangement).

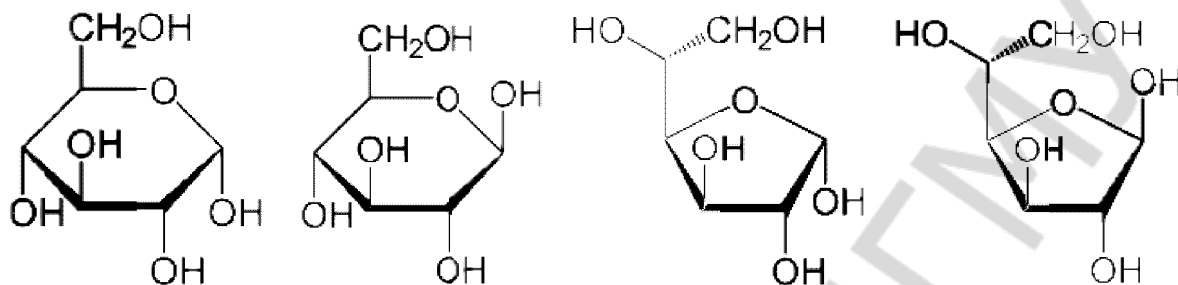


Figure 10.3. Structural formulas of α -D-glucopyranose, β -D-glucopyranose, α -D-glucofuranose, and β -D-glucofuranose

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 10.4).

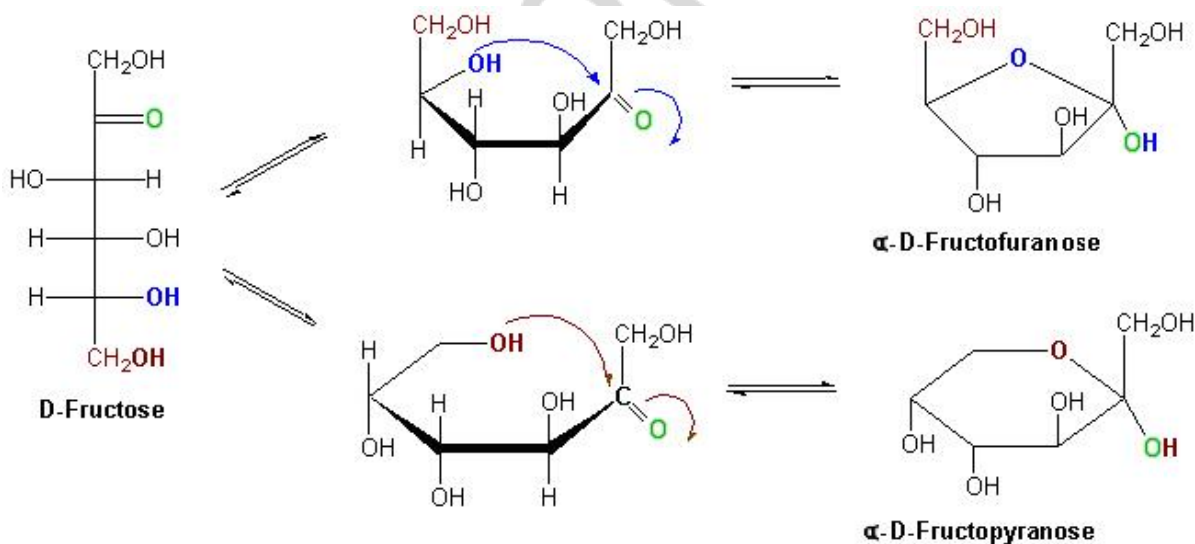


Figure 10.4. Isomeric forms of fructose

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 10.5). The word was formed in the mid-19th century from Latin *sucrum* = “sugar” and the chemical suffix *-ose*.

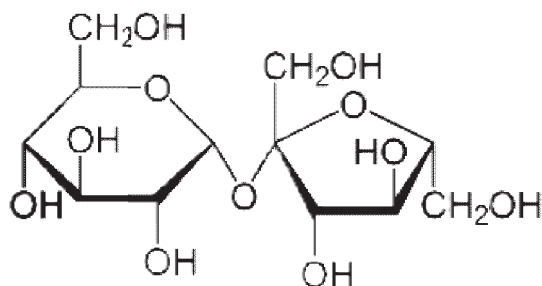


Figure 10.5. Structural formula of sucrose

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 10.6), and the branched amylopectin (figure 10.7). 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.

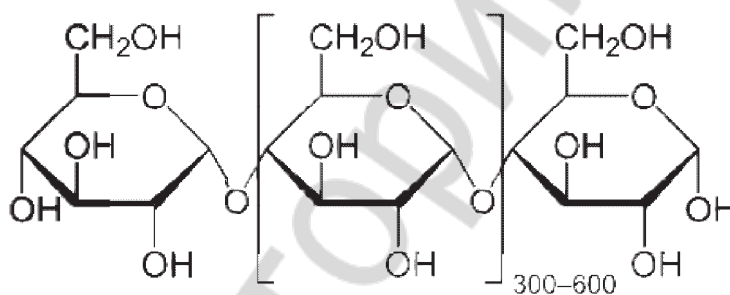


Figure 10.6. Schematic representation of amylose

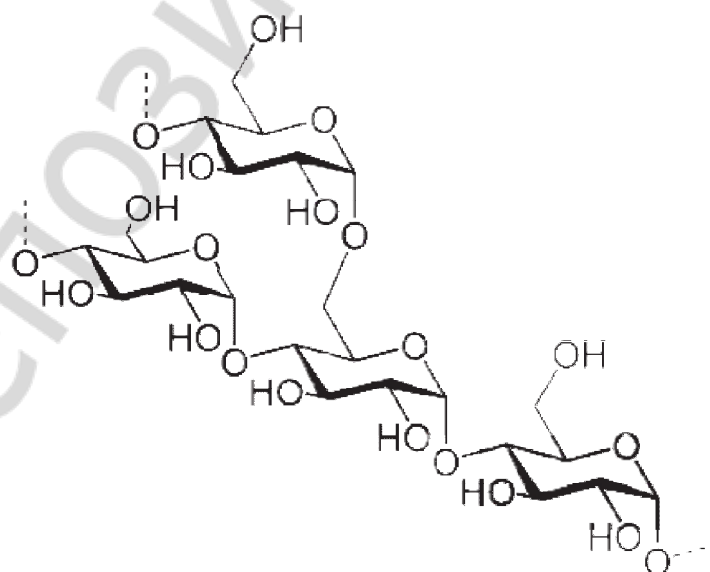


Figure 10.7. Schematic representation of amylopectin

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 10.8). 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*.

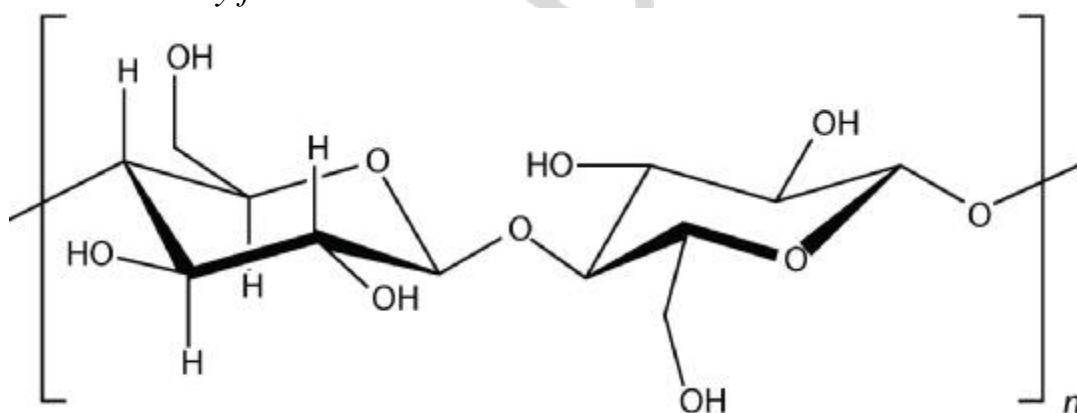


Figure 10.8. Schematic representation of cellulose

10.2 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 β -N₉-glycosidic bond (figure 10.9).

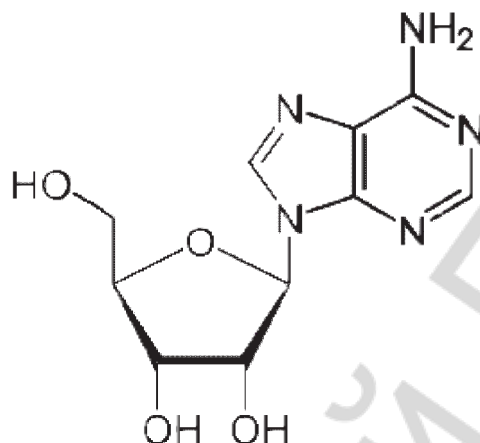


Figure 10.9. Structure of adenosine

Deoxyadenosine is a deoxyribonucleoside which is one of the four building blocks of DNA (figure 10.10). 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.

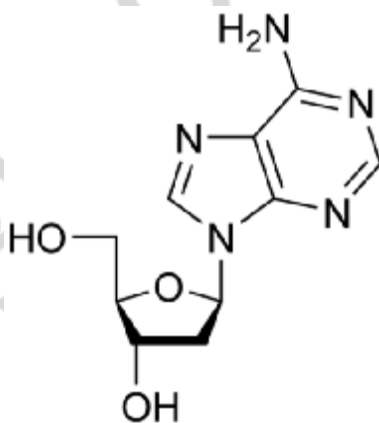


Figure 10.10. Structure of deoxyadenosine

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 10.11) 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.

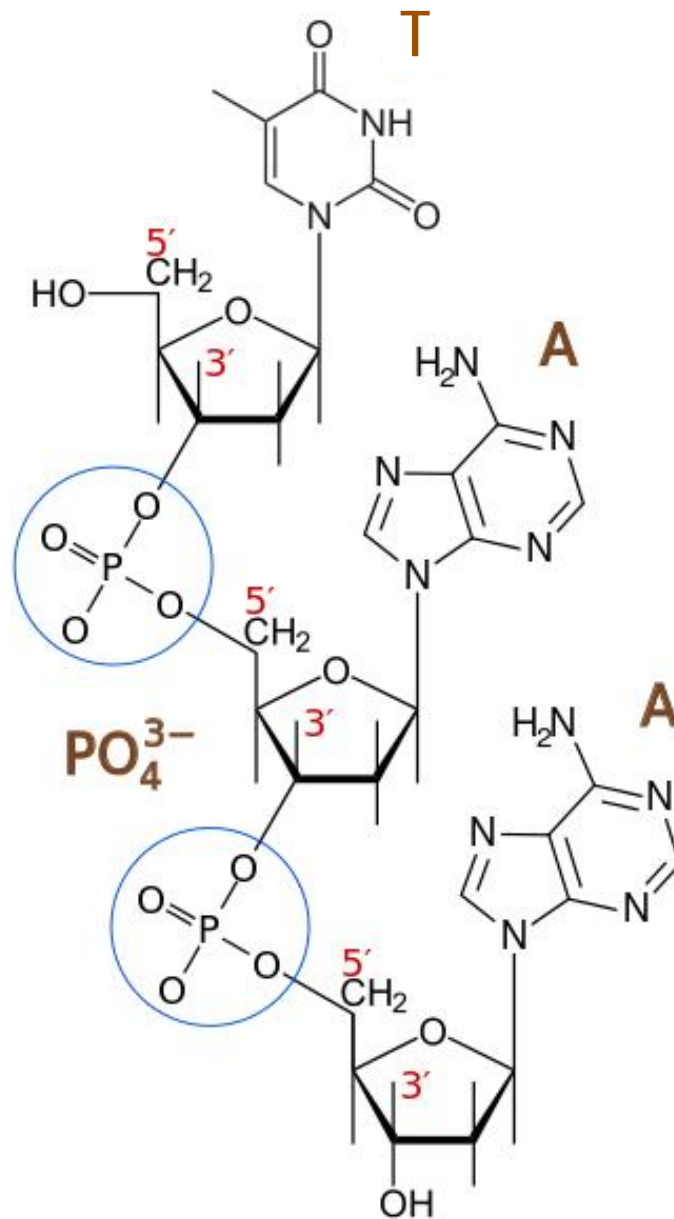


Figure 10.11. Scheme of the single strand of DNA

Two strands of DNA are connected together by hydrogen bonds formed between bases (figure 10.12). 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 10.13).

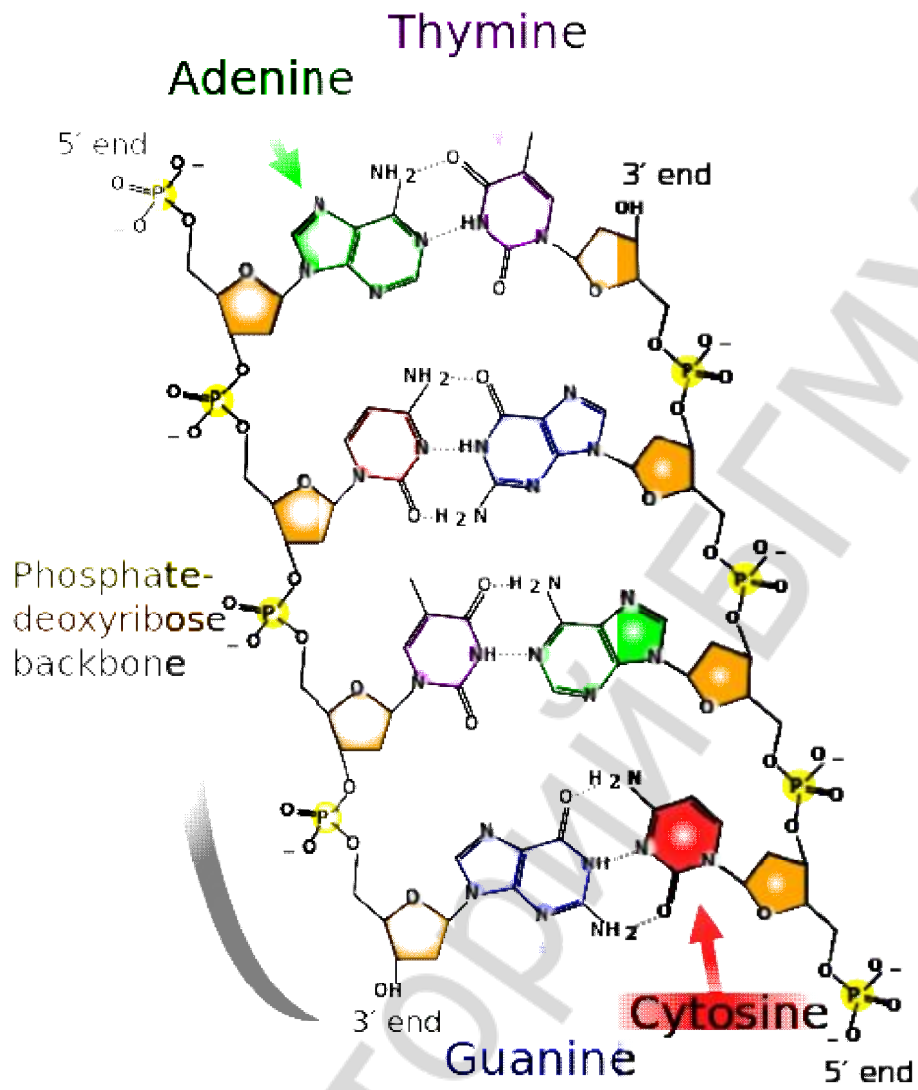


Figure 10.12. Scheme of the two strands of DNA connected together

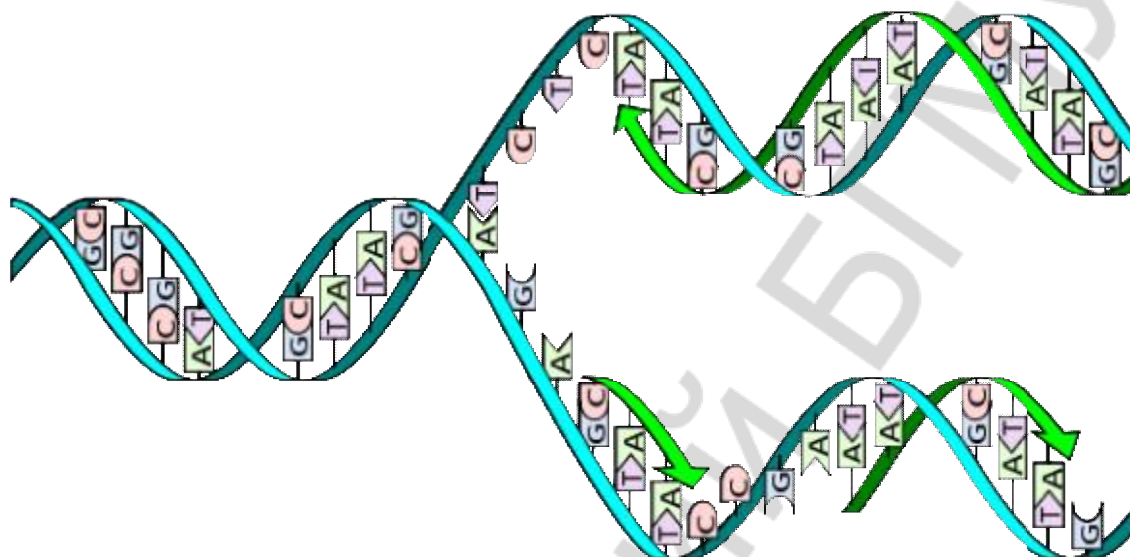
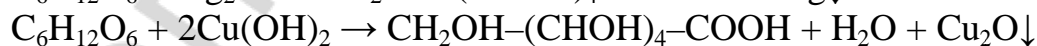
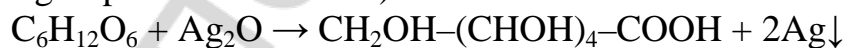


Figure 10.13. Scheme of DNA replication

10.3 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).



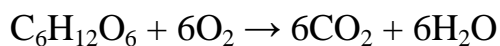
Glucose can react with hydrogen gas and form a six-atom alcohol.



Since glucose (as well as other hydrocarbons) has several hydroxyl (OH) groups, it can react with $\text{Cu}(\text{OH})_2$. Those 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 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.



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

a. Calculate the mass of silver which can be produced in the reaction between 18 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) and Ag_2O . The yield of the reaction is equal to 75 %.

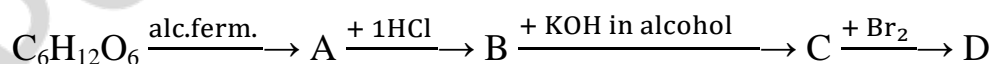
b. What is the volume of carbon dioxide (CO_2) produced in the process of alcoholic fermentation of 38 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$). The yield of the reaction is equal to 60 %.

c. What is the mass of fructose ($\text{C}_6\text{H}_{12}\text{O}_6$) which can be produced from 1 kg of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$)?

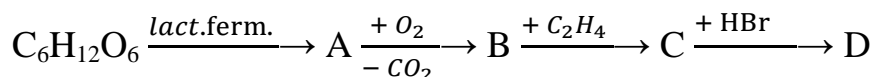
d. One ton of potatoes contain 20 % of the starch. 100 liters of 96 % ethanol have been produced from that mass of potatoes after the alcoholic fermentation. The density of 96 % ethanol is equal to 0.8 g/ml. Determine the yield of the reaction.

e. Determine the number of monomers ($\text{C}_6\text{H}_{10}\text{O}_5$) in the polymeric molecule of cotton fiber with molecular mass equal to 1750000.

f. Calculate the molar mass for the organic compound D



g. Calculate the sum of molar masses for the organic compounds A and D



LESSON 11

11.1 AMINES

An amine is an organic derivative of ammonia (NH₃). In amines, one or more of the H atoms in NH₃ is substituted with an organic group. A *primary* amine has one H atom substituted with an R group (figure 11.1).



Figure 11.1. Structural formula of methylamine

A *secondary* amine has two H atoms substituted with R groups (figure 11.2).

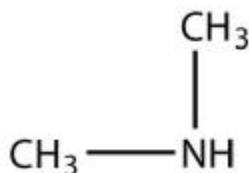


Figure 11.2. Structural formula of dimethylamine

A *tertiary* amine has all three H atoms substituted with R group (figure 11.3).

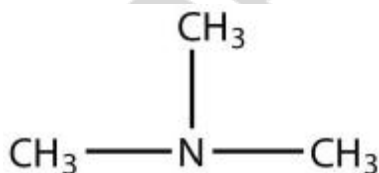


Figure 11.3. Structural formula of trimethylamine

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 11.4).

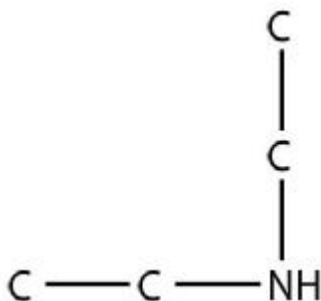


Figure 11.4. Structural formula of diethylamine (hydrogen atoms connected to carbon atoms are not shown)

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 11.5).

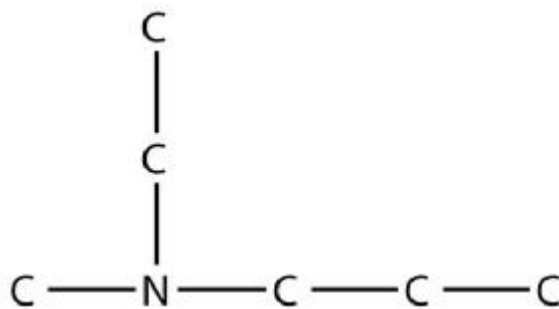


Figure 11.5. Structural formula of ethylmethylpropylamine (hydrogen atoms connected to carbon atoms are not shown)

As with NH_3 , the N atom in amines can accept a proton onto the lone electron pair on the N atom. That is, amines act as bases (i. e., proton acceptors):

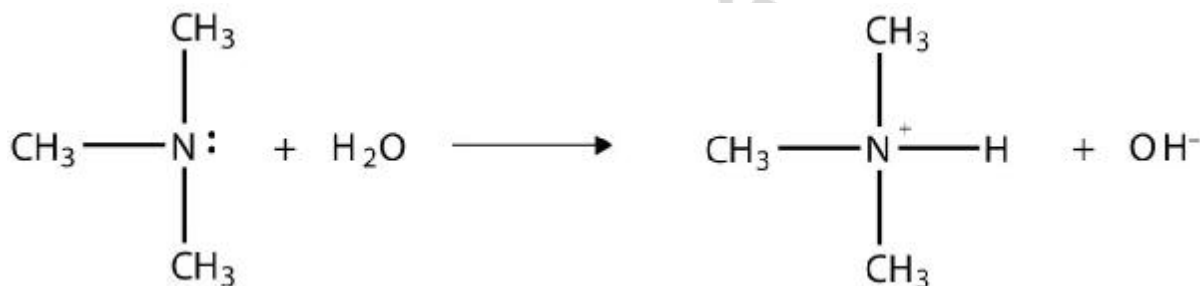
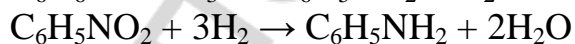
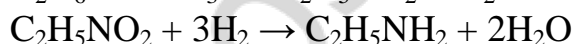
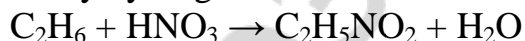


Figure 11.6. Reaction of trimethylamine and water

The amine becomes an ion similar to the ammonium (NH_4^+) ion. Remember that all amines are weak bases, as well as ammonium hydroxide.

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 11.7).

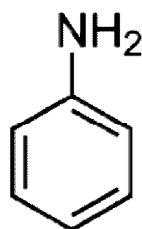
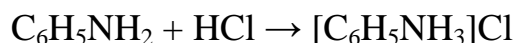
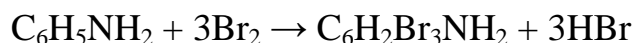


Figure 11.7. Structural formula of aniline

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.



11.2 AMIDES

An *amide functional group* is a combination of an amine group and a carbonyl group (figure 11.1).

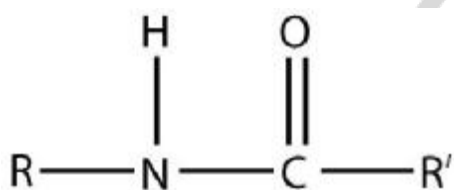


Figure 11.1. Scheme of amide functional group

Amides are actually formed by bringing together an amine containing molecule and a carboxylic acid containing molecule. A molecule of H_2O is lost in that process (figure 11.2).

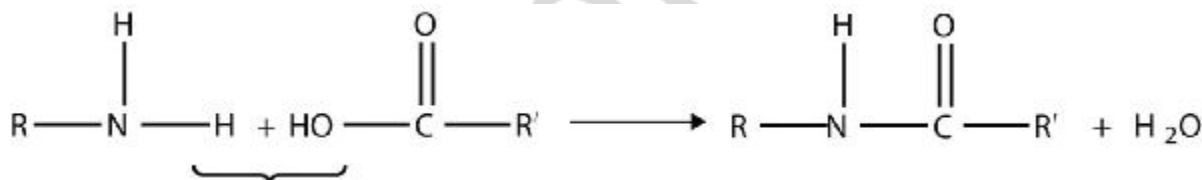


Figure 11.2. Scheme of amide bond formation

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 11.3).

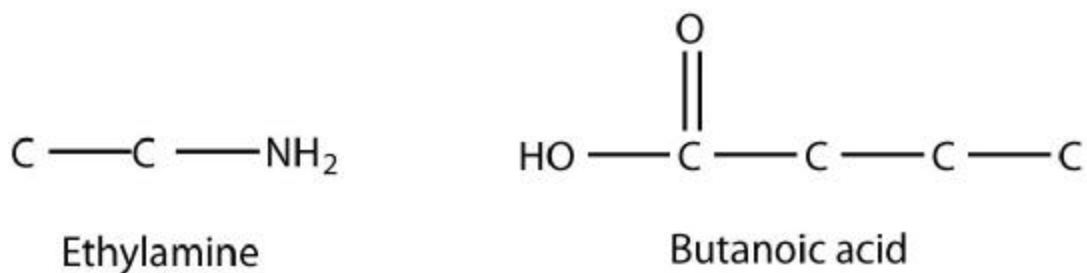


Figure 11.3. Ethylamine and butanoic acid, hydrogen atoms are not shown

When they come together to make an amide, an H_2O 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 11.4.

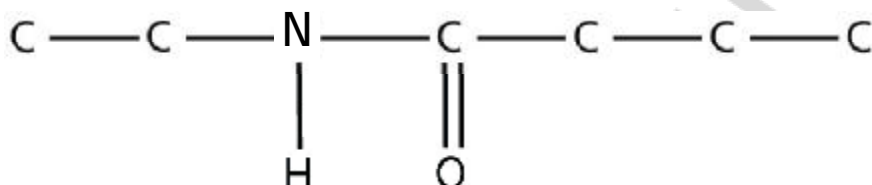


Figure 11.4. The product of the reaction between ethylamine and butanoic acid, hydrogen atoms are not shown

11.3 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 11.5).

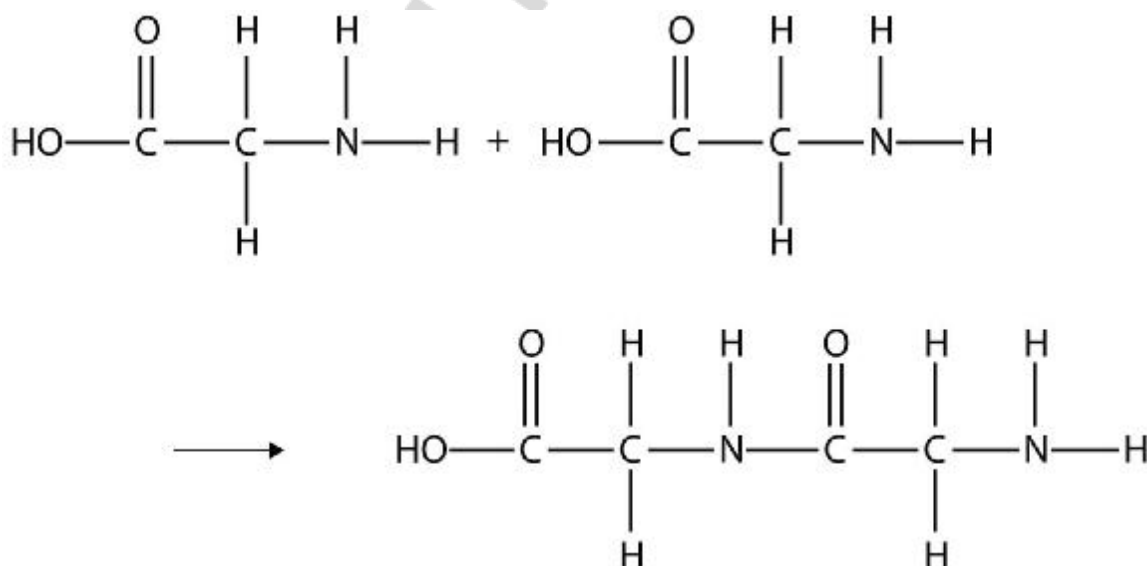


Figure 11.5. Formation of glycyl glycine

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 11.6).

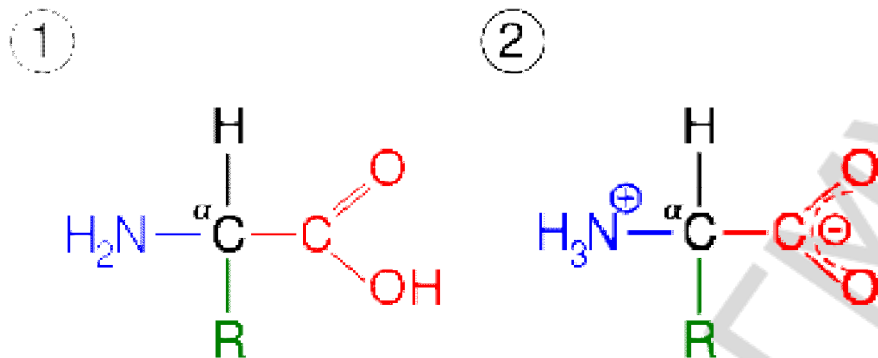


Figure 11.6. Zwitterion formation

Proteins are formed when hundreds or even thousands of amino acids form amide bonds to make polymers. Proteins play a crucial role in living organisms. Structures of the “bricks” of proteins are given below (figure 11.7).

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. Arginine and lysine has additional amino groups. 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.

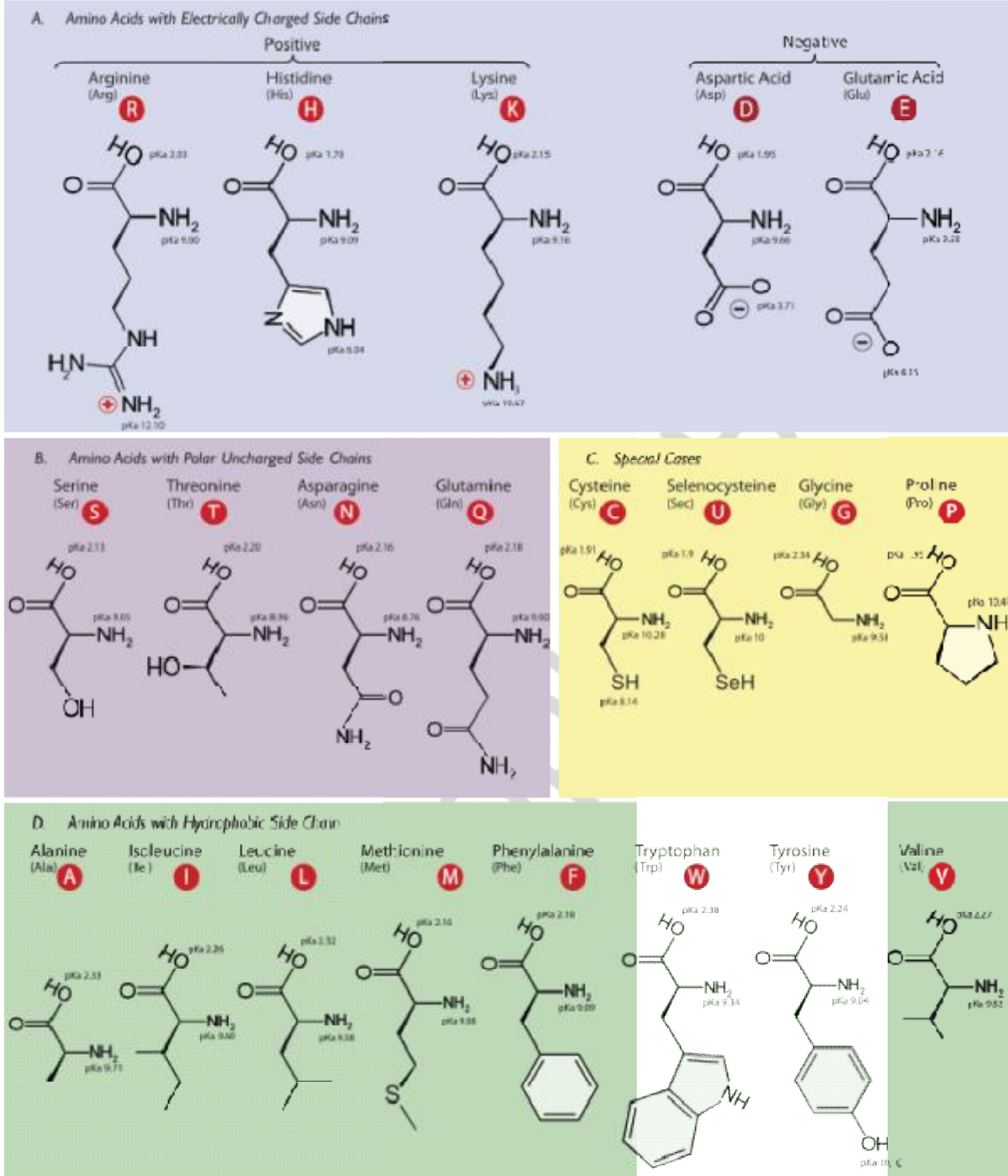
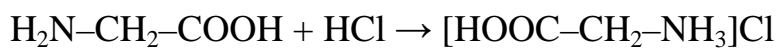
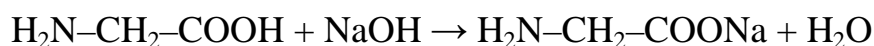


Figure 11.7. Proteinogenic amino acids

11.4 CHEMICAL PROPERTIES AND PRODUCTION OF AMINO ACIDS

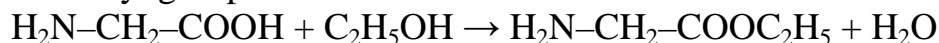
Amino acids can react with both acids and alkali.





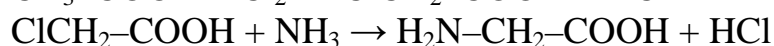
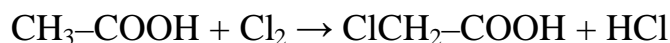
Amino groups become protonated if pH is low. Carboxyl groups become deprotonated if pH is high.

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



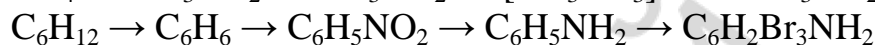
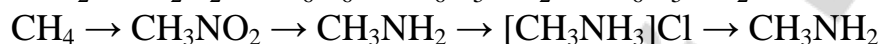
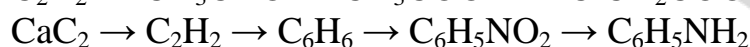
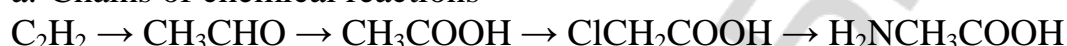
One of the ways to synthesize amino acid is as follows.

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



Exercises

a. Chains of chemical reactions



b. 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.

c. Determine the mass of HCl required for reaction with 20 g of:

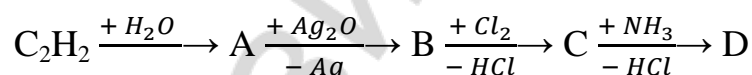
a) glycine, b) alanine, c) aspartic acid.

d. Calculate the mass of glycyL alanine formed from 4 g of glycine.

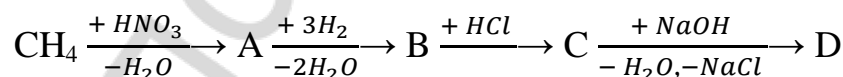
e. Calculate the mass of alanyl valine formed from 3 g of alanine.

f. 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.

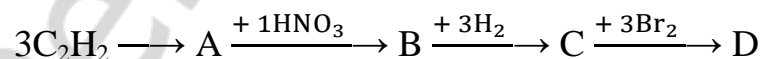
g. Calculate the sum of molecular masses for compounds A, B, C and D from the chain of chemical reactions.



h. Calculate the sum of molecular masses for compounds A, B, C and D from the chain of chemical reactions.



i. Calculate the molar mass for the organic compound D



LESSON 12

12.1 SAMPLE TASKS FROM THE CONTROL WORK

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

b. 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.

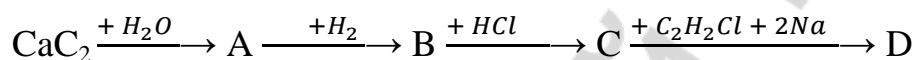
c. 7.8 g of nitrobenzene reacted with hydrogen gas. As a result 4.5 g of aniline have been produced. Determine the yield of the reaction.

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

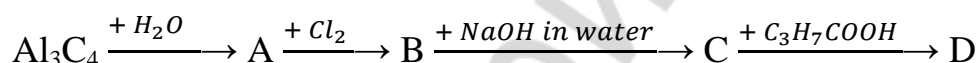
e. What is the volume carbon dioxide (CO₂) produced in the process of alcoholic fermentation of 38 g of glucose (C₆H₁₂O₆). The yield of the reaction is equal to 60 %.

12.2 SAMPLE CHAINS OF CHEMICAL REACTIONS FROM THE CONTROL WORK

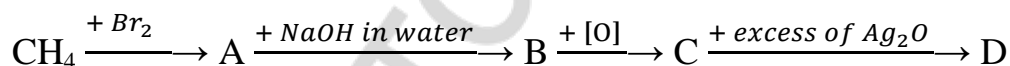
a. Calculate the sum of molecular masses for organic compounds A, B, C and D from the chain of chemical reactions.



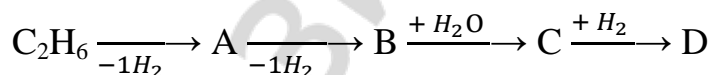
b. Calculate the sum of molecular masses for organic compounds A, B, C and D from the chain of chemical reactions.



c. Calculate the sum of molecular masses for compounds A, B, C and D from the chain of chemical reactions.



d. Calculate the sum of molecular masses for organic compounds A, B, C and D from the chain of chemical reactions.



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