МИНИСТЕРСТВО НАУКИ И ВЫСШЕГО ОБРАЗОВАНИЯ РОССИЙСКОЙ ФЕДЕРАЦИИ

ФЕДЕРАЛЬНОЕ ГОСУДАРСТВЕННОЕ БЮДЖЕТНОЕ ОБРАЗОВАТЕЛЬНОЕ
УЧРЕЖДЕНИЕ ВЫСШЕГО ОБРАЗОВАНИЯ

«СЕВЕРНО-КАВКАЗСКАЯ ГОСУДАРСТВЕННАЯ АКАДЕМИЯ»

МЕДИЦИНСКИЙ ИНСТИТУТ

КАФЕДРА ХИМИИ

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БИООРГАНИЧЕСКАЯ ХИМИЯ

Учебно-методическое пособие
для студентов I курса обучающихся по специальностям
31.05.01 «Лечебное дело»;
Часть I

Черкесск – 2024 г.

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А-13 **Абалмасова, О.В.** Биоорганическая химия: учебно-методическое пособие для студентов I курса обучающихся по специальностям 31.05.01 «Лечебное дело»; Часть I / О.В. Абалмасова, Ф.А. Бостанова. – Черкесск: БИЦ СКГА, 2024. – 132 с

Издание включает основные программные теоретические разделы биоорганической химии. Содержит теоретический материал для подготовки к лабораторным занятиям. К каждой теме даны цель занятия, вопросы для обсуждения, письменные задания. Приведены описания и протоколы лабораторных опытов. Предназначено для студентов первого курса высших учебных заведений по медицинским специальностям.

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SEMESTER II.

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3	Reactivity of hydrocarbons/ Laboratory work 1. Properties of hydrocarbons	2
4.	Control work 1.	2
Section III. **Monofunctional derivatives of hydrocarbons**		**10**
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6.	Acidity and basicity of organic compounds	2
7	Nucleophilic substitution of a saturated carbon atom Laboratory work 2. Properties of alcohols, phenols, amines	2
8	Nucleophilic reactions of carbonyl compounds Laboratory work 3. Properties of aldehydes, ketones, carboxylic acids	2
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14.	Amino acids, peptides and proteins	4
15.	Laboratory work 4. Properties of amino acids	2
16.	Carbohydrates	2
17.	Laboratory work 5. Properties of carbohydrates	2
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19.	Laboratory work 6. Properties of lipids. Fatty acids	2
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Итого во II семестре		**50**

SAFETY INSTRUCTIONS FOR WORK IN THE CHEMICAL LABORATORY

Students are required to come to classes in the chemical laboratory in cotton overalls. Students are assigned permanent jobs, which they must keep in order. During the experiment, each student must be at his workplace. During work in the laboratory, silence, order and cleanliness should be observed, and haste should not be allowed.

It is strictly forbidden:

– performing experiments not related to the implementation of the training workshop;

- work with reagents in the absence of a teacher;

- eat in the laboratory;

- Taste the chemicals.

After completing the experiment, each student must report for the work done, then wash the dishes, clean the workplace and hand it over to the duty officer, who is appointed by the head of the group before the start of the lesson.

Responsibilities of the duty student

- get the necessary equipment from the laboratory assistant on duty;

- keep order in the laboratory;

- the student on duty must be the last to leave the laboratory, having received permission from the teacher.

Alcohol lamp precautions

Careless work with an alcohol lamp can lead to a fire, so the following requirements must be observed when working:

1) the wick of the spirit lamp must fit tightly into the hole of the metal sleeve, it must be pulled out from above by 1 cm and fluffed up;

2) the sleeve must tightly close the opening of the spirit lamp, which is filled with alcohol no more than 2/3 of the volume;

3) light the spirit lamp only with matches;

4) in the lit state, the spirit lamp should be located in a place convenient for work;

5) it is possible to extinguish the flame of an alcohol lamp only by covering it with a cap;

6) it is necessary to heat substances in glassware only in the upper or middle part of the flame, without touching the wick, since the wick is always cold, and hot glass bursts upon contact with it.

Precautions for handling glassware

Heating of substances in glassware should be done gradually, slightly rotating it and, from time to time, gently shaking the contents. When a test tube with a liquid is heated over an open flame, liquid may be ejected from it. In this regard, the opening of the test tube should be directed away from yourself and from your neighbors. It is especially necessary to beware of splashes in the eyes, so you can not bend over and look into the test tube. When heated, the test tube

should be in an inclined position (45°), then the splashes will hit the walls of the dish and will not be thrown out.

When working with a gas outlet tube, make sure that the end of the outlet tube is in the liquid through which the gas passes. It is possible to remove the spirit lamp from under the test tube with the reaction mixture only after the lower end of the gas outlet tube is removed from the liquid. If the liquid begins to rise through the vent tube, immediately lower the test tube so that the liquid level in it falls below the end of the vent tube, and continue heating until the escaping gas pushes the liquid out of the vent tube.

Chemical Handling Precautions

Reagents necessary for work, except for flammable liquids, potent and toxic substances, are on the desktop and placed in racks with numbered sockets. The same number is on the bottle with the corresponding reagent. Bottles with liquids are closed with rubber stoppers, in which pipettes are mounted. It is not recommended to remove the bottles from the tripod sockets. To collect the substance with your left hand, press the bottle to the bottom of the nest, and carefully remove the cork with a pipette with your right hand, collect the required amount of reagent with a pipette and close the bottle with the same cork. For a set of crystalline reagents, a spatula (glass spatula) is mounted in the cork.

Precautions for handling flammable liquids (FL)

Flammable liquids (diethyl ether, alcohol, toluene, acetone, acetoacetic ether) are in small quantities in a fume hood. Work with these substances is carried out under draft, away from open flames and switched on tiles. If a flammable liquid ignites in a vessel, it should be quickly covered with a fire blanket. If a burning liquid spills, it is extinguished with sand, which is then removed. If a person's clothing catches fire, they are quickly and tightly wrapped in a fire blanket.

Precautions when working with acids and alkalis

Concentrated solutions of nitric, sulfuric, hydrochloric acids, nitrating mixture are in the fume hood. All work with concentrated acids and alkalis is carried out only in a fume hood. Concentrated acids can only be diluted by adding acid to water, and not vice versa. Accidentally spilled acids and alkalis on the floor must be covered with sand and then cleaned up.

Precautions when working with toxic substances

Toxic organic substances - aniline, methylamine, toluene, picric acid are in the fume hood. Care must be taken when handling these substances, do not inhale their vapors, avoid contact with hands, as they can penetrate the skin. If these substances come into contact with your hands, wash your hands quickly with soap and warm water. If vapors are inhaled, move immediately to fresh air.

First aid in case of accidents

1) when cutting hands with glass, it is necessary, first of all, to remove pieces of glass from the wound with tweezers, then treat the wound with an iodine alcohol solution and apply a bandage.

2) in case of thermal burns, the burned area should be treated with a 70% solution of ethyl alcohol.

3) in case of burns with solutions of acids, alkalis, you need to quickly rinse the affected area with water, apply an aseptic bandage.

4) if acids or alkalis get into the eyes, they should be thoroughly rinsed with water and the victim should be sent to the clinic.

5) in case of skin burns with bromine, you should quickly wash it off with ethyl alcohol and apply an anti-burn emulsion to the affected area.

6) in case of burns with hot organic liquids, it is necessary to wash the burned area with ethyl alcohol.

7) in case of burns with liquid phenol, rub the whitened area of the skin with glycerin until the normal color of the skin is restored, then rinse with water and apply a gauze bandage moistened with a solution of glycerin.

8) after providing first aid, if necessary, you should contact the university health center or polyclinic.

SECTION I.

ACTIVITY №1

Topic:

THEORETICAL FOUNDATIONS OF THE STRUCTURE AND REACTION ABILITIES OF ORGANIC COMPOUNDS

Purpose of the lesson:

To form knowledge of the basic principles of the classification of organic compounds, types of nomenclature, types of isomerism; to study the chemical bond in organic compounds and the types of hybridization of the carbon atom.

Issues for discussion

1. Subject of bioorganic chemistry
2. Classification of organic compounds:
- by the structure of the carbon skeleton;
– by the nature and number of functional groups
3. Principles of the nomenclature of organic compounds
- trivial nomenclature
- substitute nomenclature
- IUPAC systematic nomenclature (IUPAC)
4. Isomerism of organic compounds
– structural isomerism
– stereoisomerism
5. Chemical bond in organic compounds
6. Classification signs of reactions in organic chemistry

Theoretical material

Bioorganic chemistry is a fundamental discipline, the theoretical basis of medical education, a field of science that studies the electronic and spatial structure and mechanisms of functioning of biologically active molecules from the standpoint of organic chemistry.

The goal of bioorganic chemistry as an academic discipline is to form systematic knowledge about the relationship between the structure and chemical properties of biologically important classes of organic compounds, biopolymers and their structural components as a basis for perception and understanding of the essence of metabolism and its regulation at the molecular level.

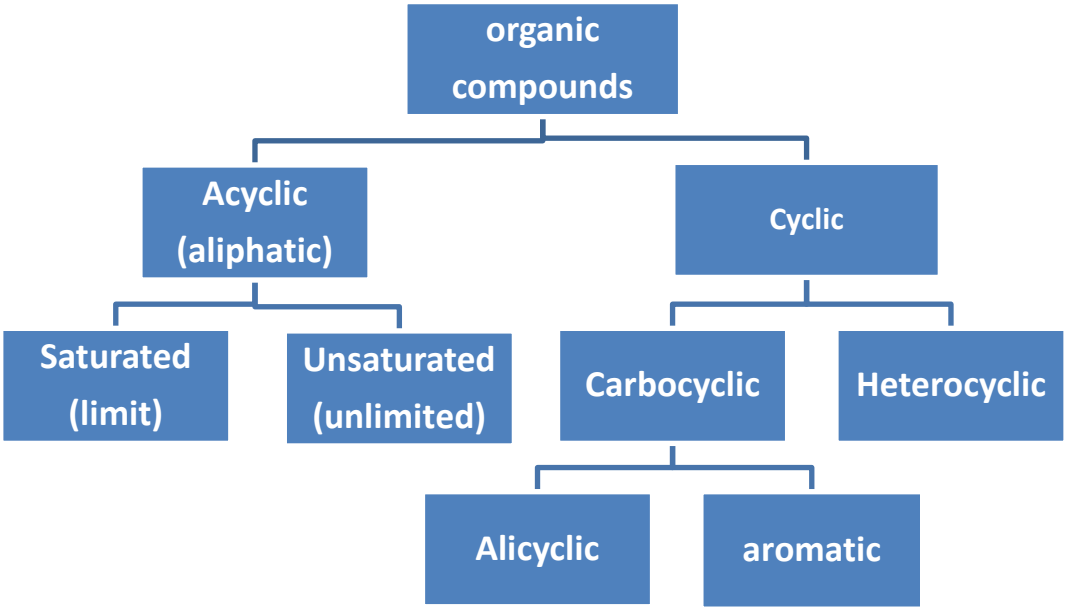
Bioorganic chemistry is based on theoretical data and methods of organic chemistry. Modern organic chemistry is generally defined as the chemistry of carbon compounds. Currently, about 17 million organic compounds are known. Such a huge number of organic compounds predetermines the need for strict classification and uniform international nomenclature rules. For medicine, the value of the general rules of nomenclature is also of great importance, since in accordance with them the names of medicines are built, which doctors meet in their professional activities.

Classification of organic compounds. Organic compounds are classified according to the structure of the carbon skeleton and functional groups.

Classification of organic compounds according to the structure of the carbon chain

Acyclic compounds are compounds with an open (open) carbon chain. They are based on aliphatic hydrocarbons. Aliphatic hydrocarbons contain only carbon and hydrogen atoms and can be saturated (limiting) and unsaturated (unsaturated).

Cyclic compounds are compounds with a closed circuit. They are divided into carbocyclic and heterocyclic. Carbocyclic compounds contain only carbon atoms in the cycle and are divided into two groups: aliphatic cyclic (abbreviated as alicyclic) and aromatic, which are based on benzene. Heterocyclic compounds contain in the cycle, in addition to carbon atoms, one or more atoms of other elements, heteroatoms - oxygen, nitrogen, sulfur, etc.



Classification of organic compounds by functional groups

All organic compounds can be considered as derivatives of hydrocarbons obtained by introducing functional groups into them.

A functional group is a group of atoms or a structural fragment of a molecule that is characteristic of a given class of organic compounds and determines the chemical properties of a substance.

Compounds with one functional group are called monofunctional, with several identical functional groups - polyfunctional, with several different functional groups - heterofunctional.

Functional groups and their designation

1.	Halogens	–F, –Cl, –Br, –I
2.	Hydroxyl	–OH
3.	Alkoxy	-OR
4.	Carbonyl	>C=O
5.	Carboxyl	-COOH
6.	Alkoxycarbonyl	-COOR
7.	Carboxamide	$-CONH_2$
8.	Amino	$-NH_2$; >NH; >N–
9.	Nitro	$-NO_2$
10.	Cyano	–C≡N
11.	Thiol	-SH
12.	Alkylthiol	-SR
13.	Sulfonic	$–SO_3H$

Depending on the structure of the carbon skeleton and the nature of the functional group, organic compounds are divided into classes.

Main classes of organic compounds

I. HYDROCARBONS

1. Alkanes 2. Alkenes
3. Acadienes 4. Alkynes
5. Cycloalkanes 6. Arenas

II. HOMOFUNCTIONAL HYDROCARBON DERIVATIVES

– halogenated derivatives of hydrocarbons

– oxygen-containing derivatives of hydrocarbons

1. Alcohols 2. Phenols
3. Ethers 4. Carbonyl compounds
5. Carboxylic acids 6. Esters

– nitrogen-containing derivatives of hydrocarbons

1. Amines
2. Nitro compounds 3. Nitriles
4. Amides

– sulfur-containing derivatives of hydrocarbons

1. Thiols
2. Thioesters 3. Sulfonic acids

III. HETEROFUNCTIONAL HYDROCARBON DERIVATIVES

1. Hydroxy acids 2. Oxoacids
3. Amino acids 4. Amino alcohols
5. Aminophenols

IV. HETEROCYCLIC COMPOUNDS

V. BIOPOLYMERS

1. Carbohydrates 2. Peptides, proteins
3. Lipids 4. Nucleic acids
5. Low molecular weight bioregulators

Nomenclature of organic compounds. Nomenclature is a set of names of individual chemicals, their groups and classes, as well as the rules for compiling these names.

In organic chemistry, especially in bioorganic and biological, conditional "trivial" names of substances are still used. The origin of these names is random and is not related to the structure of the substance. Some compounds are named after the natural source from which they were isolated or from which they were synthesized.

Currently, the international or systematic IUPAC nomenclature (IUPAC - International Union of Pure and Applied Chemistry) is generally accepted. When compiling the names of organic compounds according to the IUPAC systematic nomenclature, 4 general concepts are used: organic radical, parent structure, characteristic group, substituent.

An organic radical is a residue of an organic molecule from which one or more hydrogen atoms have been formally removed, leaving one or more valences free.

The parent structure in acyclic compounds is the main carbon chain, which includes the highest characteristic group, as well as the maximum number of other functional groups, radicals and multiple bonds. In carbo- and heterocyclic compounds, the parent structure is the cycle.

A characteristic group is a functional group associated with the parent structure or partially included in its composition.

A substituent is any atom or group of atoms that replaces a hydrogen atom in the parent compound.

Substitutive and radical-functional nomenclature are most widely represented in the IUPAC rules of systematic nomenclature.

Substitutive nomenclature

To form a name according to substitutive nomenclature, it is necessary to follow the following order: choose the main carbon chain or the main cyclic structure; determine the senior functional group; number the atoms of the main chain or cycle; construct the name of an organic compound.

Radical-functional nomenclature

The use of radical-functional nomenclature is more limited than that of substitutive nomenclature. It is mainly used to name the simplest mono- and bifunctional compounds and some classes of natural substances. The radical-functional nomenclature largely resembles and replaces the previously used rational nomenclature.

Isomerism of organic compounds. In organic chemistry, some substances with the same qualitative and quantitative composition have different properties. Back in 1830, Alexander Mikhailovich Butlerov called such a phenomenon isomerism. One of the provisions of Butlerov's theory of structure is connected with the existence of isomers.

Isomerism is the phenomenon of the existence of isomers.

Isomers are substances that have the same molecular formula but different molecular structure with different properties.

types of isomerism						
structural isomerism					spatial isomerism	
carbon skeleton	multiple bond position isomerism	isomerism of the position of functional groups	Tautomerism	interclass isomerism	configuration isomerism	conformational isomerism
			1.keto-enol		1.geometric (cis-, trans-)	
			2.lactim lactamnaya		2.optical	
			3.cyclo-oxo			
			4.emino-imine			

Currently, two types of isomerism are known in organic chemistry: structural and spatial (stereoisomerism).

Structural isomers are called isomers with a different order of connection of atoms in a molecule.

Structural isomers are divided into a number of groups: chain isomers, position isomers of multiple bonds and functional groups, interclass isomerism.

Spatial isomers are those with the same order of structure, but with a different arrangement of atoms in space. To describe spatial differences, two most important concepts in stereochemistry are used - the configuration and conformation of molecules.

A configuration is a specific spatial arrangement of atoms in a molecule. Configuration is subdivided into geometric and optical.

Conformational isomerism. The spatial forms of molecules formed as a result of rotation around simple single bonds are called rotational (rotational) isomers or conformations. In other words, conformation is the spatial arrangement of atoms and groups of atoms of molecules of a certain configuration, resulting from rotation around a single C–C bond. Separate conformations are distinguished when some groups are rotated relative to others along the σ-bond line through an angle of 60°. Different conformations differ in the amount of potential energy. The transition between different conformations is carried out without breaking σ-bonds. There are two types of conformations. In eclipsed conformations, the substituents on adjacent carbon atoms are eclipsed. In hindered conformations, the torsion angle between adjacent substituents is 60°. This form of connection is more stable. Newman's projection formulas (Newman's projections) are used to represent different conformation forms. These formulas are used to depict conformations in a plane. They are obtained by projecting promising formulas of molecules onto a plane perpendicular to the C–C bond under consideration. The nearest carbon atom is represented by a dot, the far one by a circle. Ethane conformations in the form of Newman projections arising from rotation around the C–C bond (every 60° for a full 360° rotation)

Classification of organic reactions. Organic reactions are classified: according to the method of breaking the bond; by structural type.

According to the type of bond breaking, organic reactions are divided into homolytic and heterolytic.

Homolytic (radical) reactions are accompanied by a homolytic cleavage of a covalent bond. In this case, the pair of electrons that form the bond is divided so that each of the particles receives one electron. As a result of homolytic rupture, free radicals are formed. Radicals are neutral particles containing unpaired electrons. A homolytic gap is characteristic of low-polar or non-polar bonds.

Heterolytic (ionic) reactions are accompanied by heterolytic bond decay, when both electrons of the chemical bond remain with one of the formed particles. As a result of heterolytic bond breaking, charged particles are formed - positive, that is, electrophile and negative, that is, nucleophile. Heterolytic bond breaking is characteristic of highly polar bonds.

According to the structural type, the following organic reactions are distinguished:

1. addition reactions - this is when one new substance is formed from two or more molecules. Addition reactions are characteristic of compounds with multiple bonds.

2. substitution reactions - this is when one atom (or group of atoms) in a molecule is replaced by another atom (or group of atoms), as a result of which a new compound is formed.

3. cleavage (elimination) reactions - this is when a simpler molecule is cleaved off from a molecule and a multiple bond is formed.

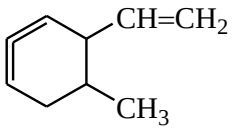
4. decomposition reactions - this is the decomposition of a substance into simpler ones.

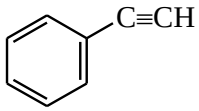
5. redox reactions.

EXERCISES

1. Specify the type of hybridization of all carbon atoms in the compounds:

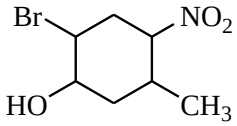
1) $CH_3-C\equiv CH$ 2) $CH_2=CH-CH_2-CN$ 3) $CH_2=C=CH-NH-CH_3$ 4) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

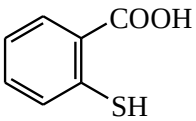
5)  6) 

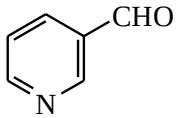
7) 

2. Classify the organic compounds below according to the following criteria:
a) the structure of the carbon chain;
b) the nature of the functional group;
c) the number of functional groups.

1) $CH_2=CH-\overset{\overset{CH_3}{|}}{C}=CH_2$ 2) $CH_2=CH-CH_2-OH$ 3) $\overset{\overset{NH_2}{|}}{CH_2}-CH_2-CH_2-\overset{\overset{NH_2}{|}}{CH_2}$ 4) $\overset{\overset{Cl}{|}}{CH_2}-CH_2-\overset{\overset{OH}{|}}{CH_2}$

5) 

6) 

7) 

3. Classify organic compounds according to the nature of the carbon skeleton and functional groups. Rewrite the structural formulas, select the carbon skeleton and functional groups, name them. Define the class of each connection:

1) $CH_2=CH-CH=CH_2$ butadiene-1,3

2) $CH_3-CH_2-CH_2-SH$ propanethiol-1

3) $CH_2=CH-CHO$ acrolein

4) $NH_2-CH_2-CH_2-OH$ colamine

5) $CH_3-O-CH_2-CH_3$ methoxyethane

6) $CH_2=CH-CH_2-Cl$ 1-chloropropene-2

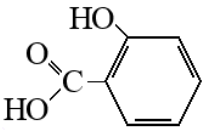
7) $\begin{matrix} | & | & | \\ CH_2-CH-CH_2 \end{matrix}$

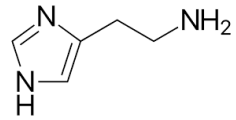
8) $CH_3-S-CH_2-CH_2-\overset{\overset{|}{}}{CH}-COOH$

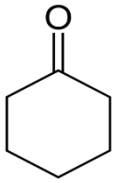
OH OH OH
glycerol

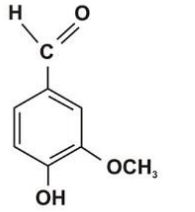
NH_2
methionine

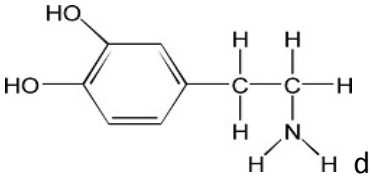
9) CH_3-CH-COOH
OH lactic acid

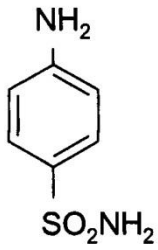
10)  salicylic acid

11)  histamine

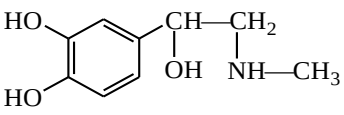
12)  cyclohexanone

13)  vanillin

14)  dopamine

15)  Streptocide

4. Write down the functional groups from the formulas of medicines, and name them.

1) 
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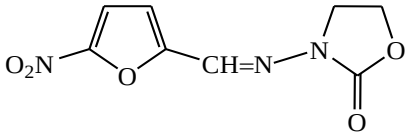
4) 
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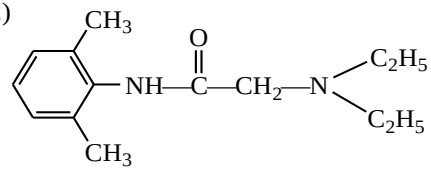
2) 
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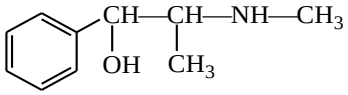
5) 
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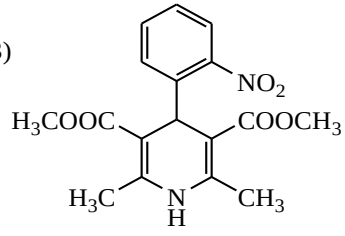
3) 
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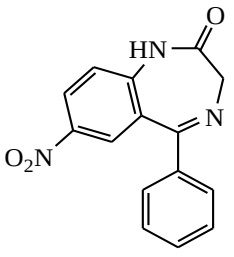
6) 
нитразепам

SECTION II

ACTIVITY № 2

HYDROCARBONS

Topic:

GENERAL CHARACTERISTICS, NOMENCLATURE, ISOMERISM OF HYDROCARBONS.

Purpose of the lesson:

To define the classes of hydrocarbons, to form knowledge of the basic principles of the nomenclature of hydrocarbons and the ability to use them when composing names and writing formulas. To form knowledge about the types of isomerism characteristic of each class of hydrocarbons and the ability to formulate compounds according to these types of isomerism

Questions for discussion

1. General characteristics, nomenclature of alkanes
2. General characteristics, nomenclature of alkenes
3. General characteristics, nomenclature of alkadienes
4. General characteristics, nomenclature of alkynes
5. General characteristics, nomenclature of cycloalkanes
6. General characteristics, nomenclature of arenes
7. Isomerism of alkanes
8. Isomerism of alkenes
9. Isomerism of alkadienes
10. Alkyne isomerism
11. Isomerism of cycloalkanes
12. Isomerism of arenes

Theoretical material

Hydrocarbons (HC) are organic substances whose molecules consist of carbon and hydrogen atoms. Hydrocarbons include saturated and unsaturated acyclic, alicyclic aromatic compounds.

Limit or saturated hydrocarbons (alkanes, paraffins) contain only simple carbon-carbon bonds, all other valences of carbon atoms in their molecules are "used up" on bonds with hydrogen atoms. The general formula is C_nH_{2n+2}. The ancestor of the series is methane CH_4.

Unsaturated or unsaturated hydrocarbons have multiple (double or triple) carbon-carbon bonds.

Alkenes (olefins, ethylene hydrocarbons) contain one double bond. The general formula is C_nH_{2n}. The ancestor of the series is ethylene $CH_2=CH_2$.

Alkynes (acetylenic hydrocarbons) have a triple bond. The general formula is C_nH_{2n-2}. The ancestor of the series is acetylene $CH{\equiv}CH$.

Alkadienes (diolefins, diene hydrocarbons) contain two double bonds. The general formula is the same as for C_nH_{2n-2} alkynes:

1) Alkadienes with isolated double bonds, for example:

$H_2C=CH–CH_2–CH=CH_2$ pentadiene-1,4

2) alkadienes with conjugated double bonds, for example:

$H_2C=CH–CH=CH–CH_3$ pentadiene-1,3

3) alkadienes with cumulated double bonds, for example:

$H_2C=C=CH–CH_2–CH_3$ pentadiene-1,2

4) alkenines - compounds with one double and one triple bonds, for example:

$H_2C=CH–C\equiv CH$ butene-1-in-3

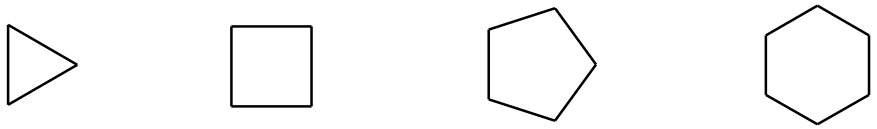
5) alkadiins - compounds with two triple bonds, for example:

$HC\equiv C–C\equiv CH$ butadiine-1,3

6) polyenes (polyolefins) - compounds with many double bonds, for example:

$H_2C=CH–CH=CH–CH=CH–CH_3$ heptatriene-1,3,5

Cycloalkanes (cycloparaffins, polymethylenes, cyclanes) - cyclic compounds contain only simple single bonds. The general formula is C_nH_{2n}:

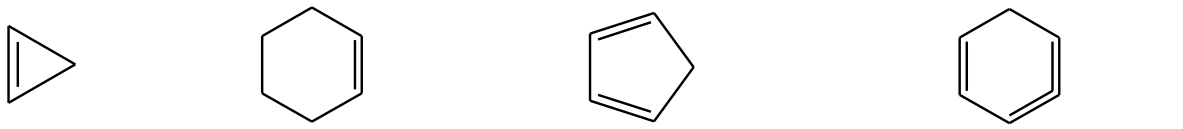


циклопропан циклобутан циклопентан циклогексан

cyclobutane cyclopropane cyclopentane cyclohexane

Cycloalkenes (cycloolefins, cyclenes) - cyclic compounds contain a double bond. The general formula is C_nH_{2n-2}:

Cycloalkadienes - cyclic compounds contain 2 double bonds. The general formula is C_nH_{2n-4}:



циклопропен циклогексен циклопентадиен-1,3 циклогексатриен-1,2,4

cyclopropene cyclohexene cyclopentadiene-1,3 cyclohexatriene-1,2,4

Alicyclic compounds may contain 1, 2 or more cycles.

Aromatic compounds (arenes) - a group of carbocycles characterized by the presence of an aromatic system. Aromatic compounds are of 2 types:

1) benzoid aromatic compounds - an obligatory component of the molecule is the benzene nucleus;

2) non-benzenoid aromatic compounds - structures that meet the requirements of aromaticity, but lack six-membered aromatic rings.

Nomenclature. Nomenclature is used to designate the structure of a substance and the spatial arrangement of atoms in their molecules. The principle of the systematic nomenclature of a compound is based on the designation of the main carbon chain of an organic molecule associated with various substituents. Compounds of each class constitute a homologous series.

A homologous series is a group of related compounds with the same structure, each subsequent member of which differs from the previous one by a homologous difference (–CH_2–).

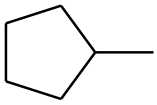
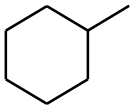
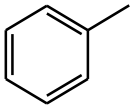
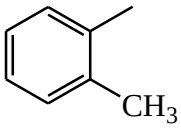
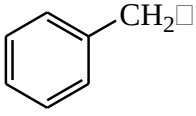
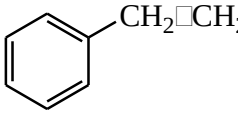
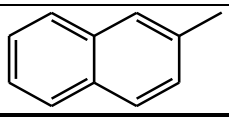
Homologues have similar chemical properties and regularly varying physical properties. For example, consider the homologous series of alkanes.

Names of saturated straight hydrocarbons

CH_4 – methane	C_6H_{14} – hexane	$C_{11}H_{24}$ –dodecane	$C_{18}H_{38}$ – octadecane
C_2H_6 – ethane	C_7H_{16} – heptane	$C_{12}H_{26}$ – undecane	$C_{20}H_{42}$ – eicosan
C_3H_8 – propane	C_8H_{18} – octane	$C_{13}H_{28}$ – tridecane	$C_{30}H_{62}$ – triacontan
C_4H_{10} – butane	C_9H_{20} – nonane	$C_{14}H_{30}$ – tetradecane	$C_{60}H_{122}$ – hexacontane
C_5H_{12} – pentane	$C_{10}H_{22}$ – decane	$C_{16}H_{34}$ – hexadecane	$C_{100}H_{202}$ – hectane

Saturated unbranched hydrocarbons form monovalent radicals. Monovalent radicals - are obtained by detaching a hydrogen atom from a carbon atom, they are called by replacing the suffix -an in the name of the original hydrocarbon with -il.

Names of the most important hydrocarbon radicals

Formula	Name	Formula	Name
CH_3–	methyl	CH_3–CH=CH–	propen-1-yl
CH_3–CH_2–	ethyl	CH_2=CH–CH_2–	allyl
CH_3–CH_2–CH_2–	propyl	CH≡C–	ethynyl
CH_3–CH(–CH_3)–	isopropyl		cyclopentyl
CH_3–CH_2–CH_2–CH_2–	butyl		cyclohexyl
CH_3–CH(–CH_3)–CH_2–	isobutyl		phenyl
CH_3–CH_2–CH(–CH_3)–	sec-butyl		Tolil (given o-isomer)
CH_3–C(–CH_3)(–CH_3)–	tert-butyl		benzyl
CH_3–CH_2–CH_2–CH_2–CH_2–	pentyl		phenethyl
CH_2=CH–	vinyl		naphthyl

Branched alkanes are named based on the longest carbon chain, with the addition of prefixes denoting side chain radicals (see Table 2). The chain is numbered in such a way that the substituent locants are the smallest.

Unsaturated acyclic hydrocarbons having one double bond are given the generic name alkenes. Their names are formed by replacing the suffix -an in the corresponding alkane with -ene. In the presence of two or more double bonds, the suffixes -adiene, -atriene, etc. are used. Hydrocarbons containing one triple bond have the generic name alkynes. The presence of a triple bond is reflected in the name by the suffix –in. The carbon chain is numbered so that the multiple bond has the smallest locant.

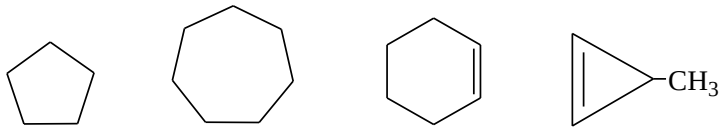
Unsaturated unbranched acyclic hydrocarbons, having both double and triple bonds, receive suffixes -enine, -adienine, etc., replacing -an in the corresponding alkanes. When numbering the carbon chain, the double bonds should be given the lowest number.

$CH \equiv C — CH = CH — CH_2 — CH_3$ $CH \equiv C — CH = CH — CH = CH_2$

гексен-3-ин-1 гексадиен-1,3-ин-5

hexen-3-**ene**-1 hexadiene-1,3-**ene**-5

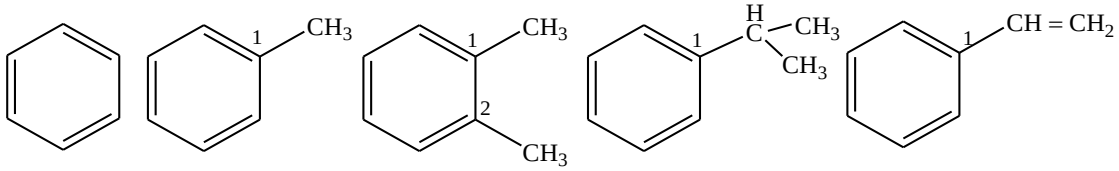
The names of saturated monocyclic hydrocarbons are formed by adding the prefix cyclo– to the name of an acyclic saturated straight hydrocarbon with the same number of carbon atoms. The generic name of such hydrocarbons is cycloalkanes. When writing cyclic structures, the symbols for carbon and hydrogen atoms are often omitted. Unsaturated cyclic hydrocarbons are called by replacing the suffix -ane in cycloalkanes with -ene, -ine, -adiene, etc. The position of multiple bonds is indicated by smaller numbers. Monovalent radicals formed from cyclic hydrocarbons are named similarly to the radicals of acyclic hydrocarbons (see Table 2). The numbering in such a radical is carried out from a carbon atom with a free valence.



циклопентан циклогептан циклогексен 2-метилциклопентен-1

cyclopentane cycloheptane cyclohexene 2-methylcyclopentene-1

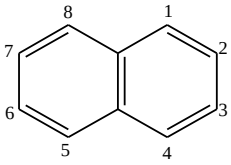
In the series of aromatic hydrocarbons, the generic name of which is arenes, the following non-systematic names are preserved for monocyclic compounds:



бензол толуол орто-ксилол кумол стирол

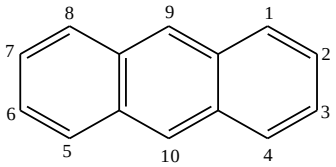
benzene toluene ortho-xylene cumene styrene

Other monocyclic substituted arenes are named as derivatives of benzene or one of the given hydrocarbons, unless the introduced substituent is identical to the one already present. In the latter case, such a compound is named as substituted benzene. Substituent positions are indicated by the smallest numbers, and for disubstituted compounds in positions 1,2-, 1,3- and 1,4-, the designations o- (ortho-), m- (meta-) and p- (para-) can be used, respectively . Of the more than 30 parent structures of condensed arenes, four are the most common:



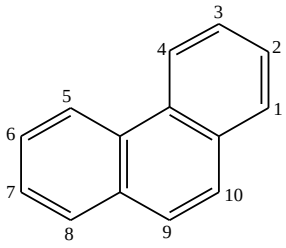
нафталин

naphthalene



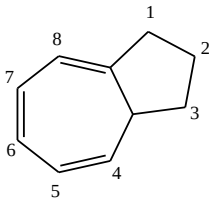
антрацен

anthracene



фенантрен

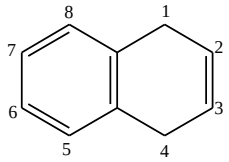
phenanthrene



азулен

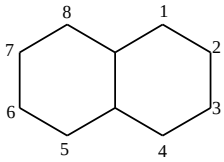
azulene

Condensed hydrocarbons with a lower degree of unsaturation than in aromatic systems (partially or fully hydrogenated) are given the names of the corresponding aromatic hydrocarbons with the prefixes dihydro-, tetrahydro-, etc.; the prefix perhydro- means full saturation:



1,4-дигидронафталин

1,4-dihydronaphthalene



декагидронафталин
или пергидронафталин

perhydronaphthalene

Isomerism of alkanes

Alkanes are characterized

– Structural isomerism: isomerism of the carbon skeleton.

– spatial isomerism: conformational isomerism; configuration isomerism.

In the homologous series of alkanes, structural isomerism, namely, the isomerism of the carbon skeleton, is manifested in the fourth homologue - butane. It is characterized by the presence of isomers with a linear (unbranched) and branched carbon chain.

$CH_3–CH_2–CH_2–CH_3$ n-бутан

$CH_3–\underset{\displaystyle CH_3}{\underset{|}{CH}}–CH_3$ изобутан

Linear alkanes are called normal and are preceded by the letter n. The number of possible isomers increases with the number of carbon atoms. So, for hexane, 5 isomers are known, for octane, the number of possible isomers is 18, for decane - 75, and for eikazane - more than 300 thousand.

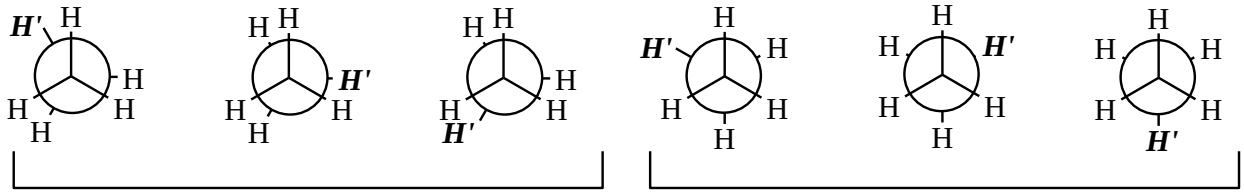
The carbon atoms of alkanes are in sp^3-hybridization and are capable of forming four σ-bonds with hydrogen atoms or with other carbon atoms. With such

compounds, groups of atoms can freely rotate around the C-C bond, forming various rotational isomers - conformations.

Conformations arise due to internal rotations around σ-bonds without breaking them.

As the length of the carbon chain increases, alkanes have more opportunities for free rotation around C-C bonds, which leads to the appearance of a greater number of conformers. The carbon chain can take on a zigzag (the atoms are in an advantageous hindered conformation) or a pincer conformation (energetically less favorable due to the obscured arrangement of atoms in the molecule). There are also irregular conformations.

Ethane is one of the simplest molecules for which the existence of conformations is possible. As a result of a complete rotation performed by one methyl group relative to another, an infinite number of conformations arise, six of them with torsion angles that are multiples of 600 - three eclipsed and three hindered.



заслоненные конформации

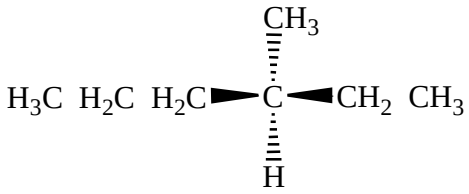
eclipsed conformation

заторможенные конформации

hindered conformations

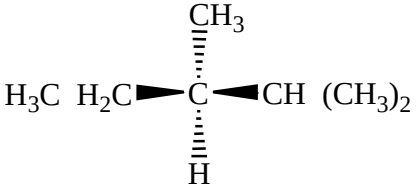
Thus, alkanes are characterized by conformational isomerism, which is one of the types of spatial isomerism.

Some structural isomers of alkanes may contain asymmetric carbon atoms, which leads to the appearance of stereoisomers. For example, among the 9 isomers of heptane, two have an asymmetric carbon atom, and each of these chiral heptanes can exist as a pair of enantiomers, that is, configurational isomers.



(S)□3□метилгексан

(S)- 3-methylhexane



(R)□2,3□диметилпентан

(R) – 2,3-dimethylpentane

For the branched hydrocarbon 3,4-dimethylhexane, the existence of diastereomers is also possible.

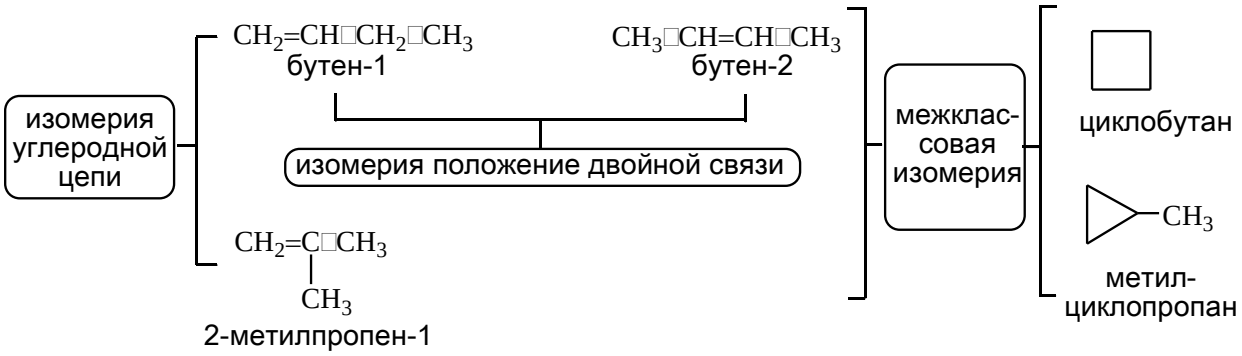
Isomerism of alkenes

Alkenes are characterized

– structural isomerism: isomerism of the carbon skeleton; isomerism the position of a multiple bond (milk); interclass isomerism (isomeric to cycloalkanes).

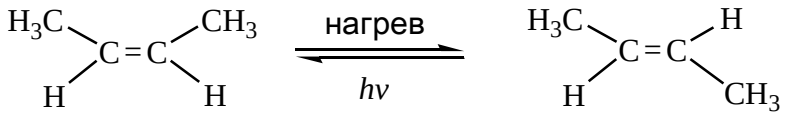
– spatial isomerism: geometric isomerism.

Structural isomerism in the alkene series is represented by chain isomerism, double bond position isomerism, and interclass isomerism. The first homologue, which has all kinds of structural isomerism, is the C_4H_8 alkene.



carbon chain isomerism **double bond position isomerism** **interclass isomerism**

Alkenes can form configurational, so-called geometric isomers. Rotation around the double bond is difficult and can only occur when the π-bond is broken. Therefore, alkenes with different substituents at the ends of the double bond can exist in the form of spatial isomers that differ in the arrangement of substituents relative to the double bond: in the cis isomer, both substituents are located on the same side, in the trans isomer, on opposite sides of the double bond.



цис-бутен-2 ***cis*-butene-2** *транс*-бутен-2 ***trans*-butene-2**

Cis-, *trans*-isomers are individual substances and differ in physicochemical properties, that is, they are stable under normal conditions. Their interconversions are possible at relatively high temperatures or irradiation with ultraviolet light, or under the action of high-energy reagents capable of breaking the π-bond.

The phenomenon of geometric isomerism is inherent in classes of organic compounds that have double bonds.

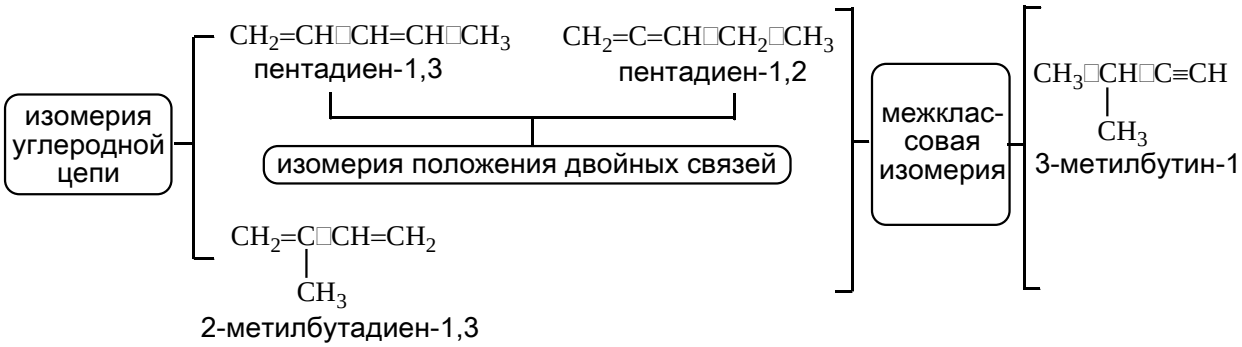
Isomerism of alkadienes

Alkadienes are characterized

– structural isomerism: isomerism of the carbon skeleton; isomerism of the position of multiple bonds (milk); interclass isomerism (isomeric to alkynes).

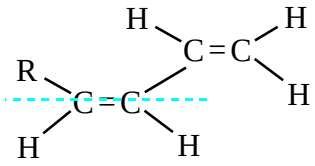
– spatial isomerism: geometric isomerism.

The structural isomerism of alkadienes, like alkenes, is determined by the structure of the carbon skeleton, the position of double bonds, and interclass isomerism. Starting with compounds containing 5 carbon atoms, all types of structural isomerism are characteristic.



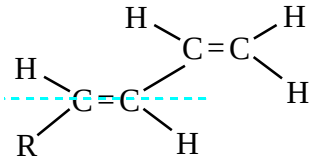
carbon chain isomerism | double bond position isomerism | interclass isomerism

Dienes having various substituents at carbon atoms at double bonds exist in the form of *cis*-, *trans*-isomers.



цис-изомер

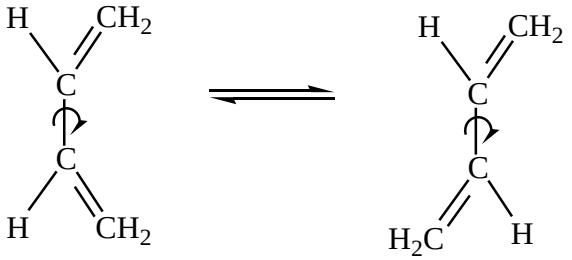
Cis-isomer



транс-изомер

trans-isomer

In addition, due to rotation along the σ-bond separating double bonds, rotational (conformational) isomerism is manifested.



цис-конформация

Cis-conformation

транс-конформация

trans-conformation

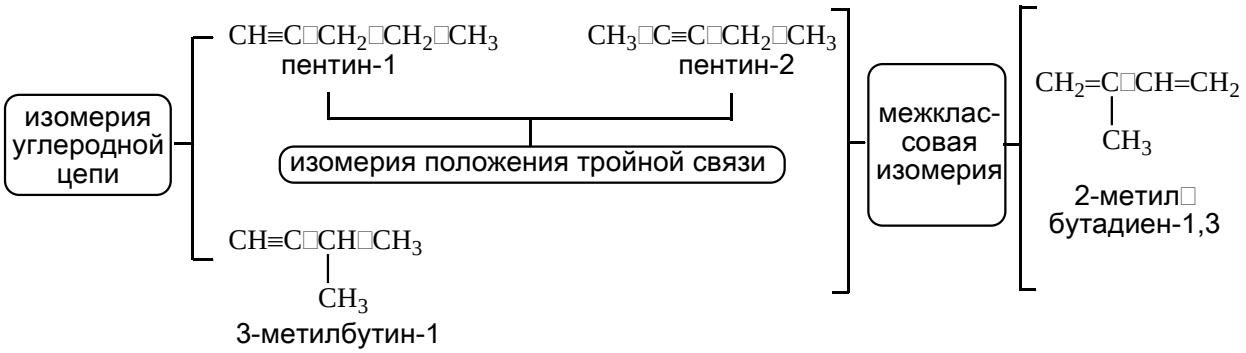
Some chemical reactions of conjugated dienes are selective only with a certain rotational isomer.

Alkyne isomerism

Alkynes are characterized

– structural isomerism: isomerism of the carbon skeleton; isomerism the position of a multiple bond (triple); interclass isomerism (isomeric to alkadienes).

The structural isomerism of acetylenic hydrocarbons is determined by three factors: the structure of the main carbon chain, the position of the triple bond in it, and interclass isomerism. The first homologue, which has all kinds of structural isomerism, is the C_5H_8 alkyne.

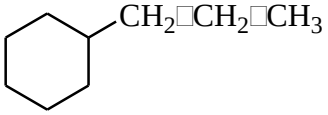


carbon chain isomerism double bond position isomerism interclass isomerism

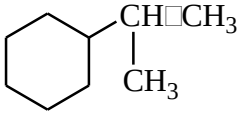
Isomerism of cycloalkanes

A number of cycloalkanes are interesting in that all types of isomerism are found here. Among the structural ones, isomers are distinguished that differ:

1) the structure of the side chain

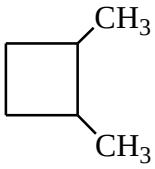


пропилциклогексан
Propylcyclohexane

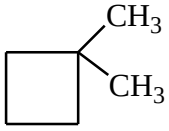


изопропилциклогексан
isopropylcyclohexane

2) the position of deputies

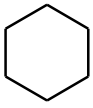


1,2-диметилциклобутан
1,2-Dimethylcyclobutane

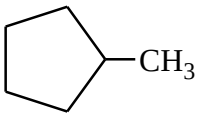


1,1-диметилциклобутан
1,1-Dimethylcyclobutane

3) ring size

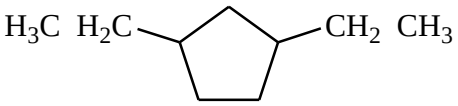


циклогексан
Cyclohexane

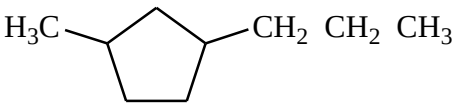


метилциклопентан
methylcyclopentane

4) the size of radicals (metamerism)



1,2-диэтилциклопентан
1,2-diethylcyclopentane



1-метил-2-пропилциклопентан
1-methyl 2-propylcyclopentane

5) interclass isomerism: cycloalkanes are isomeric to alkenes

CH_2=CH□CH_3

циклопропан пропен

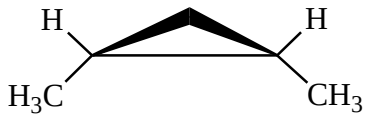
Cyclopropane propene

Spatial isomerism is also widespread in the cycloalkanes series. They are characterized by:

1) geometric cis-trans isomerism

In cycloalkanes with two substituents located at adjacent carbon atoms in the ring, the cis-trans isomerism is due to the different mutual arrangement of substituents in space relative to the plane of the ring. In cis-isomers, the substituents are located on one side of the ring plane, in trans-isomers, the substituents are located on opposite sides.

For example: in a 1,2-dimethylcyclopropane molecule, two CH_3 groups can be on the same side of the ring plane (*cis*-isomer) or on opposite sides (*trans*-isomer):



цис-1,2-диметилциклопропан

Cis-1,2-dimethylcyclopropane

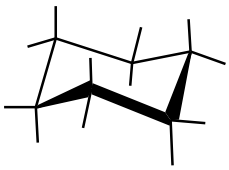
транс-1,2-диметилциклопропан

trans -1,2-dimethylcyclopropane

For 1,1-dimethylcyclopropane, cis-trans isomerism is not typical.

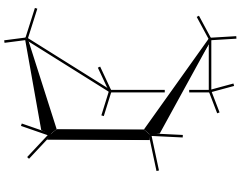
2) rotational (conformational) isomerism of cycloalkanes

All rings, except for cyclopropane, have a non-planar structure, which is due to the tendency of carbon atoms to form normal (tetrahedral) angles between bonds. This is achieved by rotations along the C–C σ-bonds included in the cycle. In this case, various conformations (rotation isomers) with different energies arise, and those that have the lowest energy, i.e., are most often realized. more sustainable. For example, cyclohexane can take three conformations: "armchair", "bath","twist".



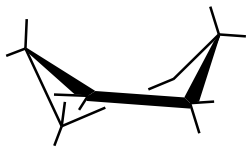
кресло

"armchair"



ванна

"bath"



твист

"twist".

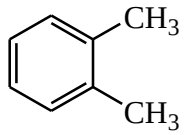
There is no angular tension in these conformations. However, they are not energetically equivalent. Among them, the chair conformation is the most stable, since all neighboring carbon atoms in it are in an energetically more favorable hindered conformation. It is not possible to separate the conformations of cyclohexane, since at ordinary temperatures they quickly turn into each other.

However, the chair conformation, being more stable, makes up 99% of the equilibrium mixture under normal conditions.

Isomerism of arenes

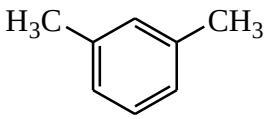
Arenas are characterized

1) isomerism of the position of substituents in the benzene ring



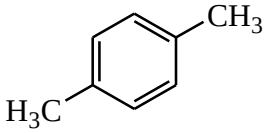
1,2-диметилбензол
орто-ксилол

1,2-dimethyl benzene
ortho-xylene



1,3-диметилбензол
мета-ксилол

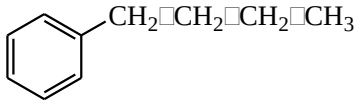
1,3-dimethyl benzene
meta-xylene



1,4-диметилбензол
пара-ксилол

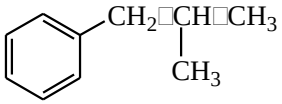
1,4-dimethyl benzene
para-xylene

2) side chain isomerism (radical structure and number of radicals).



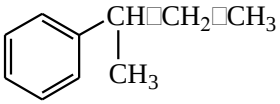
бутилбензол

butylbenzene



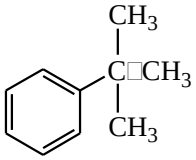
изо-бутилбензол

iso-butylbenzene



втор-бутилбензол

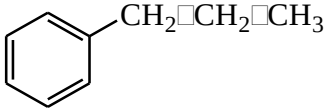
sec-butylbenzene



трет-бутилбензол

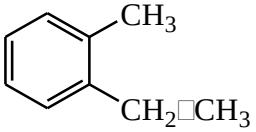
tert-butylbenzene

3) isomerism of radicals (metamerism).



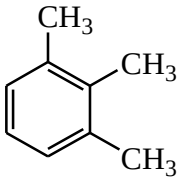
пропилбензол

propylbenzene



1-метил-2-этилбензол

1-methyl-2-ethylbenzene



1,2,3-триметилбензол

1,2,3-trimethylbenzene

EXERCISES

1. Make structural formulas of hydrocarbons:

1) 4-isopropyl-3-ethylheptane;
2) 2,3,7-trimethyl-5-ethyloctane;
3) 5-methylhexadiene-1,4;
4) 1-methyl-4-propylbenzene;
5) 2,5-dimethylhexene-1;
6) 3,3-dimethylbutyne-1;
7) allylnaphthalene;
8) ethylcyclobutane;
9) 2,3-dimethylhexadiene-1,3-yn-5;
21) 5,6-diethylcyclohexadiene-1,3;
22) 5-isobutyl-4-cyclopentyldecane;
23) 2-benzyl-3-methylhexadiene-1,4;
24) o-propylethylbenzene;
25) 2,3-dimethylnaphthalene;
26) 4-allyltoluene;
27) 3-phenyloctadiine-4,6-diene-1,2;
28) 2,7-dimethyl-3-ethyloctyne-4;
29) 5-methylcumene;

10) 2-phenyl-3,6-diethyloctene-4;
11) hexamethylbenzene;
12) 5-methylcyclohexadiene-1,3;
13) 1,1-dimethylcyclopropane;
14) 3-propylstyrene;
15) 5-ethynylheptatriene-1,3,6;
16) 4-butyl-2-cyclopropyloctane;
17) 4-propyl-2-ethyltoluene;
18) 2-methyl-5-tert-butylheptin-3;
19) 2-propylbutene-1-in-3;
20) 1-butyl-3-ethynyl-5-ethylbenzene;
30) 3,4,6-trimethylcyclohexene-1;
31) 2,4-dimethyl-6-vinylbenzene;
32) 3-naphthylhexadiene-1.5;
33) 1-ethynyl-5-isobutylcyclopentane;
34) 1-propyl-4-tert-butylbenzene;
35) 3-methylhexadiine-1.5;
36) 1-pentyl-3-ethylcycloheptane;
37) 2,4-dimethyl-4-phenethyloctane;
38) 3-isopropylheptatetraene-1,2,4,5;
39) 1,3-diethylazulene;
40) perhydroanthracene.

2. An alkane in the molecule of which there are only primary and tertiary carbon atoms, and there are twice as many primary ones as tertiary ones - these are:

1) 2-methylpentane;
2) 2-methylbutane;
3) 2,3-dimethylpentane;
4) 2,3-dimethylbutane.

3. An alkane that does not have a quaternary carbon atom in its molecule is:

1) 2,2-dimethylpropane;
2) 3,4-diethylhexane;
3) 2,2-dimethylbutane;
4) 3,3-diethylpentane.

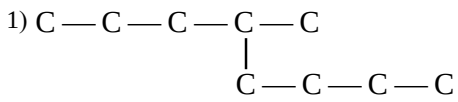
4. One tertiary carbon atom contains:

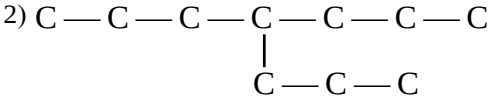
1) butane;
2) 2,2-dimethylbutane;
3) 2,2,3,3-тетраметилбутан;
4) 2-метилбутан.

5. An alkane whose molecule has three secondary carbon atoms is:

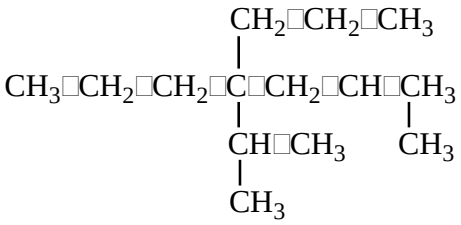
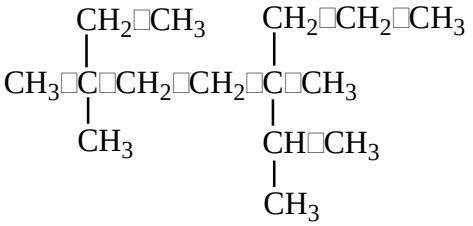
1) hexane;
2) 2-methylpentane;
3) pentane;
4) butane.

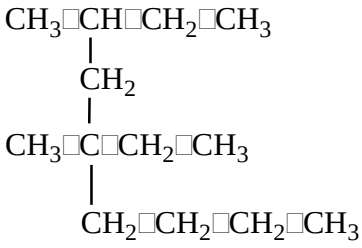
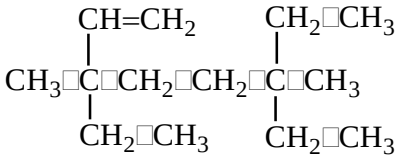
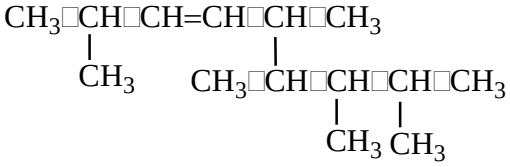
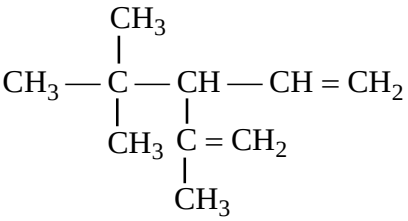
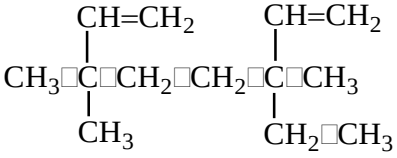
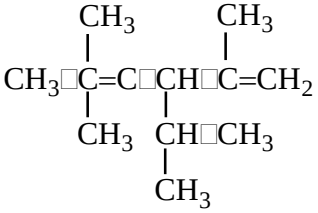
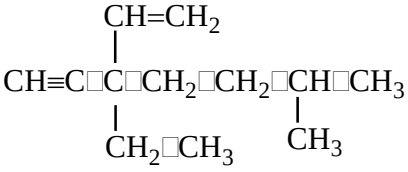
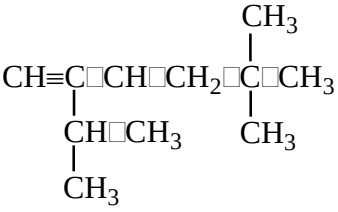
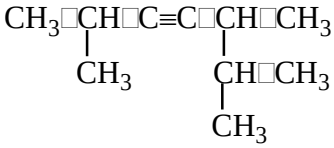
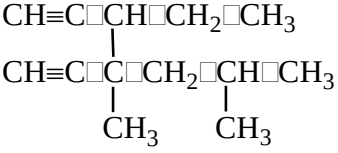
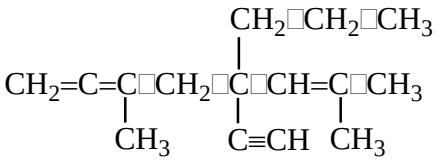
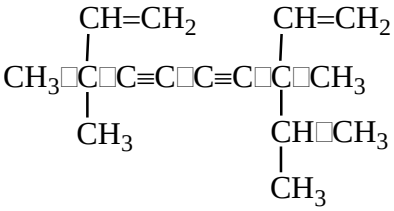
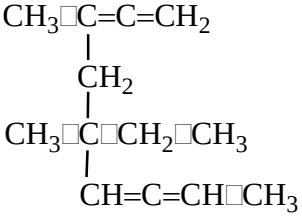
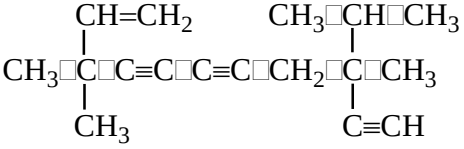
6. How many alkadienes with cumulated, conjugated, isolated bonds can have such carbon skeletons:

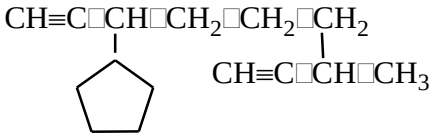
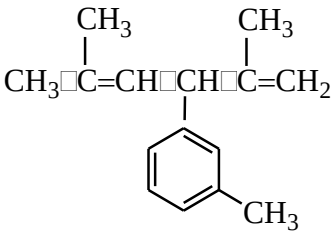
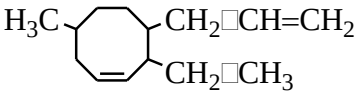
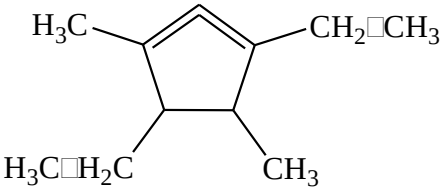
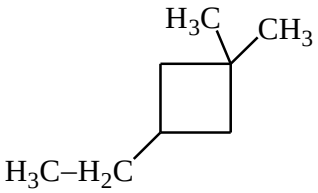
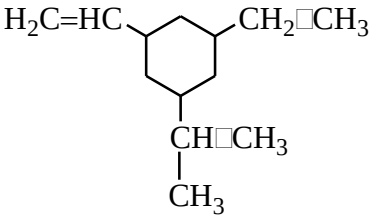
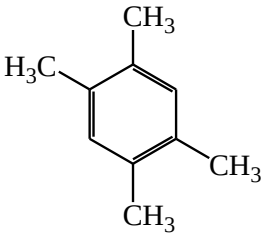
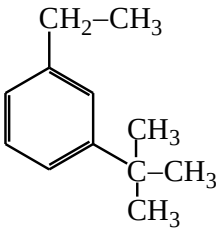
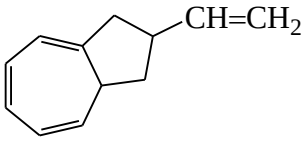
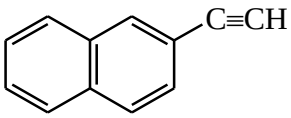
1) 

2) 

7. Name the following hydrocarbons according to the systematic nomenclature:

1. 	2. 

3. 	4. 
5. 	6. 
7. 	8. 
9. 	10. 
11. 	12. 
13. 	14. 
15. 	16. 

17. 	18. 
19. 	20. 
21. 	22. 
23. 	24. 
25. 	26. 

8. Write the structural formulas of the isomers of the following hydrocarbons and name them:

1) C_6H_{14}; 2) C_6H_{12}; 3) C_5H_8; 4) C_9H_{12}; 5) C_4H_{10}; 6) C_5H_{10}; 7) $C_{10}H_{14}$; 8) C_6H_{10}.

9. Draw the structural formulas of 2-methylpentene-2 and pentine-1. Bring for them:

1) carbon skeleton isomer;
2) the isomer of the position of the multiple bond;
3) interclass isomer;

4) geometric isomers (if possible);
5) optical isomers (if possible).
Name all compounds.

10. Write the projection formulas for the geometric isomers of the following hydrocarbons:

1) $CH_3–CH=CH–CH_3$

2) $CH_3–CH=CH–CH_2–CH_3$

3) $CH_2=CH–CH_3$

4) $CH_3–\underset{\displaystyle CH_3}{\underset{|}{CH}}–CH=CH–\underset{\displaystyle CH_3}{\underset{|}{CH}}–CH_3$

5) $CH_3–CH=CH–\underset{\displaystyle CH_3}{\underset{|}{CH}}–CH_3$

6) $CH{\equiv}C–CH_3$

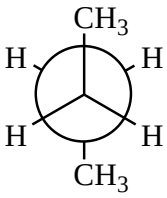
7) $CH_3–CH=CH–CH_2–CH_2–CH_3$

8) $CH_3–CH=\underset{\displaystyle CH_3}{\underset{|}{C}}–CH_2–CH_3$

11. Using Newman's projection formulas, write the eclipsed and hindered conformations of the following compounds:
1) arising from rotation around the C_1-C_2 bond for ethane;
2) arising from rotation around the C_1-C_2 bond for butane;
3) arising from rotation around the C_2-C_3 bond for isobutane;
4) arising from rotation around the C_1-C_2 bond for 2-methylbutane;
5) arising from rotation around the C_3–C_4 bond for pentene-1.

12. Determine the type of conformation (shielded or hindered), write the structural formulas of hydrocarbons, the conformations of which are given below:

1)



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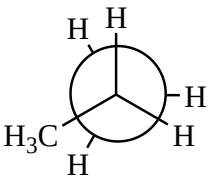

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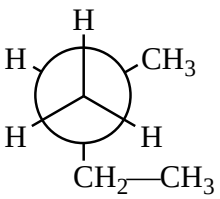

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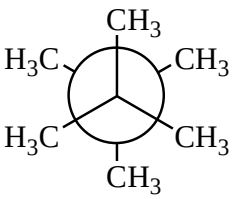

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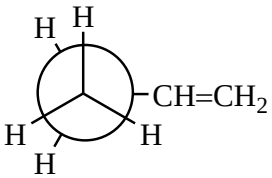

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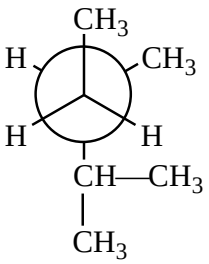

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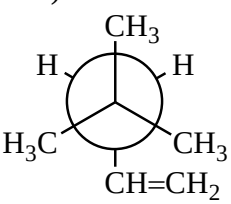

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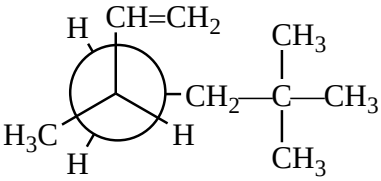


ACTIVITY № 3

Topic:

THE ELECTRONIC STRUCTURE OF CONJUGATED AND AROMATIC SYSTEMS. MUTUAL INFLUENCE OF ATOMS IN AN ORGANIC MOLECULE

Purpose of the lesson:

To form knowledge about the electronic structure of molecules with conjugated bonds as thermodynamically stable systems used in the construction of biologically active compounds; mutual influence of atoms as a factor in the formation of reaction centers; the ability to determine the type of conjugated systems, the type and sign of the inductive and mesomeric effects of functional groups in organic compounds, electron-donating and electron-withdrawing substituents.

Issues for discussion

1. Hybridization of the carbon atom in organic compounds
a) sp^3 hybridization
b) sp^2 hybridization
c) sp hybridization
2. Types of chemical bonds in organic compounds
a) σ-bond
b) π bond
3. Conjugated systems with an open chain, their types
a) π,π-conjugation
b) p,π-conjugation.
4. Systems with a closed circuit of conjugation.
5. Criteria for aromaticity. Hückel's rule.
6. Electronic effects
a) inductive effect
b) mesomeric effect
7. Electron donor and electron acceptor substituents.

Theoretical part

Conjugated open circuit systems

π-bond can be localized and delocalized. A localized, two-center is a double bond, in which the electron density of the π-bond covers only two nuclei of the bonded atoms. A delocalized π bond spans more than two atoms. Delocalized coupling is characteristic of conjugated systems. If in organic molecules there are two double bonds (or more) separated by one single bond, or, in general, the atom adjacent to the double bond has a p-orbital (vacant, populated by one or two p-electrons), then p-orbitals neighboring atoms can overlap with each other, forming a common π-electron system. Such a system is called a conjugate system.

Conjugation is the formation of a single delocalized electron cloud in a molecule as a result of overlapping of non-hybridized p-orbitals.

There are two types of conjugation: π-π-conjugation and p-π-conjugation.

π-π-Conjugation is a conjugation in which π-electrons of a multiple bond participate.

Signs of π-π-conjugation:

– the presence of 2 or more multiple bonds in the molecule;

– alternation of multiple and single bonds.

π-π-conjugate systems

π,π-Сопряженные системы

бутадиен-1,3 акролеин винилацетилен

butadiene -1,3 acrolein vinylacetylene

An example of the simplest π-π-conjugated system is the 1,3-butadiene molecule. In a 1,3-butadiene molecule, two π-bonds are separated by one σ-bond. All carbon atoms are in sp2 hybridization, and the molecule has a planar structure. The unhybridized pz orbitals of each carbon atom are located perpendicular to this plane, i.e. parallel to each other. This creates conditions for their mutual overlap. The overlapping pz-orbitals leads to the socialization of p-electrons, the formation of a single π-electron cloud. In this case, they say that delocalization of π-electrons occurs, i.e., a π-π-conjugated system is formed.

p-π-Conjugation is a conjugation in which π-electrons of a multiple bond and p-electrons of a lone electron pair of heteroatoms participate: oxygen, nitrogen, halogens, sulfur.

Signs of p-π-conjugation:

– the presence of at least one multiple bond in the molecule;

– the presence in the molecule of a heteroatom with an unshared electron pair;

– the bond of the heteroatom directly with the sp2-hybrid carbon atom, which forms a double bond.

p-π-conjugated systems

ρ,π-Сопряженные системы

винилметиловый эфир винилдиметиламин винилхлорид

vinyl methyl ether vinyl dimethylamine vinyl chloride

Conjugation can be carried out not only in neutral molecules, but also in free radicals, ions:

аллил-радикал аллил-катион аллил-анион

allyl radical allyl cation allyl anion

An example of a p-π-conjugated system is the vinyldimethylamine molecule. In the vinyldimethylamine molecule, the conjugation chain includes three sp2 hybridized atoms. Two of them are carbon atoms forming a multiple bond and one more is a nitrogen atom with a lone electron pair. Each of these atoms has one non-hybrid pz-orbital, which will be located perpendicular to the plane of σ-bonds and parallel to each other. The interaction of the pz-orbitals of the π-bond with the pz-orbital of the heteroatom leads to the delocalization of the electron density, that is, p,π-conjugation occurs.

Conjugated closed circuit systems. Aromaticity

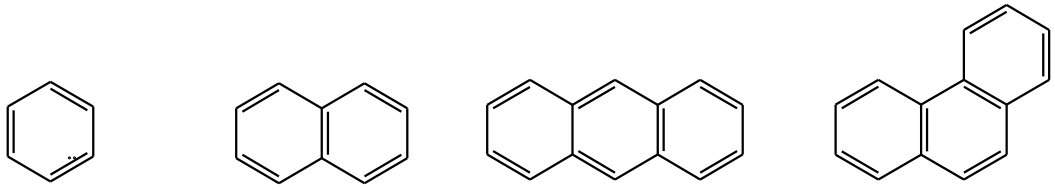
In closed conjugated systems, conditions are created for the circular delocalization of p-electrons, and they have special aromatic properties. Aromaticity is understood as the ability of planar cyclic systems with a closed conjugation system, covering all atoms of the cycle, to enter into substitution reactions under normal conditions, rather than addition, and to have an increased resistance of the cycle to cleavage and oxidation. A typical carbocyclic aromatic system is the benzene molecule. All carbon atoms in the molecule are in the sp2-hybridized state, the σ-skeleton of the molecule is planar, p-orbitals are located perpendicular to the σ-skeleton and parallel to each other. As a result, a single 6-center π-π-π-conjugated system is formed. Its formation leads to alignment of all distances between carbon atoms up to 0.140 nm and stabilization of the molecule. Aromatic properties are possessed not only by benzene and its homologues, but also by compounds with condensed benzene rings (naphthalene, anthracene), some ions (cyclopentadienyl anion, cycloheptatrienyl cation), heterocyclic compounds, if they meet the aromaticity criteria.

The criteria for aromaticity were established by Hückel in 1931 and are called the Hückel rule. A system is aromatic if it has all of the following features:

– all atoms in the cycle are in sp^2 hybridization (hence the σ-skeleton is planar);

– the molecule has a cyclic conjugation system;

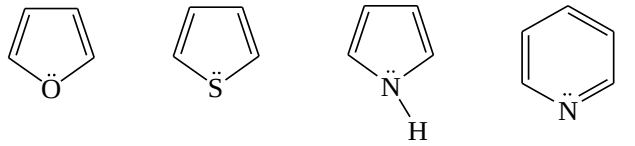
– (4n+2) p-electrons are involved in conjugation, where n is an integer.



бензол 6 р-электронов (n=1)	нафталин 10 р-электронов (n=2)	антрацен 14 р-электронов (n=3)	фенантрен 14 р-электронов (n=3)
benzene 6 p-electrons (n=1)	**naphthalene 10 p-electrons (n=2)**	**anthracene 14 p-electrons (n=3)**	**phenatrene 14 p-electrons (n=3)**

In these systems, all carbon atoms are in sp2 hybridization, therefore, the σ-skeleton is planar, and the p-orbitals are arranged in parallel. The conjugation is closed and 6, 10 and 14 p-electrons, respectively, participate in the conjugation. Therefore, these systems exhibit aromatic properties.

In heterocyclic molecules, a single π-electron system is formed with the participation of p-orbitals of carbon atoms and p-orbitals of heteroatoms. The most important aromatic heterocycles are furan, thiophene, pyrrole, pyrimidine.



фуран тиофен пиррол пиридин

furan **thiophene** **pyrrole** **pyridine**

However, not all conjugated closed chain systems are aromatic. So, for example, cyclooctatetraene-1,3,5,7 does not belong to aromatic ones, since Hückel's rule is not satisfied, 4n+2=8 p-electrons, n=1.5.

Electronic Effects

Electronegativity - the ability of atoms to shift the electron density of a covalent bond towards itself. In molecules containing atoms of different electronegativity, the electron density of chemical bonds is distributed unevenly, which leads to polarization of the covalent bond and the appearance of partial charges, denoted δ.

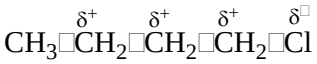
In organic molecules, two types of electronic effects of functional groups (substituents) are distinguished: shift of electron density in σ-bonds (inductive effect) and shift of electron density along the conjugated system (mesomeric effect).

The inductive effect is the transfer of the electronic influence of the substituent along the chain of σ-bonds, caused by the difference in the electronegativity values of the atoms. The inductive effect is denoted by the letter I and is graphically represented by an arrow, the tip of which is directed towards the more electronegative element.

The –I effect is manifested by substituents that contain atoms with a higher electronegativity than carbon: –F, –Cl, –Br, –OH, $–NH_2$, –CHO, –COOH, etc. These are electron-withdrawing substituents. They reduce the electron density in the carbon chain. The higher the electronegativity of the heteroatom included in the substituent, the greater the negative inductive effect.

The +I effect is exhibited by alkyl radicals $–CH_3$, $–CH_2–CH_3$….. Moreover, the electron-donor properties of alkyl radicals increase with the length of the hydrocarbon chain ($–C_4H_9$> $–CH_3$) and increase in the series from primary to tertiary radicals . The latter is explained by the fact that the inductive effect is attenuated in the circuit.

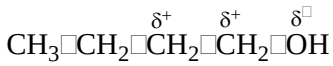
The benzene ring and similar aliphatic substituents containing –C=C– exhibit the –I effect (and not the +I effect, like all other hydrocarbon radicals, without alternating double and single bonds). This can be explained by the fact that the carbon atoms in the benzene ring are in the sp^2 hybrid state. And the electronegativity of carbon atoms in different types of hybridization is different:



-I (Cl)

1-хлорбутан

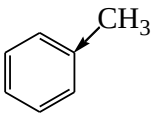
1-chlorobutane



-I (OH)

бутанол-1

butanol-1



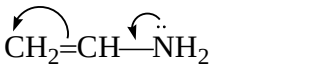
-I (C_6H_5)

+I (CH_3)

толуол

toluene

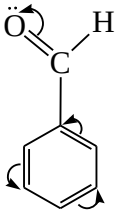
The mesomeric effect is the transfer of the electronic influence of a substituent along the conjugation chain. It manifests itself only in the presence of a conjugate system and is undamped (propagates throughout the conjugate system). It is customary to consider such a conjugation effect to be positive, in which the substituent (functional group) displaces electrons along the conjugation chain away from itself (+ M-effect), and negative if the substituent displaces electrons along the conjugation chain towards itself (–M-effect). The direction of electron density shift under the influence of the M-effect is indicated by curved arrows from the middle of the π-bond or a pair of p-electrons from or to the substituent.



-M (NH_2)

виниламин

Vinylamine



-M (CHO)

бензальдегид

benzaldehyde

The +M effect is exhibited by all heteroatoms that have lone electron pairs, if their participation in conjugation is carried out precisely due to this lone electron pair (p-π-conjugation).

The –M effect is exhibited by all substituents having a vacant orbital, and substituents having a π-bond between atoms with different electronegativity, while the substituent is attached to the conjugated system by a less electronegative atom. Due to the shift of electrons towards the more electronegative atom, the less electronegative atom has a deficit of electrons, i.e. it has a partial positive charge.

mesomeric effect	**Deputy**
+M-effect	–OH; –OR; –NH_2; –NHR; –NR_2; –F; –Cl; –Br; –I; –SH; –SR; –O^-
–M-effect	–COOH; –COOR; –CHO; >C=O; –NO_2; –SO_3H; –C≡N

Groups that have bonds between identical atoms, such as the benzene ring, are conductors of mesomeric effects of both signs. They are involved in the conjugation system, but they do not have their own mesomeric effect, since they do not contain atoms with a lone pair of electrons or a vacant orbital. Thus, the

peculiarity of the benzene ring and aliphatic groups similar to it will be that they have an inductive effect and it is negative (–I), but there is no mesomeric effect.

In the molecules of organic compounds, along with the existing mesomeric effect, the inductive effect also acts simultaneously. Both effects can act either in concert or in opposite directions. As a result, a certain cumulative effect appears - an electron-donor or electron-acceptor action. If the mesomeric and inductive effects have different signs, then the mesomeric effect significantly prevails over the inductive effect, the only exceptions are halogens, for them the inductive effect is predominant, therefore they are always electron-withdrawing substituents.

EXERCISES

1. Write the structural formulas and determine the type of hybridization of the carbon atom:

1) cyclohexane;
2) methylbenzene;
3) 2-ethylpenten-2-in-4;
4) methylonitrile;
5) 2-methylbutadiene-1,3;
6) cyclopentene;
7) butadiene-1,2;
8) butin-1.

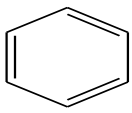
2. Find among the given compounds those that have conjugated systems, and in conjugated systems determine the type of conjugation. Name all these compounds:

1) $CH_2=CH—CH=CH—CH=CH_2$

2) $CH_2=CH—O—CH_3$

3) $CH_2=CH—CH_3$

4) $CH_2=CH—CH=CH—CH_3$

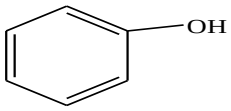
5) 

6) $CH_2=CH—N—(CH_3)_2$

7) $CH_3—CH=CH—CH_3$

8) $CH_2=CH—COOH$

9) $CH_3—COOH$

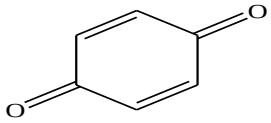
10) 

11) $CH_2=CH—O—CH=CH_2$

12) $CH≡C—CH=CH_2$

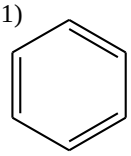
13) $CH_2=CH—Cl$

14) $CH_3—CH_2—CHO$

15) 

3. Choose aromatic structures among the given compounds, using aromaticity criteria for proof:

benzene **purine** **cyclopentadiene -1,3** **naphthalene** **furan**

1) 

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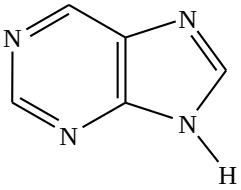
2) 

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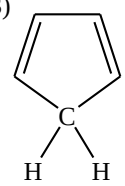
3) 

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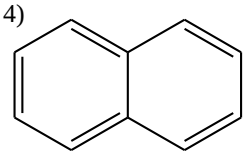
4) 

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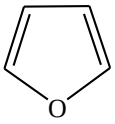
5) 

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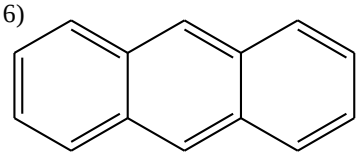
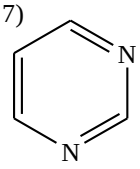
6) 

антрацен

7) 

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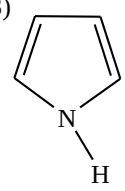
8) 

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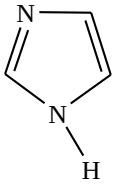
9) 

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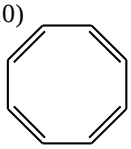
10) 

циклооктатетраен

Anthracene **pyrimidine** **pyrrole** **imidazole** **cyclooctatetraene**

4. Indicate the direction of displacement and the sign of the inductive effect of functional groups, as well as their character (electrodonor or electroacceptor) in the following compounds:

1) $CH_3—CH_2—CH_2—CH_2—F$

2) $CH_3—CH_2—CH_2—OH$

3) $CH_2=CH—CH_3$

4) $CH_3—CH_2—CH(Cl)—CHO$

5) $CH_2—CH_2—NH—CH_3$

6) $H_2N—CH_2—CH_2—SO_3H$

7) $CH_3—CH_2—COOH$

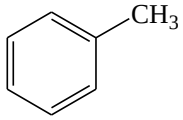
8) $Cl—CH_2—COOH$

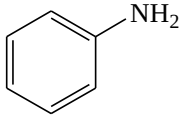
9) $CH_3—O—CH_2—CH_3$

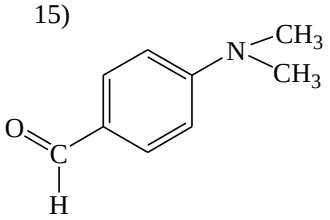
10) $CH_3—CH_2—CH_2—Li$

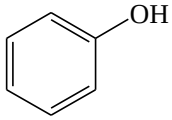
11) $OH—CH_2—CH_2—Cl$

12) $H_2N—CH_2—CH_2—CHO$

13) 

14) 

15) 

16) 

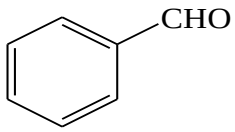
5. Select the structures in which the functional groups exhibit a mesomeric effect. Determine the sign of the mesomeric effect, as well as their nature (electrodonor or electroacceptor):

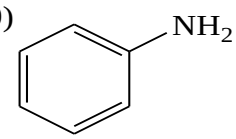
1) $CH_2=CH—NH_2$

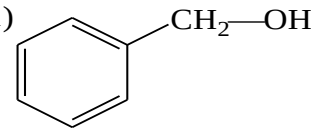
2) $CH_2=CH—CH=CH—CHO$

3) $CH_3—CH_2—CH(Cl)—CHO$

4) $CH_3—CH_2—COOH$

9) 

10) 

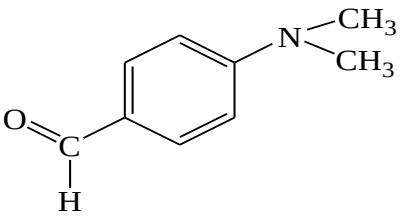
11) 

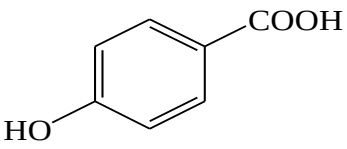
5) $H_2N—CH=CH—CH=CH—CH_2—CHO$

6) $CH_2=CH—O—CH_2—CH_2—CH_3$

7) $CH_2=CH—CH_2—CH_2—NH_2$

8) $CH_3—CH=CH—CH=CH—COOH$

12) 

13) 

ACTIVITY № 4

Topic:

REACTIVITY OF HYDROCARBONS

Purpose of the lesson:

To form knowledge about the reaction mechanism, substrate, reagent, reaction center; structure and properties of hydrocarbons; the ability to predict the ability of the main classes of hydrocarbons to enter into reactions of homolytic or heterolytic interaction, based on the electronic structure, types of hybridization and mutual influence of atoms.

Issues for discussion

1. The concept of the mechanism of an organic reaction. Substrate, reagent, reaction center.
2. Homolytic and heterolytic mechanisms of covalent bond rupture. Reagent types.
3. Classification of organic reactions according to the direction of the reaction.
4. Radical substitution reactions (S_R).
5. Reactions of electrophilic addition (A_E). Halogenation, hydrohalogenation and hydration of alkenes. Markovnikov's rules (static and dynamic factors).
6. Features of the mechanism of A_E reactions in diene hydrocarbons with conjugated double bonds.
7. Polymerization reactions of unsaturated compounds.
8. Reactions of electrophilic substitution (S_E) in aromatic compounds, their mechanism.
9. Orientants of the I and II kind. Influence of substituents in the benzene ring on the rate of the SE reaction and the nature of the resulting products.
10. Features of SE reactions in a series of heterocyclic aromatic compounds.

Theoretical part

Hydrocarbons have the simplest composition among organic compounds. They contain only carbon and hydrogen atoms. The reactivity of hydrocarbons depends on the degree of their saturation. Hydrocarbons are most characteristic of the following reactions:

for saturated ones, reactions of radical substitution S_R;

for unsaturated ones - electrophilic addition reactions A_E;

for aromatics, electrophilic substitution reactions S_E.

The same reactions are often characteristic of derivatives of hydrocarbons, i.e., compounds of other classes containing hydrocarbon fragments.

RADICAL SUBSTITUTION REACTIONS

Alkanes and cycloalkanes contain non-polar σ-bonds (C-C) and practically non-polar σ-bonds (C-H). They are characterized by a hemolytic type of bond

cleavage, accompanied by the formation of free radicals and, therefore, a radical mechanism of substitution reactions.

S_R reactions are chain and regioselective, i.e. selective to the place of substitution. First of all, the hydrogen atom is replaced at the tertiary, then the secondary and primary carbon atoms. This is due to the lower C-H bond energy at the tertiary carbon atom and the greater stability of the tertiary radical. The radical substitution reaction consists of three stages: chain initiation (nucleation), chain growth (development), and chain termination. The chain is initiated by heating, ultraviolet irradiation, or under the influence of initiators. The essence of this stage is the formation of free radicals from a molecule in the process of homolytic cleavage of a chemical bond. The chain growth stage means an increase in the number of free radicals due to the involvement of the substrate in the process. Under the stage of chain termination is meant a decrease in the number of free radicals due to their interaction.

The mechanism of the radical substitution reaction:

Stage 1: chain initiation:

$$X \therefore X \xrightarrow{h\nu} X^{\bullet} + X^{\bullet}$$

Stage 2: chain growth:

$$Alk{:}H + X^{\bullet} \rightarrow Alk^{\bullet} + HX$$

Free radical reactions are called chain reactions, because. the resulting alkyl radicals (Alk), in turn, interact with the molecules of the reagent (X_2), which leads to the formation of a substitution product (Alk–X) and a new free radical ($X^{\bullet}$), which repeats the described reaction cycle:

$$Alk^{\bullet} + X{:}X \rightarrow Alk{-}X + X^{\bullet}$$

Stage 3: open circuit:

$$X^{\bullet} + X^{\bullet} \rightarrow X_2$$

$$Alk^{\bullet} + Alk^{\bullet} \rightarrow Alk{-}Alk$$

$$Alk^{\bullet} + X^{\bullet} \rightarrow Alk{-}X$$

The theory of chain reactions was developed by the Soviet scientist, one of the founders of chemical physics, academician Nikolai Nikolaevich Semenov (1896 - 1986), for which he was awarded the Nobel Prize in 1956.

The most significant radical reactions in the alkane series are halogenation, nitration, sulfochlorination, and sulfoxidation. The oxidation reactions of hydrocarbons, phenols, thiols, double bonds in the radicals of unsaturated fatty acids and polymerization reactions can also proceed according to the free radical mechanism.

Halogenation is a reaction of radical substitution of a hydrogen atom for halogen atoms (fluorine, chlorine, bromine) with the formation of halogen derivatives:

$$Cl_2 \xrightarrow{h\upsilon} 2Cl^{\bullet}$$

$$CH_4 + Cl^{\bullet} \rightarrow CH_3^{\bullet} + HCl$$

$$CH_3^{\bullet} + Cl_2 \rightarrow CH_3Cl + Cl^{\bullet}$$

Each quantum of light that breaks the bond in a chlorine molecule leads to the formation of about 10 thousand molecules of methyl chloride. That is, each of the two formed chlorine atoms initiates about 5 thousand repetitions of the cycle before the reaction terminates.

$$Cl^{\bullet} + Cl^{\bullet} \rightarrow Cl_2$$

$$CH_3^{\bullet} + CH_3^{\bullet} \rightarrow CH_3\text{-}CH_3$$

$$CH_3^{\bullet} + Cl^{\bullet} \rightarrow CH_3Cl$$

Nitration. Alkanes are nitrated with nitric acid both in the vapor phase at a temperature of 400-500 0C and in the liquid phase. Both processes proceed according to the radical mechanism, where the active particle is the nitronium radical NO_2●.

$$HNO_3 \xrightarrow{h\upsilon} HO^{\bullet} + NO_2^{\bullet}$$

$$RH + HO^{\bullet} \rightarrow R^{\bullet} + H_2O$$

$$R^{\bullet} + HNO_3 \rightarrow R\text{-}NO_2 + HO^{\bullet}$$

Sulfochlorination and sulfoxidation. Direct sulfonation of alkanes is difficult and usually accompanied by oxidation. Alkanes are sulfonated much more easily under the combined action of sulfur dioxide and chlorine (sulfochlorination) or oxygen (sulfonation). Both processes are classified as radical substitution reactions and are initiated by UV irradiation or peroxides.

Sulfochlorination produces alkanesulfonyl chlorides.

$$R\text{-}H + SO_2 + Cl_2 \xrightarrow{h\upsilon} R\text{-}SO_2Cl + HCl$$

The mechanism of this reaction is similar to the mechanism of radical halogenation, with the only difference that there are two more stages of chain growth:

$$R^{\bullet} + SO_2 \rightarrow R\text{-}SO_2^{\bullet}$$

$$R\text{-}SO_2^{\bullet} + Cl_2 \rightarrow R\text{-}SO_2Cl + Cl^{\bullet}$$

Sulfoxidation is similar, including the mechanism, to the sulfochlorination reaction and leads to the formation of alkanesulfonic acids:

$$R\text{-}H + SO_2 + \tfrac{1}{2}O_2 \xrightarrow{h\upsilon} R\text{-}SO_3H$$

Oxidation of hydrocarbons. An important type of radical processes is the interaction of organic compounds with oxygen. The oxygen molecule is a biradical ●O-O● and can react with compounds containing C-H bonds by a radical

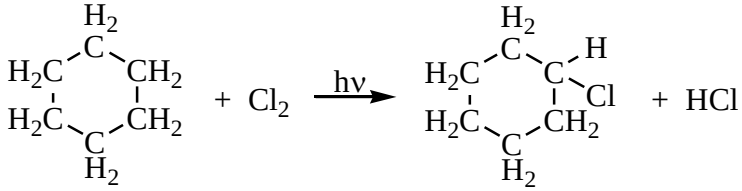
mechanism with the formation of hydroperoxides or products of their further transformations:

$$R\text{-}H + O_2 \xrightarrow{h\upsilon} R\text{-}O\text{-}O\text{-}H$$

Hydrogen peroxide derivatives in which one or two hydrogen atoms are replaced by an organic radical are called hydroperoxides (R-O-O-H) and peroxides (R-O-O-R′).

Oxidation of organic compounds by oxygen can proceed under fairly mild conditions in the body (in vivo). Such processes include lipid peroxidation, which proceeds as a free radical multistage process, resulting in mono- and dicarboxylic acids with shorter carbon chains. Lipid peroxidation is the cause of damage to cell membranes (for example, in radiation sickness).

Halogenation reactions of cycloalkanes. Cycloalkanes are divided according to the nature of the cycle: small cycles - C_3-C_4, ordinary - C_5-C_7, medium - C_8-C_{11}, macrocycles - over C_{12}. Substitution reactions occur in ordinary, medium cycles and macrocycles:

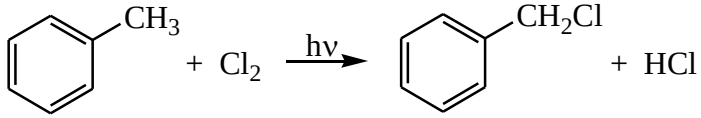


циклогексан — хлорциклогексан

Cyclohexane — chlorocyclohexane

Small cycles (cyclopropane, cyclobutane) are unstable due to high angular stress, contain a special banana σ-bond. During halogenation, the σ-bond between carbon atoms is broken, and a radical addition reaction (AR) occurs.

Halogenation of benzene homologues. Free-radical substitution at benzene homologues proceeds in the light, in the aliphatic side radical:



толуол — бензилхлорид

toluene — benzyl chloride

ELECTROPHILIC ADDITION REACTIONS BY MULTIPLE BONDS

Unsaturated hydrocarbons - alkenes, cycloalkenes, alkadienes and alkynes - are capable of addition reactions, as they contain double or triple bonds. More important in vivo is the double bond. The appearance of a double bond and its transformation are characteristic of many biochemical processes. In this regard, most reactions will be considered using the example of compounds with a double bond.

Multiple bonds contain π-bonds, which are less strong and easily polarized compared to σ-bonds. The π-bond is easily cleaved and is the reaction center through which addition reactions (A) proceed in unsaturated hydrocarbons. The π-bond is located perpendicular to the σ-bond plane, forms a region of increased electron density above and below the σ-skeleton plane, and is a nucleophilic center. The nucleophilic center can be attacked by an electrophilic particle (E +), therefore, for unsaturated hydrocarbons, the reaction mechanism AE - electrophilic addition is more characteristic. The AE reactions proceed in three stages.

Mechanism of electrophilic addition reactions:

Stage 1: formation of a π-complex.

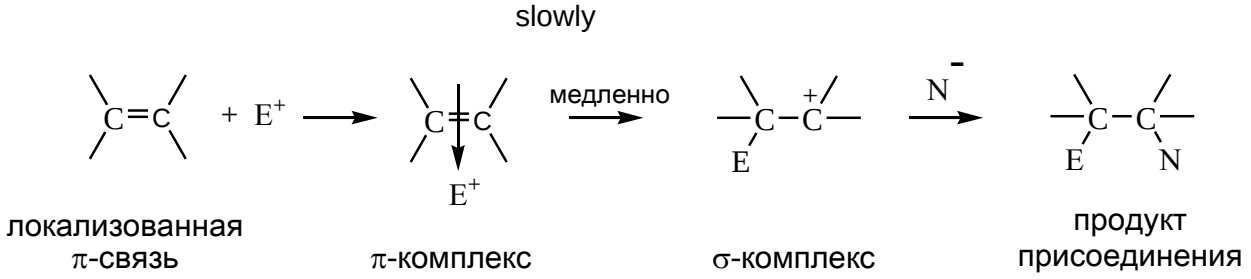
The π complex is an unstable product that results from the electrostatic attraction of a positively charged electrophile to a π bond. This step is fast and does not affect the rate of the reaction. Therefore, this stage is often omitted when describing the reaction mechanism.

Stage 2: formation of a σ-complex.

σ-Complex is an intermediate particle (carbocation) in which there are no π-bonds. This step is slow and rate limiting.

3 stage: stabilization of the σ-complex due to the addition of a nucleophile.

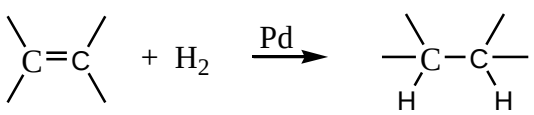
This stage is fast.



localized π bond **π-complex** **σ-complex**. **addition product**

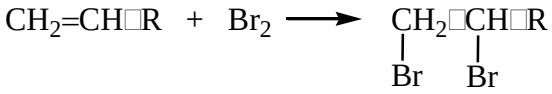
According to the mechanism of electrophilic addition, reactions of hydrogenation, halogenation, hydrohalogenation, and hydration proceed.

Hydrogenation. The hydrogenation (reduction) reaction is a reaction of hydrogen addition to a multiple bond, leading to the formation of the corresponding saturated hydrocarbons. It is carried out in the presence of a catalyst, metals are used as catalysts: Pt, Pd, Ni:



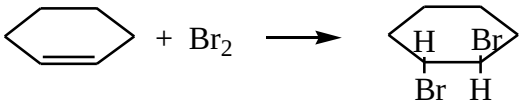
Halogenation. Chlorination and bromination of unsaturated compounds is one of the most common organic reactions, which cannot be said about fluorination and iodination. Fluorine is an extremely active reagent; it attacks not only the π-bond, but also other fragments of molecules, which leads to the breaking of C-C bonds and the formation of a mixture of products. Iodine is added slowly, some amount of iodine remains in equilibrium with the alkene even in the presence of an excess of alkene.

The addition of chlorine and bromine occurs easily at room temperature:



A solution of bromine in water is brown in color, the products of addition of bromine are colorless, so the rapid discoloration of a solution of bromine is used as a simple visual test for unsaturation.

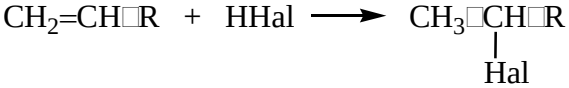
The cyclic halonium ion is more stable than the corresponding carbocation due to the fact that all atoms in its composition have a complete outer electron shell. The nucleophilic halogen ion attaches to the halonium ion from the opposite side, which leads to the trans products of the reaction and the stereoselectivity of its course. Reaction scheme for the bromination of cyclohexene:



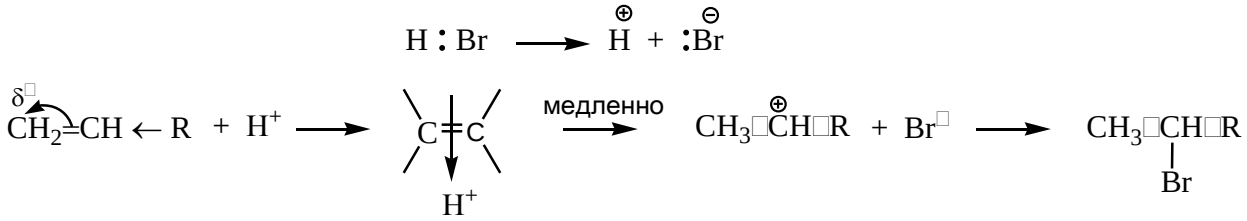
циклогексен — транс-1,2-дибромциклогексан

Cyclohexene — trans-1,2-dibromocyclohexane

Hydrohalogenation. The hydrohalogenation reaction is the addition of a hydrogen halide via a multiple bond. The reactivity of hydrogen halides in this reaction increases with increasing acid strength: HF<HCl<HBr<HI, reaction scheme:



The mechanism of the electrophilic addition reaction on the example of hydrobromination, which is carried out most often:

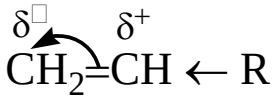


Markovnikov's rule. In the case of unsymmetrical alkenes, as a rule, one of two possible structural isomers is formed, i.e. the reaction proceeds regioselectively. V.V. Markovnikov (1869) formulated a pattern that determines the direction of addition, which entered world chemistry under the name *Markovnikov's rule:*

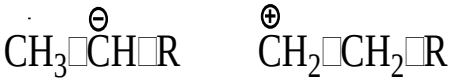
In the interaction of HX-type reagents with unsymmetrical alkenes, a hydrogen proton is added to the carbon atom associated with the maximum number of hydrogen atoms, i.e. to the most "hydrogenated" carbon atom of the double bond.

This reaction is due to two factors:

1. Static factor - the π-bond in the molecule of unsymmetrical alkenes is polarized due to the positive inductive effect of the (+I) radical. Therefore, the proton (H^+) is attached to that of the carbon atoms (more hydrogenated), at the double bond, which has a partial negative charge (δ^-).

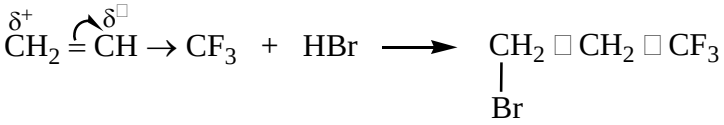


2. Dynamic factor - determines the direction of proton addition towards the formation of a more stable intermediate particle (carbocation). As a result of the addition of a proton, the formation of two types of carbocations is theoretically possible:

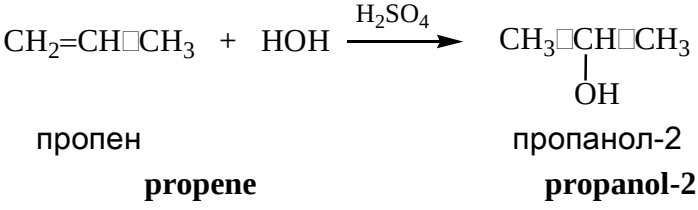


Of the two possible carbocations, the first one is more stable, since it is secondary and its charge is delocalized due to the +I-effect of two radicals.

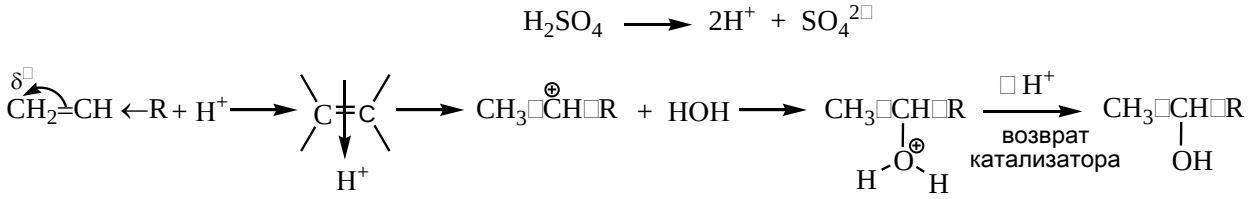
The addition of hydrogen to alkene derivatives containing electroacceptor substituents in a multiple bond occurs against the Markovnikov rule:



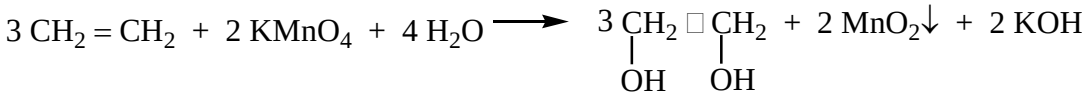
Hydration. The hydration reaction is one of the biologically important reactions, since it proceeds with unsaturated compounds in vivo. The hydration reaction is the addition of water to a multiple bond. Hydration of alkenes proceeds according to the type of electrophilic addition according to Markovnikov's rule in the presence of a catalyst - strong acids (sulfuric, nitric, etc.). Without an acid catalyst, the reaction is not possible. This is due to the fact that water is a weak electrolyte and acts as a molecular nucleophile. Reaction scheme:



Hydration Reaction Mechanism:



Oxidation (Wagner reaction). During the oxidation of alkenes under mild conditions under the action of a cold neutral solution of potassium permanganate, the solution of potassium permanganate becomes discolored and a brown precipitate of manganese (IV) oxide precipitates, and this reaction is also qualitative for a double bond. The reaction is stereospecific and results in a cis product: vicinal dihydric alcohol (vicinal dihydric alcohols contain hydroxyl groups at adjacent carbon atoms):



этилен — этиленгликоль

Ethylene — **ethylene glycol**

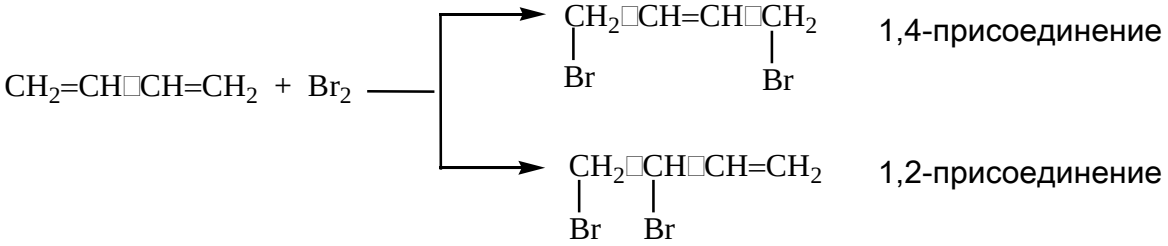
AE reactions in the alkadiene series. Alkadienes, depending on the mutual arrangement of double bonds, are divided into dienes:

a) with cumulated double bonds: $H_2C=C=CH_2$,

b) with conjugated double bonds: $H_2C=CH–CH=CH_2$,

c) with isolated double bonds: $H_2C=CH–(CH_2)_n–CH=CH_2$.

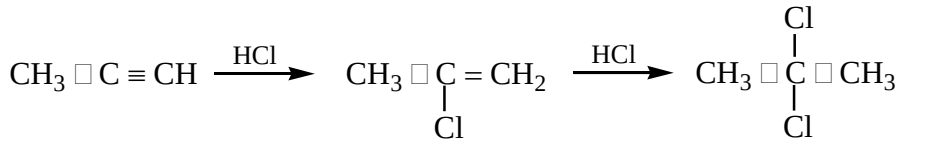
The most common are dienes with conjugated double bonds, i.e. compounds with alternating single and double bonds. The chemical properties of dienes depend on the location of the double bonds. The properties of non-conjugated alkadienes are identical to those of simple alkenes. Conjugated dienes differ from simple alkenes in that they are more thermodynamically stable and more reactive, and reactions of AE with such dienes proceed with the formation of two 1,4- and 1,2-addition products.



The ratio between the 1,4- and 1,2-addition products depends on the reaction conditions, but, as a rule, the 1,4-addition product in the mixture is greater than the 1,2-addition product. Such a feature in the reactions of AE with alkadienes is associated with the formation of two carbocations with a mesomeric structure, which easily transform into each other.

AE reactions to alkynes. Alkynes are also characterized by electrophilic addition reactions, but alkynes are less active than alkenes. The mechanisms of

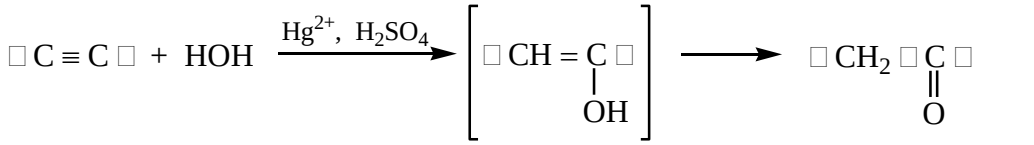
these reactions are basically similar to the mechanisms of the corresponding reactions of alkenes. The difference is that, depending on the conditions, an alkyne can attach one or two molecules of hydrogen, halogen or hydrogen halide, while an alkene can only add one. In this case, Markovnikov's rule is also observed:



пропин — 2-хлорпропен — 2,2-дихлорпропан

propyne — 2-chloropropene — 2,2-dichloropropane

The hydration of alkynes proceeds similarly (Kucherov's reaction). Alkynes are hydrated in dilute sulfuric acid in the presence of catalysts. In the first stage, unstable vinyl alcohol (enol) is formed, which quickly isomerizes to aldehyde:



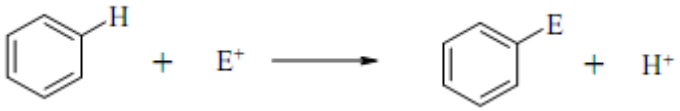
енол — альдегид или кетон

Enol — **aldehyde and ketone**

Hydration of substituted acetylenes always leads to the formation of ketones, and aldehyde is obtained in the only case - by adding water to acetylene. This reaction is of national economic importance, since ethyl alcohol is formed during the reduction of acetaldehyde, and acetic acid is formed during the oxidation of acetaldehyde.

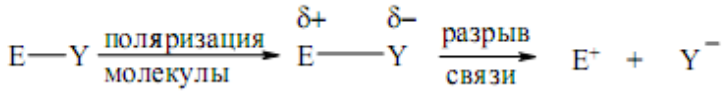
ELECTROPHILIC SUBSTITUTION REACTIONS

Electrophilic reactions occur when a molecule (substrate) is exposed to an electrophilic reagent - a particle with a positive charge. Electrophilic substitution is characteristic of aromatic compounds. The presence of π-electron density on both sides of the planar aromatic ring leads to the fact that aromatic compounds of the benzene series (arenes) are nucleophiles and, therefore, tend to undergo electrophilic attack. In general, for benzene, the proton substitution reaction for other electrophiles can be represented as follows:



Mechanism of electrophilic substitution reactions:

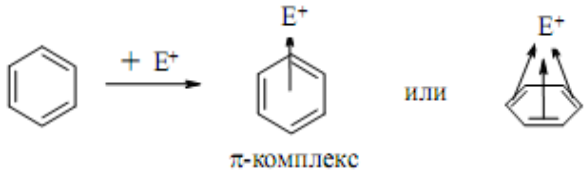
Stage 1: generation of an electrophilic particle in the presence of a catalyst.



polarization of a molecule — molecular bond breaking

Stage 2: formation of a π-complex.

The electrophilic particle attacks the aromatic substrate, forming an unstable π-complex, in which it is simultaneously bound to all the π-electrons of the aromatic system.

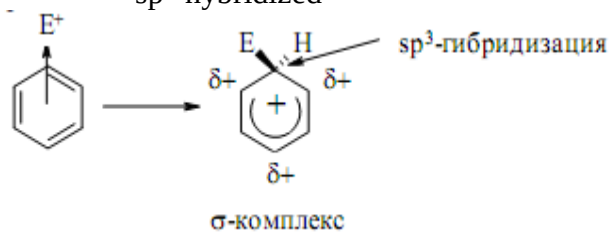


π-complex

Stage 3: transformation of the π-complex into a σ-complex (slow stage of the reaction).

The electrophile takes two electrons from the π-system, forming a σ-bond with one of the carbon atoms of the benzene ring:

sp^3-hybridized

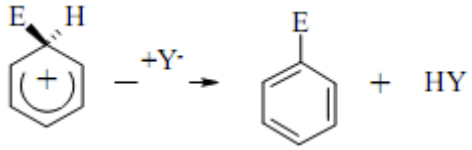


σ-complex

In the σ-complex, the aromatic system is broken, since one of the carbon atoms of the ring has become sp^3-hybridized. The four remaining π-electrons are distributed among five carbon atoms, with the greatest deficit of electron density in the ortho- and para-positions with respect to the substituent.

4th stage: elimination of a proton from the σ-complex.

The aromatic system is restored (the pair of electrons missing from the sextet returns to the nucleus), so this process is energetically favorable. The split off proton binds to the nucleophile:

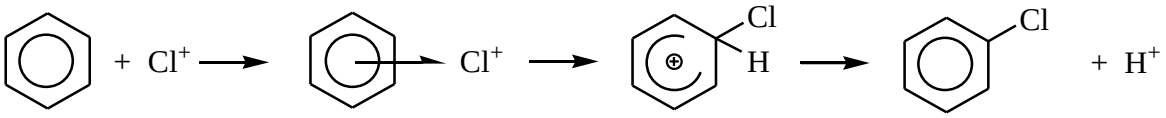


The most significant electrophilic substitution reactions are halogenation, nitration, sulfonation, alkylation, and acylation.

Halogenation. The halogenation reaction is carried out in the presence of halogen carrier catalysts (FeCl3, AlCl3, Cl2). The role of the catalyst is to polarize the halogen-halogen bond to form a positively charged ion (electrophile), which then attacks the benzene ring:

$$Cl_2 + FeCl_3 \rightleftharpoons \overset{\delta^+}{Cl}\ \square\ \overset{\delta^-}{Cl}....FeCl_3 \rightleftharpoons Cl^+ + FeCl_4^-$$

The halogenation reaction proceeds according to the mechanism discussed above:



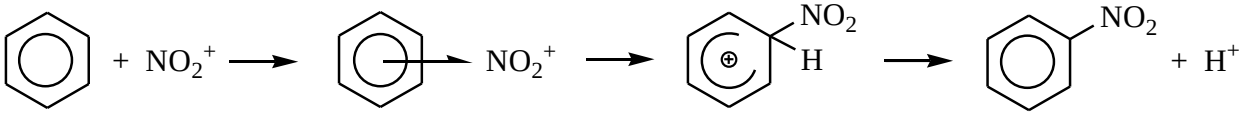
$H^+ + FeCl_4^- \longrightarrow HCl + FeCl_3$

Nitration. Aromatic nitro compounds with a nitro group in the core are obtained by nitration of aromatic hydrocarbons with a nitrating mixture (a mixture of concentrated nitric and sulfuric acids) at a temperature of 40-50°C.

As a result of the interaction of sulfuric and nitric acids, a nitrating agent is formed - the nitronium ion - NO^{2+}:

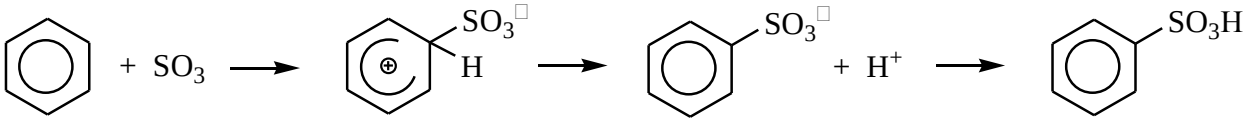
$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$

The nitronium ion attacks the benzene ring:



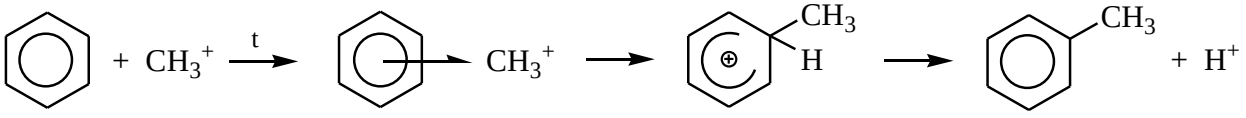
$H^+ + HSO_4^- \longrightarrow H_2SO_4$

Sulfonation. Benzene is sulfonated with fuming sulfuric acid containing an excess of sulfur oxide (IV) dissolved in it. It is assumed that he is the sulfonating agent in this reaction.



Alkylation. Alkyl derivatives of aromatic hydrocarbons are usually obtained by the action of haloalkyls on benzene in the presence of an AlCl3 catalyst. This reaction has much in common with halogenation reactions. The role of the catalyst is to form a positively charged cation that electrophilically attacks the benzene ring:

$CH_3-Cl_2 + AlCl_3 \rightleftharpoons \overset{\delta+}{CH_3}-\overset{\delta-}{Cl}....AlCl_3 \rightleftharpoons CH_3^+ + AlCl_4^-$



$H^+ + AlCl_4^- \longrightarrow HCl + AlCl_3$

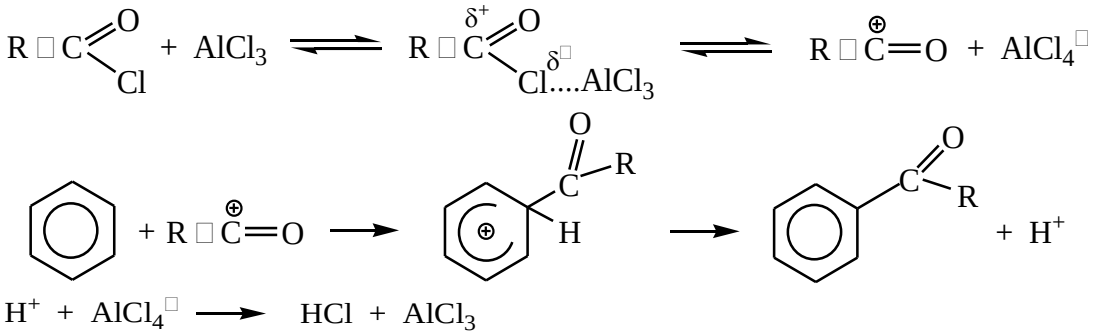
Instead of haloalkyls, unsaturated hydrocarbons and alcohols can be used as alkylating agents. In this case, catalysts are used (H_3PO_4, H_2SO_4, HF, BF_3, etc.), which convert alkenes or alcohols into the corresponding carbocations:

$CH_2=CH_2 + H^+ \rightleftharpoons CH_3-CH_2^+$

$CH_3-CH=CH_2 + H^+ \rightleftharpoons CH_3-CH^+-CH_3$

$CH_3-OH + H^+ \rightleftharpoons CH_3-\overset{+}{O}H_2 \rightleftharpoons CH_3^+ + H_2O$

Acylations. Anhydrides and acid halides are used as acylating agents, and AlCl3 is used as a catalyst. In the presence of a catalyst, anhydrides and acid chlorides form a carbocation, which then interacts with a benzene molecule:

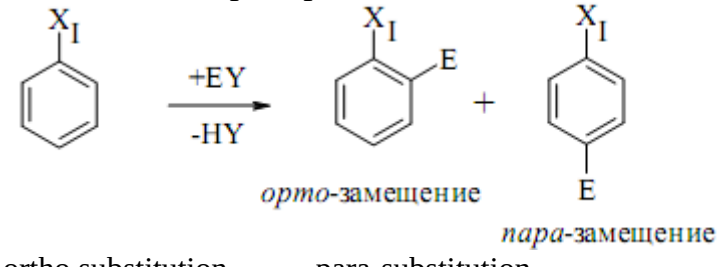


Orienting action of substituents in the benzene ring

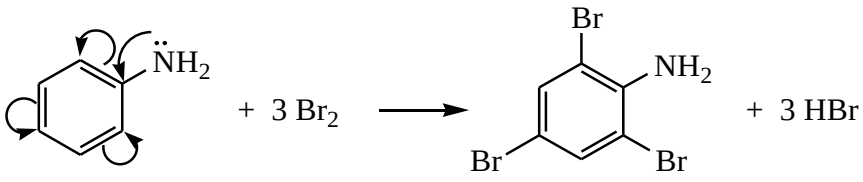
If benzene itself enters the SE reaction, then the place of orientation of the electrophile does not matter, because the electron density in the benzene ring is evenly distributed. However, if homologues or substituted derivatives of benzene enter into such reactions, then the symmetry of the π-electron cloud is broken in them and the electrophile (E^+) can be oriented in ortho-, meta-. or it's time-position to the deputy. The factor determining the direction of the electrophilic substitution reaction to the benzene ring is often the mesomeric effect. If there is no mesomeric effect, then the orientation into the benzene ring depends on the sign of the inductive effect.

According to the nature of the orientation of the electrophilic particle (E^+), all substituents in the benzene ring are divided into two groups:

1. Substituents (orientants) of the first kind. These include alkyl groups having a positive inductive effect (-R: $-CH_3$; $-C_2H_5$, etc.); groups showing a positive mesomeric effect (–OH; –OR; $–NH_2$; –NHR; $–NR_2$; –F; –Cl; –Br; –I; –SH; –SR; $–O^–$) to the benzene nucleus. Type I substituents (X_I) facilitate electrophilic substitution compared to unsubstituted benzene and direct the incoming group to the ortho or para positions:



ortho substitution para-substitution

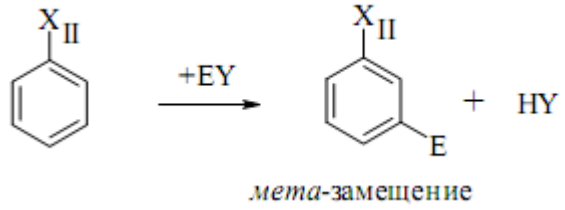


анилин
Aniline

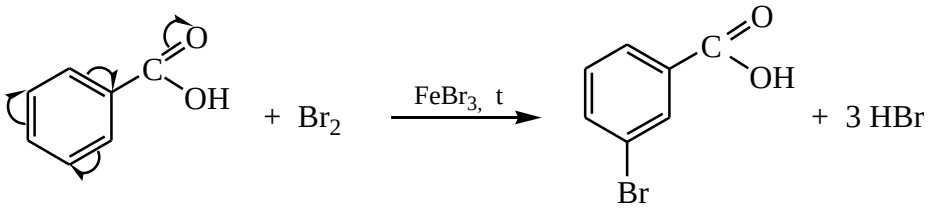
2,4,6-трибромanилин
2,3,6-tribromaniline

The bromination reaction is qualitative for phenol, aniline, and is widely used in pharmaceutical analysis.

2. Substituents (orientants) of the second kind. These include groups: –C≡N, –SO_3H, –CHO, –COR, –COOH, –COOR, –NH_3^+, –NR_3^+, –CF_3, –CCl_3, –NO_2. Showing an electron-withdrawing character with respect to the benzene nucleus due to negative inductive or negative mesomeric effects. Substituents of the II kind (XII) complicate electrophilic substitution reactions in comparison with unsubstituted benzene. If, under more severe conditions, the reaction still passes, the incoming group enters the meta position:



мета-замещение



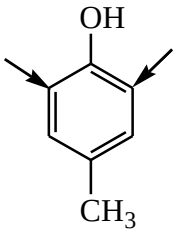
бензойная кислота

benzoic acid

м-бромбензойная кислота

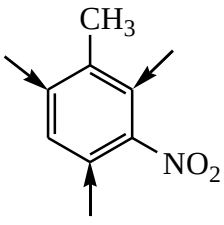
m-bromobenzoic acid

Orientation in disubstituted benzene. In disubstituted benzene, the influence of substituents on the core can be coordinated if both substituents direct the entry of the next one into the same positions. If the orienting action of the substituents does not match, then they speak of inconsistent orientation. In this case, the direction of entry of the third substituent is determined by the stronger activator. In a nucleus containing two activators, the direction of substitution is controlled by the stronger activator:



n-крезол
-OH, как более сильный активатор
(по сравнению с -CH_3)
контролирует направление S_E

n-cresol
-OH as a stronger activator
(compared to CH_3)
controls the direction S_E



м-нитротулуол
-CH_3 □ активатор,
-NO_2 □ дезактиватор, поэтому -CH_3
контролирует направление S_E

m-nitrotoluene
-CH3 activator,
-NO_2 -deactivator therefore -CH3
controls direction S_E

EXERCISES

1. Write the equations for the reactions of obtaining hydrocarbons and name the reaction products:

1) chloromethane + Na $\xrightarrow{t}$

2) $CaC_2 + H_2O \rightarrow$

3) $CH_3\text{-}CH_2\text{-}CH(Cl)\text{-}CH_3 + KOH_{\text{alcohol solution}} \xrightarrow{t}$

4) 1,4-dichlorobutane + Mg $\xrightarrow{t}$

5) $CH_3\text{-}COONa + NaOH \xrightarrow{t}$

6) chlorobenzene + Na + chloromethane $\xrightarrow{t}$

7) 1,2-dichloropropane + $2KOH_{\text{alcohol}}$. $\xrightarrow{t}$

8) $CH_3\text{-}CH_2\text{-}CH(OH)\text{-}CH_3 \xrightarrow{t,\ Al_2O_3,\ H_2SO_{4\text{конц.}}}$

9) benzene + chloropropane $\xrightarrow{t,\ AlCl_3}$

10) 1-bromopropane + Na $\xrightarrow{t}$

2. Complete the reaction equations, indicate the reaction mechanism:

1) $CH_3\text{-}C{\equiv}CH + HCl \rightarrow$

2) $CH_3\text{-}CH_2\text{-}CH_3 + Cl_2 \xrightarrow{h\nu}$

3) $CH_2{=}CH\text{-}CH{=}CH_2 + HCl \xrightarrow{t}$

4) toluene + $3HNO_{3\ (\text{conc.})} \xrightarrow{t,\ p,\ H_2SO_{4(\text{конц.})}}$

5) cyclopropane + $Cl_2 \xrightarrow{h\nu}$

6) ethene + $Br_2 \rightarrow$

7) 2-methylbutane + $HNO_{3\ (\text{dil.})} \xrightarrow{t,\ p}$

8) ethyne + $H_2O \xrightarrow{t,\ Hg^{2+},\ H^+}$

9) propene + $H_2O \xrightarrow{t,\ H^+}$

10) butadiene-1,3 $\xrightarrow{\text{полимеризация}}$

11) cyclohexane + $Cl_2 \xrightarrow{h\nu}$

3. Write a reaction scheme for the radical substitution of alkanes using the example of methane chlorination, describe the mechanism of this reaction

4. Write a scheme for the reaction of electrophilic addition to unsaturated hydrocarbons, describe the mechanism of this reaction

1) hydrogen bromide to ethene;

2) chlorine to ethine.

5. Using Markovnikov's rule, write the reaction equations for the following additions

1) $CH_2=CH-CH_3 + HCl \rightarrow$

2) $CH_2=CH-CH_2-CH_3 + H_2O \rightarrow$

3) $CH_3-CH=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-CH_2-CH_3 + HBr \rightarrow$

4) $CH_2=CH-CH_2-CH_2-CH_3 + HI \rightarrow$

5) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-CH=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-CH_3 + H_2O \rightarrow$

6) $CH_2=CH-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-CH_3 + HCl \rightarrow$

6. Write a scheme for the reaction of benzene halogenation using the example of its bromination, describe the mechanism of this reaction in the presence of a FeBr3 catalyst.

7. Write a diagram and describe the mechanism of the benzene nitration reaction in the presence of a mixture of nitric and sulfuric acids (nitrating mixture).

8. Write a diagram and describe the mechanism of benzene alkylation reactions with chloromethane and propene.

9. Write a scheme and describe the reaction mechanism of benzene acylation with acetic acid chloride in the presence of AlCl3 catalyst (Friedel-Crafts acylation).

10. What isomers (ortho-, meta- or para-) will be predominantly formed during the nitration of C6H5Cl (chlorobenzene) and what will be the rate of this reaction compared to the nitration of benzene?

11. Write a scheme and describe the reaction mechanism of toluene chlorination in the presence of AlCl3.

12. Write a diagram and describe the mechanism of the nitrobenzene sulfonation reaction.

13. Write the reaction equations for the following transformations:

1) $CO \xrightarrow{t,\ кат.} CH_4 \xrightarrow{Cl_2 \parallel h\nu} CH_3Cl \xrightarrow{Na \parallel t} CH_3\text{-}CH_3 \xrightarrow{t,Ni} CH{\equiv}CH \xrightarrow{t,\ C_{(акт.)}} X_5.$

2) $CH_3\text{-}CH_2\text{-}OH \xrightarrow{t,\ Al_2O_3,\ H_2SO_{4конц.}} CH_2{=}CH_2 \xrightarrow{HBr} CH_3\text{-}CH_2\text{-}Cl \rightarrow C_6H_5\text{-}CH_2\text{-}CH_3.$

3) cyclohexane $\xrightarrow{t,\ Pt}$ benzene $\xrightarrow{O_2\ в\ недостатке} CO \xrightarrow{t,\ кат.}$ propane $\xrightarrow{Br_2 \parallel h\nu} X_5$

4) 1,2 dibromoethane $\xrightarrow{Zn \parallel t} C_2H_4 \xrightarrow{HBr} C_2H_5Br \xrightarrow{Na \parallel t} C_4H_8$ → butene-1.

5) cyclopropane $\xrightarrow{H_2 \parallel t,\ Ni}$ propane $\xrightarrow{t, Ni}$ propene $\xrightarrow{Br_2}$ 1,2-dibromopropane $\xrightarrow{KOH_{спирт\,р-р} \parallel t}$ propyne $\xrightarrow{H_2O \parallel t,\ Hg^{2+},\ H^+} CH_3\text{-}C(O)\text{-}CH_3$.

6) 1-bromobutane $\xrightarrow{KOH_{спирт\,р-р} \parallel t}$ butene-1 $\xrightarrow{HBr}$ 2-bromobutane $\xrightarrow{Na \parallel t}$ X_4.

7) Al_4C_3→ methane → acetylene → benzene → toluene → spent

8) 1,4-dibromobutane → cyclobutane → 1-chlorobutane → butene-1 → butadiene-1,3

9) calcium carbide → ethyn → ethene → ethane → nitroethane.

10) 1-bromopropane → hexane → benzene → methylbenzene → benzoic acid.

11) cyclobutane $\xrightarrow{H_2 \parallel t,\ Ni} X_1 \xrightarrow{Cl_2 \parallel h\nu} X_2 \xrightarrow{KOH_{спирт\,р-р} \parallel t} X_3 \xrightarrow{Br_2} X_4$.

12)1,2-dichlorobutane $\xrightarrow{Zn \parallel t} X_1 \xrightarrow{HBr \parallel H_2O_2} X_2 \xrightarrow{t,\ p,\ Pt} X_3 \xrightarrow{t,\ KMnO_4,\ H^+} X_4$.

LABORATORY WORK №1

Topic:

PRODUCTION METHODS, REACTIVITY HYDROCARBONS

Goal of the work:

Get acquainted with laboratory methods for obtaining some representatives of the homologous series of ethylene and acetylenic hydrocarbons and study their properties. Study some physical properties and compare the reactivity of alkanes, alkenes, alkynes and arenes.

Reagents:

1.	benzene	C_6H_6	–
2.	hexane	C_6H_{14}	–
3.	hexene-1	$CH_2{=}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$	–
4.	toluene	$C_6H_5\text{-}CH_3$	–
5.	ammonia solution of copper (I) chloride	$[Cu\ (NH_3)_2]Cl$	–
6.	calcium carbide	CaC_2	crystal
7.	potassium permanganate	$KMnO_4$	2% solution
8.	sulfuric acid	H_2SO_4	1M solution
9.	phenolphthalein	$C_{20}H_{14}O_4$	1% alcohol solution
10.	distilled water		–

Equipment:

- copper wire
- glass rod
- tweezers
- filter paper
- spirit lamp
- stand with test tubes

Experience 1. Obtaining acetylene

In a test tube, pour 20 drops of potassium permanganate and place a small piece of calcium carbide.

What are you observing? Write the chemistry of the production and oxidation of acetylene.

Process chemistry:

$$CaC_2 + H_2O \rightarrow$$

$$CH \equiv CH + KMnO_4 + H_2O \rightarrow$$

Answer questions about experience:

1. What gas is released when calcium carbide interacts with water?
2. What external signs are characteristic of the oxidation reaction of alkyne with potassium permanganate?
3. What reaction products are formed during the oxidation of alkynes?

Experience 2. Combustion of hydrocarbons

Take three test tubes. In the first place 10 drops of hexane, in the second - 10 drops of hexene-1, in the third - 10 drops of toluene. In the flame of a burner, burn

a loop of copper wire until the extraneous color disappears. Then place it in a test tube with hexane and bring it back into the burner flame. Repeat the experiment with other hydrocarbons.

What are you observing? Write the chemistry of combustion of hexane.

Process chemistry:

$$CH_3 — CH_2 — CH_2 — CH_2 — CH_2 — CH_3 + O_2 \rightarrow$$

Answer questions about experience:

What hydrocarbons burn with a sooty flame? Why?

Experience 3. Comparison of the chemical properties of hydrocarbons

Take 4 test tubes, put 10 drops of potassium permanganate solution and 8 drops of sulfuric acid solution into each test tube. Then add:

- in the first test tube 10 drops of hexane,
- in the second 10 drops of hexene-1,
- in the third 10 drops of benzene,
- in the fourth 10 drops of toluene.

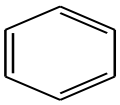
Shake all tubes and heat.

What are you observing? Write the chemistry of hydrocarbon oxidation.

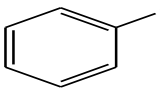
Process chemistry:

$$CH_3 — CH_2 — CH_2 — CH_2 — CH_2 — CH_3 + KMnO_4 + H_2SO_4 \xrightarrow{t}$$

$$CH_2 = CH — CH_2 — CH_2 — CH_2 — CH_3 + KMnO_4 + H_2SO_4 \xrightarrow{t}$$



$$+ KMnO_4 + H_2SO_4 \xrightarrow{t}$$



$$+ KMnO_4 + H_2SO_4 \xrightarrow{t}$$

Answer questions about experience:

1. How to explain the discoloration of the KMnO4 solution in this experiment?
2. Does hexane oxidize under normal conditions? Why?
3. What compound is formed during the oxidation of hexene-1?
4. At what structural fragment of the toluene molecule does the oxidation reaction take place, and under what conditions?
5. Evaluate the ability to oxidize in a series of arenes: benzene, toluene.
6. Which of the studied classes of compounds are chemically more active?

Experience 4 Formation of copper (I) acetylenide

Place a small piece of calcium carbide into a test tube, to which add 2 ml of distilled water. Insert a strip of filter paper moistened with an ammonia solution of copper (I) chloride into the opening of the test tube. At the end of the release of acetylene, add 1 drop of phenolphthalein to the test tube

What are you observing? Write the chemistry of formation of acetylene and copper (I) acetylenide.

Process chemistry:

$CaC_2 + H_2O \rightarrow$

$H - C \equiv C - H + [Cu(NH_3)_2]Cl \rightarrow$

Answer questions about experience:

1. What compound is formed on a strip of filter paper?
2. Note the changes that occur during the interaction of acetylene with ammonia solutions of copper (I) chloride.
3. What alkynes cannot react with this reagent?
4. What observations did you note after adding the acetylene indicator to the test tube? Why?

QUESTIONS FOR PROTECTION OF LABORATORY WORK 1.

1. Conjugate systems: π, π-conjugation, p, π-conjugation.
2. Aromaticity. Hückel's rule.
3. Inductive effect.
4. Mesomeric effect.
5. Reaction mechanism. Substrate, reagent, reaction center.
6. Classification of organic reactions.
7. Types of reagents: radical, electrophilic, nucleophilic.
8. Mechanism of radical substitution reactions (SR).
9. Reactions of halogenation, nitration, oxidation of alkanes. The mechanism of these reactions.
10. Mechanism of electrophilic addition (AE) reactions.
11. Reactions of halogenation, hydrohalogenation, hydration, oxidation of alkenes. The mechanism of these reactions.
12. Markovnikov's rule. Is it possible to deviate from this rule?
13. Reactions of halogenation, hydrohalogenation, hydration of alkynes. The mechanism of these reactions.
14. Features of the mechanism of AE reactions in alkadienes with conjugated double bonds.
15. Reactions of electrophilic substitution (SE) of aromatic hydrocarbons. The mechanism of these reactions.
16. Orientants of the I and II kind in the benzene ring.
17. Reactions of halogenation, nitration, sulfonation, alkylation, acylation, oxidation of arenes. The mechanism of these reactions.
18. Write the nitration reaction of toluene (methylbenzene). By what mechanism does it proceed? Show the orienting action of the methyl group.
19. Write the sulfonation reaction of aminobenzene (aniline). By what mechanism does it proceed? Show the orienting action of the amino group.
20. Write the reaction of bromination of benzoic acid. Describe the mechanism and show the orienting action of the carboxyl group.
21. Write the naphthalene nitration reaction. By what mechanism does it proceed?

ACTIVITY №5

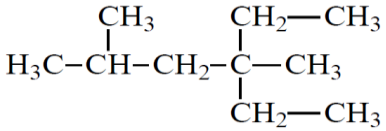
CONTROL WORK № 1

Purpose of the lesson:

Assess the assimilation by students of the program material on the topic "Hydrocarbons" and the ability to use the knowledge gained to solve practical problems.

Exemplary test ticket 1.

1. Give a name according to the international nomenclature to the compound:



2. Write the formulas of substances in the molecules of which the hydroxyl group is an electron-withdrawing substituent:

1) glycerin
2) phenol
3) ethylene glycol
4) 2-aminoethanol-1.

Write formulas.

3. Give the equation for chlorination of 2-methylpropane and indicate the reaction mechanism

4. Give the formula of the compound corresponding to the following name:

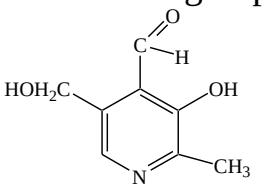
2,5,5-trimethylheptene-3

5. A nucleophile is a particle that:

1) attaches a proton
2) attacks a positively charged carbon atom
3) supplies a pair of electrons to form a chemical bond
4) supplies a free orbital for the formation of a chemical bond

6. Write the equations for the reactions of benzene and ethylbenzene with chlorine under ultraviolet irradiation

7. Indicate the type and sign of the electronic effects of substituents in the molecule of pyridoxal, a vitamin of group B (vitamin B6).



SECTION III.

HOMOFUNCTIONAL HYDROCARBON DERIVATIVES.

ACTIVITY №6

Topic:

GENERAL CHARACTERISTICS, CLASSIFICATION, NOMENCLATURE OF HOMOFUNCTIONAL HYDROCARBON DERIVATIVES. ISOMERISM OF HYDROCARBON DERIVATIVES

Purpose of the lesson:

To form modern knowledge of the classification and rules of the international chemical nomenclature of biologically active organic compounds and the ability to use them. To form knowledge about the types of isomerism characteristic of each class of monofunctional derivatives of hydrocarbons and the ability to formulate compounds according to these types of isomerism

Issues for discussion

1. Isomerism of halogenated derivatives of hydrocarbons
2. Isomerism of oxygen-containing derivatives of hydrocarbons
3. Isomerism of nitrogen-containing derivatives of hydrocarbons
4. Isomerism of sulfur-containing derivatives of hydrocarbons

Theoretical part

All organic compounds can be considered as derivatives of hydrocarbons obtained by introducing functional groups into them.

A functional group is an atom or group of atoms that determines the characteristic chemical properties of a given class of organic compounds.

Compounds with one functional group are called monofunctional, with several identical functional groups - homofunctional, with several different functional groups - heterofunctional.

Depending on the nature of the functional groups, hydrocarbon derivatives are divided into classes.

Monofunctional derivatives of hydrocarbons include halogen derivatives, hydroxyl compounds (alcohols and phenols), carbonyl compounds (aldehydes and ketones), carboxylic acids, ethers and esters, nitrogen-containing compounds (amines, nitro compounds and nitriles), sulfur-containing compounds (thiols and sulfonic acids).

Halogenated hydrocarbons are derivatives of hydrocarbons in which one or more hydrogen atoms are replaced by halogen atoms.

According to the degree of substitution, there are:

1) monohalogen derivatives:

CH_3C1 - chloromethane (methyl chloride);

CH_3-CH_2-Br - bromoethane (ethyl bromide);

2) dihalogen derivatives:

geminal - both halogen atoms are on the same carbon atom, for example

CH_3-CH_2-Cl_2 - 1,1-dichloroethane;

vicinal - halogen atoms are located at neighboring carbon atoms, for example

Cl-CH_2-CH_2-Cl - 1,2-dichloroethane;

3) polyhalogen derivatives, for example

$CHCl_3$ - trichloromethane (chloroform),

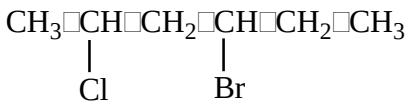
CCl_4 - carbon tetrachloride (carbon tetrachloride).

Of the halogen derivatives of the unsaturated series, compounds of two types are of theoretical and practical interest: the vinyl chloride type, when the halogen atom is near the multiple bond (CH_2=CH-Cl - chloroethene); allyl chloride type, when the halogen atom is separated from the multiple bond by one methylene unit (CH_2=CH-CH_2-Cl - 3-chloropropene-1).

Depending on the type of carbon atom to which the halogen is bound, primary, secondary and tertiary haloalkanes are distinguished.

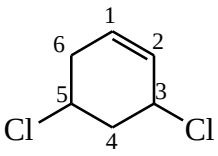
Compounds in which the double bond and the halogen atom are far apart do not differ chemically from ordinary alkenes and halogen derivatives of saturated hydrocarbons.

The names of halogen derivatives of hydrocarbons are formed by adding the prefix halo- (bromo-, chloro-, etc.) to the name of the parent hydrocarbon. The chain or cycle is numbered so that the halogen gets the lowest number. In unsaturated compounds, preference in numbering is given to a multiple bond. In halogen derivatives of condensed hydrocarbons, the numbering of condensed systems is retained.



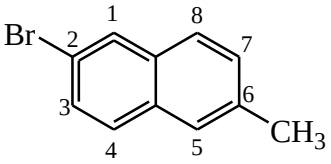
4-бром-2-хлоргексан

4-bromine 2-chlorhexane



3,5-дихлоргексен-1

3,5 – dichlorohexene



2-бром-6-метилнафталин

2-bromine-6-methylnaphthalene

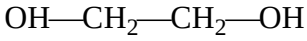
Halogen derivatives that are simple in structure are often named according to the radical-functional nomenclature, for example: isopropyl bromide - $(CH_3)_2CHBr$, benzyl chloride - $C_6H_5CH_2Cl$.

Alcohols are oxygen-containing derivatives of acyclic hydrocarbons, in the molecules of which one or more hydrogen atoms are replaced by a hydroxyl group.

Depending on the number of hydroxyl groups, alcohols are one-, two-, trihydric, etc. Alcohols containing two or more hydroxyl groups are called polyhydric

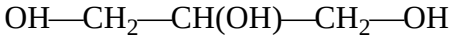
этанол

ethanol



этандиол-1,2
этиленгликоль

ethanediol-1,2



этантриол-1,2,3
глицерин

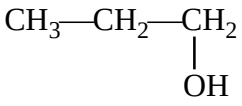
ethantriol-1,2,3

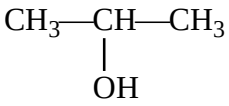
ethylene glycol **glycerin**

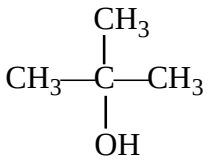
Alcohols are also divided into primary, secondary and tertiary, depending on which carbon atom the hydroxyl group is attached to:

primary alcohols **secondary alcohols** **tertiary alcohols**

Первичный спирты Вторичный спирты Третичный спирты





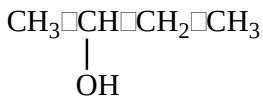


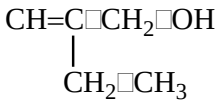
пропанол-1 пропанол-2 2-метилпропанол-2

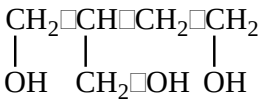
propanol-1 **propanol-2** **2-methylpropanol-2**

In the series of lower alcohols, a trivial nomenclature is often used, in which the word "alcohol" is added to the name of the radical associated with the hydroxyl group. Methyl alcohol is also called wood alcohol, since until 1925 it was obtained by dry distillation of wood. Ethyl alcohol is found in grape wine, hence its trivial name - wine spirit. Trivial names are preserved for a number of polyhydric alcohols: ethylene glycol, glycerin, etc.

In the names of monohydric alcohols, the hydroxyl group, if it is the eldest in the compound, is denoted by the suffix *-ol*. The suffixes *-diol, -triol,...* are used in the name of polyhydric alcohols. The number indicates the number of the carbon atom at which the *–OH* group is located, which should be the smallest. The hydroxyl group, if it is not a senior group or is in the side chain, is denoted by the prefix *hydroxy-*.







бутанол-2 2-этилпропен-2-ол-1 2-гидроксиметилбутандиол-1,4

butanol-2 **2-methylpropene-2-ol-1** **2-hydroxymethylbutanediol-1,4**

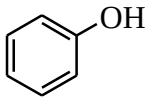
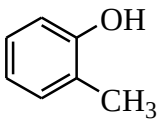
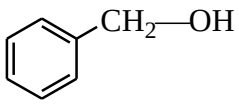
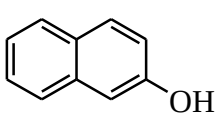
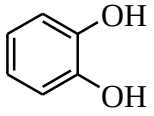
In the systematic nomenclature of alcohols, they proceed from the name of the corresponding saturated hydrocarbon with the addition of the ending -ol (in the case of dihydric alcohols, diol, triatomic alcohols, triol). The name of the hydrocarbon skeleton is compiled according to the usual rules of systematic nomenclature.

Phenols are oxygen-containing derivatives of aromatic hydrocarbons containing one or more hydroxyl groups at the carbon atom of the benzene ring.

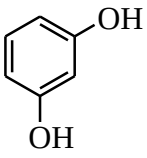
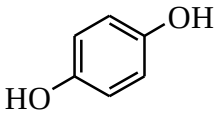
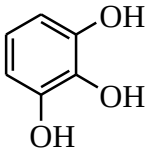
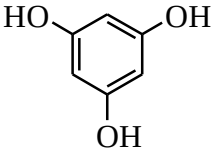
The general formula of phenols is Ar-OH, where Ar is an aromatic radical. Phenols occupy a special position among hydroxy derivatives of hydrocarbons. Due to the strongly pronounced mutual influence of the hydroxyl group and the phenyl nucleus, the properties of phenols differ so much from the properties of

alcohols that they are distinguished into a separate class of hydroxy derivatives. In the aromatic series, there are also compounds with a hydroxyl group in the side chain - the so-called aromatic alcohols (for example, benzyl alcohol). The properties of the hydroxyl group in aromatic alcohols do not differ from the properties of aliphatic alcohols. Phenols can be monatomic or polyhydric.

Phenol **o-cresol** **benzyl alcohol** **naphthol** **pyrocatechin**

фенол *o*-крезол бензиловыйспирт нафтол пирокатехин

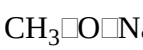
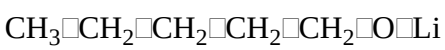
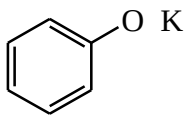





резорцин гидрохинон пирогаллол флороглюцин

resorcinol **hydroquinone** **pyrogallol** **phloroglucin**

Radicals RO- are named by adding the particle -oxy- to the name of the radical R, i.e. alkyloxy-, aryloxy-. For the simplest radicals of this type, abbreviated names are recommended: methoxy-CH_3O-, ethoxy-CH_3CH_2O-, isopropoxy- $(CH_3)_2CHO$-, phenoxy-C_6H_5O-.

Salts of alcohols and phenols, consisting of the anion RO– and a cation (usually a metal), are given names in which the name of the anion comes first, and then the cation. The anion RO– is called in two ways: by replacing the suffix -ol in the names of alcohols and phenols with -olate, or as the corresponding radical RO- with a change in the suffix -yloxin-yloxide (including the above abbreviations):

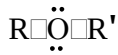
метанолят натрия
метоксид натрия

пентанолят лития
пентоксид лития

фенолят калия
феноксид калия

sodium methanolate **lithium pentanolate** **potassium phenolate**

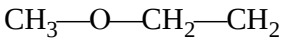
Ethers are derivatives of alcohols or phenols in which the hydrogen atom of the hydroxyl group is replaced by a hydrocarbon radical.



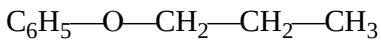
простые эфиры

simple ethers

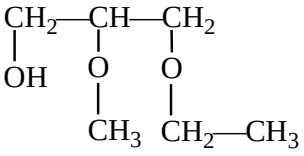
Specific names are constructed by adding a prefix denoting the radical R'O- to the name of the hydrocarbon corresponding to the radical R. The senior component is chosen as the starting compound, the names of the esters of polyhydroxyl compounds are also composed:



1-метоксиэтан



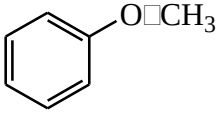
пропоксибензол
(цикл старше цепи)

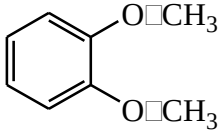


2-метокси-3-этоксипропанол-1

1-methoxyethane **propoxy benzoyl** **2-methoxy - ethoxypropanol-1**

Some esters containing an aromatic radical retain trivial names:





анизол фенетол

anisole **phenethol**

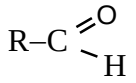
For ethers, more often than for other classes of compounds, the radical-functional nomenclature is used. In this case, the names are formed from the names of the radicals R and R' in alphabetical order, preceding the word ether, for example:

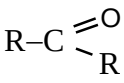
methyl ethyl ether CH_3-O-CH_2CH_3,

vinylphenyl ether C_6H_5-O-CH=CH_2.

Carbonyl compounds are oxygenated derivatives of hydrocarbons containing a carbonyl group.

Carbonyl compounds include aldehydes and ketones. In aldehydes, the carbonyl group is bonded to a radical and a hydrogen atom, while in ketones, both valences of the carbonyl group are saturated with hydrocarbon radicals.

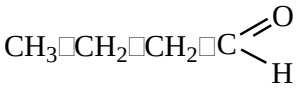




альдегиды кетоны

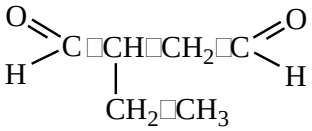
Aldehydes **ketones**

In the names of acyclic aldehydes, the -CHO group, if it is the eldest and is in the main chain, is denoted by the suffix *-al*. The numbering starts with the aldehyde group and its position is not indicated. Dialdehydes are named by adding the suffix *-dial* to the name of the parent structure. If the -CHO group is not a senior group or is not in the main chain, then the prefix formyl- is used.



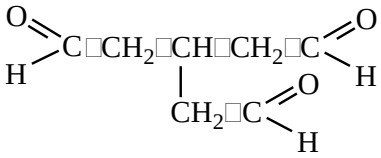
бутаналь

butanal



2-этилбутандиаль

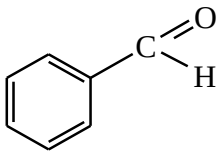
2-ethylbutanal



3-формилметилпентандиаль

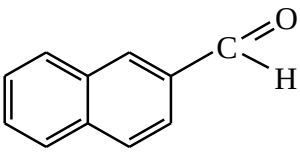
3-for mylmethylpentandial

The names of cyclic aldehydes in which the -CHO group as the eldest is linked to the cycle are constructed by adding the suffix *-carbaldehyde* to the name of the cyclic system:



циклогексанкарбальдегид

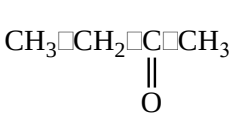
cyclohexanecarbaldehyde



нафталин-2-карбальдегид

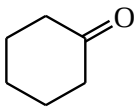
naphthalene-2-carbaldehyde

Ketones are named using the suffix -one if there is no older group. In her presence, the prefix *oxo*- is used.



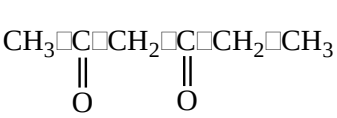
бутанон-2

butanone-2



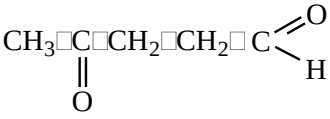
циклогексанон

cyclohexanone



гександион-2,4

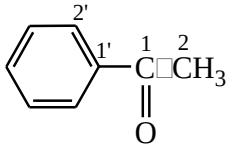
hexanedione-2,4



4-оксопентаналь

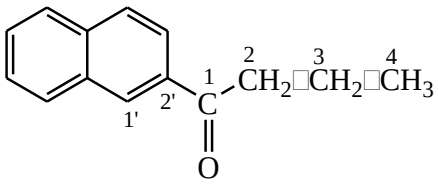
4-oxopentanal

Ar-CO-R ketones, in which the carbonyl group is attached to the benzene or naphthalene ring, are called by replacing the particle -yl in the name of the acyl radical R-CO- with the suffixes -ofenone and -onaphthone, respectively. Diketones produced from aromatic compounds by replacing two -CH= fragments with >C=O groups, followed by a rearrangement of double bonds, are called by adding the suffix -quinone to the name of the aromatic compound:



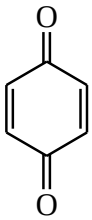
1-метанофенон

1-methanophenone



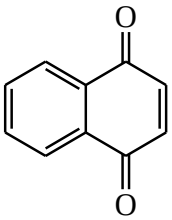
2-бутанонафтон

2-butanonaphthone



n-бензохинон

***n*-benzoquinone**

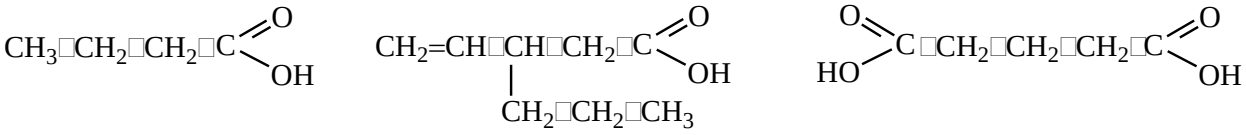


нафтохинон-1,4

naphthochenone -1.4

Carboxylic acids are oxygen-containing derivatives of hydrocarbons, in the molecules of which one or more hydrogen atoms are replaced by a carboxyl group.

Aliphatic carboxylic acids are named by adding the suffix *-noic acid* to the name of the parent hydrocarbon with the same number of carbon atoms. The names of dicarboxylic acids include the suffix *-dioic acid*. The numbering always starts from the carbon atom of the carboxyl group, and its position is not indicated:



бутановая кислота — 3-пропилпентен-4-овая кислота — пентандиовая кислота

butanoic acid — **3-propylpentene-4-ova acid** — **pentanedioic acid**

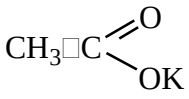
When naming complex acids, sometimes trivial names of acids corresponding to the longest straight chain are also used. In this case, the carbon atoms in the straight chain are denoted by Greek letters, starting from the second carbon atom: α (alpha), β (beta), γ (gamma), δ (delta), …

Table 7

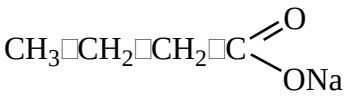
Trivial names of some carboxylic acids

№	Acid formula	Acid name	
		systematic	trivial
1.	H-COOH	methanoic acid	formic acid
2.	CH_3-COOH	ethanoic acid	acetic acid
3.	CH_3-CH_2-COOH	propanoic acid	propionic acid
4.	CH_3-CH_2-CH_2-COOH	butanoic acid	butyric acid
5.	CH_3-$(CH_2)_3$-COOH	pentanoic acid	valeric acid
6.	CH_3-$(CH_2)_4$-COOH	hexanoic acid	caproic acid
7.	CH_3-$(CH_2)_5$-COOH	heptanoic acid	enanthic acid
8.	CH_3-$(CH_2)_6$-COOH	octanoic acid	caprylic acid
9.	CH_3-$(CH_2)_7$-COOH	nonanoic acid	pelargonic acid
10.	CH_3-$(CH_2)_8$-COOH	decanoic acid	capric acid
11.	CH_2=CH-COOH	propenoic acid	acrylic acid
12.	HOOC-COOH	ethanedioic acid	oxalic acid
13.	HOOC-CH_2-COOH	propanedioic acid	malonic acid
14.	HOOC-$(CH_2)_2$-COOH	butanedioic acid	succinic acid
15.	HOOC-$(CH_2)_3$-COOH	pentanedioic acid	glutaric acid

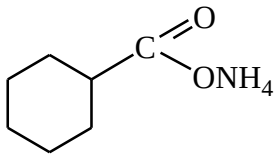
Neutral salts of carboxylic acids are named by listing the names of the acid anion and cation (in the genitive case). The names of acid anions, in turn, are formed by replacing the suffix *-yl* in the name of the acyl radical with *-at*. The anion derived from the name of an acid with the suffix *-carboxylic acid* is called R-*carboxylate.*



ацетат калия

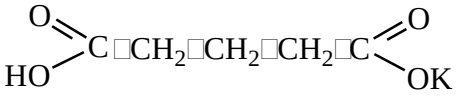


бутаноат натрия



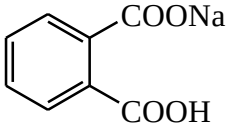
циклогексанкарбоксилат аммония

Acid salts of dicarboxylic acids are called similarly neutral. The presence of a hydrogen ion is indicated by the prefix *hydro-* before the name of the anion:



гидропентандионат калия

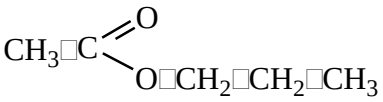
potassium hydropentanedionate



гидрофталат натрия

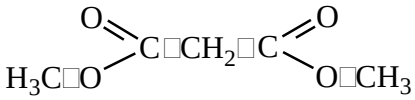
sodium hydrophthalate

Esters of carboxylic acids (as well as sulfonic acids) are named similarly to salts, only instead of the name of the cation, the name of the corresponding alkyl or aryl is used, which is placed before the name of the anion and is written together with it. The presence of the -COOR ester group can also be expressed in a descriptive way, for example, "R-ester of (such and such) acid":



пропилацетат или пропиловый эфир уксусной кислота

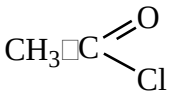
propyl acetate or propyl ether of acetic acid



диметилмалонат или диметиловый эфир малоновой кислота

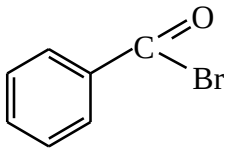
dimethylmalonate or dimethyl ether of malonic acid

The names of carboxylic acid halides RCOX (as well as sulfonic acids RSO_2X) are formed by placing the name of the halide after the name of the acyl radical. The names of symmetrical acid anhydrides come from the names of the corresponding acids with the word acid replaced by anhydride:



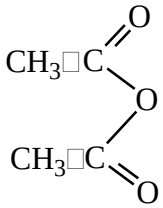
ацетилхлорид

acetyl chloride



бензоилбромид

benzoyl bromide



уксусный ангидрид

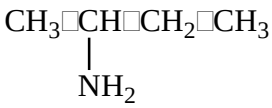
acetic anhydride

Amines are nitrogen-containing derivatives of hydrocarbons, in the molecules of which one or more hydrogen atoms are replaced by an amino group.

The generic name amines refers to the compounds RNH_2, RR'NH and RR'R''N, which are primary, secondary and tertiary amines, respectively. In a

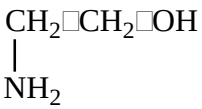
broader sense, amines also include compounds containing an –NH- group in the cycle.

The names of primary amines are formed by adding the suffix -amine to the name of the radical or to the name of the parent structure. In cases where the -NH_2 group is not the eldest, it is denoted by the prefix *amino*-:



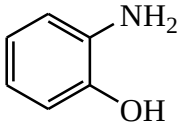
бутанамин-2

butanamine-2



2-аминоэтанол

2-aminoethanol

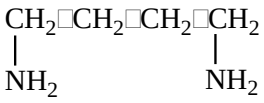


n-аминофенол

***n*-aminophenol**

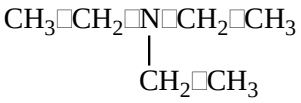
Primary diamines and polyamines, in which all amino groups are attached to an aliphatic chain or cyclic core, are named by adding the suffixes -diamine, -triamine, etc. to the name of the parent structure or polyvalent radical.

Symmetrical secondary and tertiary amines are named by adding multiplying prefixes di- or tri- to the names of alkyl radicals with the suffix -amine. Unsymmetrical compounds are named as N-substituted derivatives of primary amines, and a compound with a more complex radical is taken as the initial primary amine:



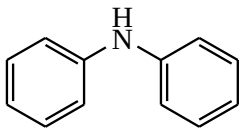
бутандиамин-1,4

butanediamine-1,4



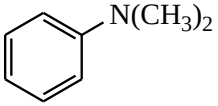
триэтиламин

triethylamine



дифениламин

diphenylamine



N,N-диметиланилин

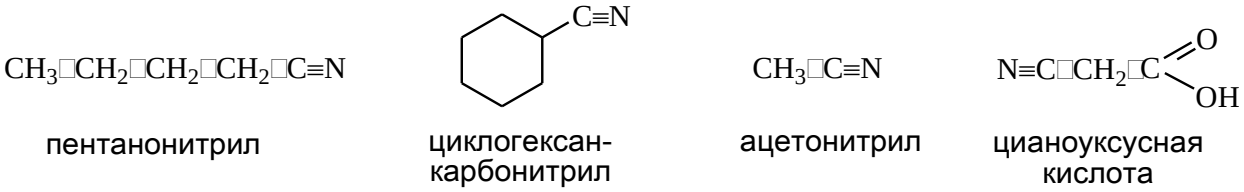
N,N-dimethylaniline

Nitro compounds are nitrogen-containing derivatives of hydrocarbons, in the molecules of which one or more hydrogen atoms are replaced by a nitro group.

The names of nitro compounds are formed only with the use of the prefix *nitro*-. Nitroso compounds are named similarly, using the prefix *nitroso*-.

Nitriles are nitrogen-containing derivatives of hydrocarbons, in the molecules of which one or more hydrogen atoms are replaced by a cyano group.

Their names are formed by adding the suffix -*nitrile* to the name of the parent hydrocarbon with the same number of carbon atoms. The names of RCN compounds, which can be considered as derivatives of RCOOH acids, are formed by replacing the suffix -*carboxylic acid* with -*carbonitrile*. If the acid RCOOH has a trivial name, then the name of the nitrile derived from it is formed by replacing the suffix -*oil* (or -*yl*) of the acyl radical with -*onitrile* (the letter o is inserted between two consonants for euphony). In the presence of an older group in the nitrile molecule, the -CN group is denoted by the prefix *cyano*-.



пентанонитрил | циклогексан-карбонитрил | ацетонитрил | цианоуксусная кислота

pentannitrile | **cyclohexanecarbonitrile** | **acetonitrile** | **cyanoacetic acid**

Sulfur derivatives of hydrocarbons

Thiols are sulfur-containing derivatives of hydrocarbons, in the molecules of which there is a thio group (-SH) directly bonded to the carbon atom.

In the name of specific compounds, the suffix -thiol is added to the name of the parent structure if the -SH group is the highest. If there is another senior group, -SH is indicated by the prefix *mercapto*-.

метантиол | 2-меркаптоэтанол

methanethiol | **2-mercaptoethanol**

Thiol salts are named similarly to salts of hydroxyl compounds: the suffix -*thiolate* is used, and the suffix -*sulfide*, for example: sodium ethanethiolate (or ethyl sulfide) CH_3CH_2SNa.

Sulfides are the generic name for R-S-R' compounds. These compounds are named like ethers: they use prefixes such as *alkylthio*- or *arylthio*-; according to the radical-functional nomenclature, the radicals R and R' are listed, added to the word *sulfide*, which is written together with the names of the radicals:

метилтиоэтан
метилэтилсульфид | 1-метилтиобутан
бутилметилсульфид

methylthioethane
methylethyl sulfide | **1-methylthiobutane**
butylethyl sulfide

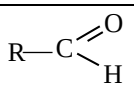
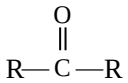
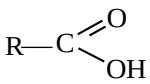
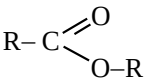
Sulfoxides and sulfones are generic names for the compounds R-SO-R' and R-SO2-R', respectively. In their names, the radicals R and R' are listed alphabetically, added to the words sulfoxide and sulfone, for example: CH_3-SO-CH_3 dimethyl sulfoxide, C_6H_5-SO_2-CH_2CH_3 phenyl-ethylsulfone.

Sulfonic acids are sulfur-containing derivatives of hydrocarbons, in the molecules of which one or more hydrogen atoms are replaced by a sulfo group (-SO_3H).

The sulfonic group is reflected by the suffix -*sulfonic acid,* and in the presence of an older group - by the prefix *sulfonic acid*.

ISOMERISM OF HYDROCARBON DERIVATIVES

Each class of monofunctional derivatives of hydrocarbons is characterized by the following types of structural isomerism.

Classes of compounds	General formula	Main types of isomerism
Halogen hydrocarbons	R—Hal	1) isomerism of the carbon skeleton; 2) isomerism of the position of the functional group (-F, -Cl, -Br, -I).
Alcohols	$C_nH_{2n+1}OH$	1) isomerism of the carbon skeleton; 2) isomerism of the position of the functional group (-OH); 3) interclass isomerism (isomeric to ethers).
Phenols	Ar—OH	1) isomerism of the position of substituents in the benzene ring; 2) side chain isomerism (radical structure and number of radicals).
Ethers	R–O–R	1) isomerism of the structure of the carbon radical; 2) interclass isomerism (isomeric to monohydric saturated alcohols).
Aldehydes		1) isomerism of the carbon skeleton; 2) interclass isomerism (isomeric to ketones).
Ketones		1) isomerism of the carbon skeleton; 2) isomerism of the position of the functional group (>C=O); 3) interclass isomerism (isomeric to aldehydes).
carboxylic acids		1) isomerism of the carbon skeleton; 2) interclass isomerism (isomeric to esters).
Esters		1) isomerism of the structure of the carbon radical; 2) interclass isomerism (isomeric to monobasic limiting carboxylic acids).
Amines	R—NH_2	1) isomerism of the carbon skeleton; 2) isomerism of the position of the functional group (-NH2).
Nitro compounds	R—NO_2	1) isomerism of the carbon skeleton; 2) isomerism of the position of the functional group (-NO_2).
Thiols	R—SH	1) isomerism of the carbon skeleton; 2) isomerism of the position of the functional group (-SH).
Sulfonic acids	R–SO_3H	1) isomerism of the carbon skeleton; 2) isomerism of the position of the functional group (-SO_3H).

EXERCISES

1. Make structural formulas of monofunctional and polyfunctional derivatives of hydrocarbons:

1) 4-nitro-3-isopropylcyclopentene-1; 2) 2-methyl-3-ethynylpentadiol-1,4; 3) methylethylpropylamine; 4) 5-isopropyl-6-(m)-tolylheptadione-3,4; 5) 1-thiol-2-cyclopropylpentadiene-3,4; 6) 1-amine-2,3-diallylbenzene; 7) benzyl benzoate; 8) 3-benzylbutene-2-dioic acid; 9) cyclooctaoctaol-1,2,3,4,5,6,7,8; 10) 2,3-diamine-4,5-diisopropyltoluene; 11) propen-1-ylbutyl ether; 12) 6-methylhexene-2-yn-4-al; 13) 3-butylhexine-5-sulfonic acid; 14) 3,4-dimethylphthalic acid; 15) 2-vinylpentene-3-dial;	16) 3-methoxypropanediol-1,2; 17) heptadiine-3,5-dioic acid; 18) 2,3,4-triamine-4-phenethylhexane; 19) 2,3-dinitro-4,4,5-triethyloctane; 20) hexahydroxabenzene; 21) 2-methyl-4-t-butylcyclohexanone; 22) 1-chloro-2-ethoxyethane; 23) 3-formylpetandial; 24) 5,5-dimethyl-3-propylhexanone-2; 25) 2-methylnonadiin-3,6-oic acid; 26) propyl acetate; 27) 2-thiobutin-3; 28) 2,3,4-trichlorophenol; 29) 3-methyl-4-nitrooctin-7-ene-1; 30) methoxybenzene.

2. Give the formulas of the following compounds by their name:

1) menthol 2-isopropyl-5-methylcyclohexanol-1 (is part of the drug validol);

2) 8-hydroxyquinoline derivative of the drug 5-NOC (antimicrobial drug);

3) meprotan (2-methyl-2-propylpropanediol-1,3), used as a tranquilizer;

4) menadione (2-methyl-1,4-naphthoquinone), a synthetic analogue of vitamin K;

5) arachidonic acid (eicosatetraen-5,8,11,14-oic acid) omega-6 fatty acid;

6) geraniol (3,7-dimethyloctadien-2,6-ol-1) terpene, which is part of the essential oils of geranium and rose;

7) inositol (hexahydroxycyclohexane) vitamin B8;

8) caffeine (1,3,7-trimethylpurindione-2,6) alkaloid, is a psychoactive substance;

9) pyridoxine (4,5-dihydroxymethyl-2-methylpyridin-ol-3) one of the forms of vitamin B6.

10) citral (3,7-dimethyloctadien-2,6-al) analgesic, anti-inflammatory agent.

3. Make formulas of substances corresponding to the characteristics:

1) limiting linear alcohol;

2) branched aminoalkene;

3) cyclic limiting ketone;

4) nitro-containing linear alkyne;

5) branched saturated carboxylic acid;

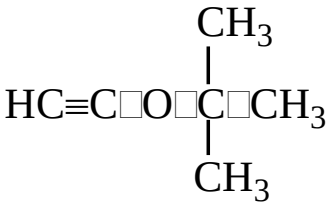
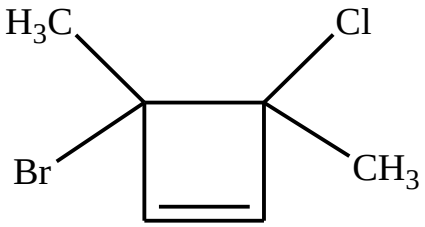
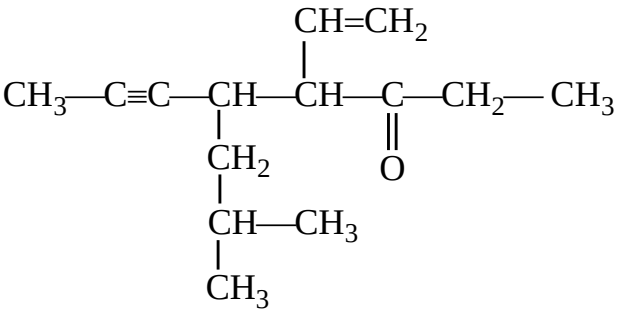
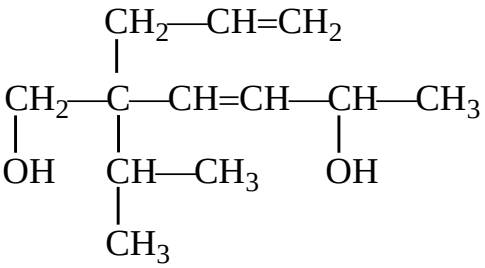
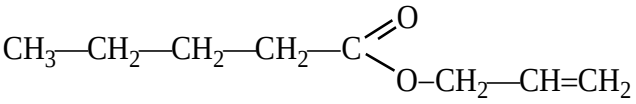
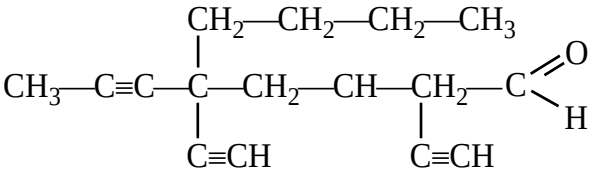
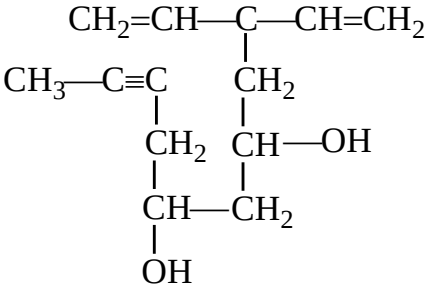
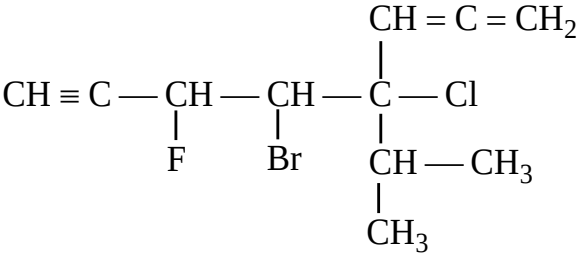
6) linear limiting simple ether;

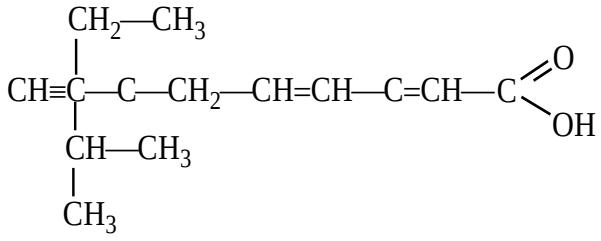
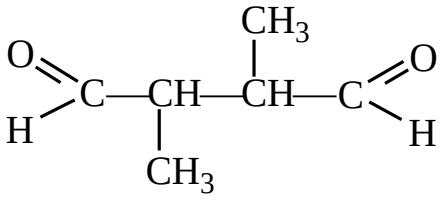
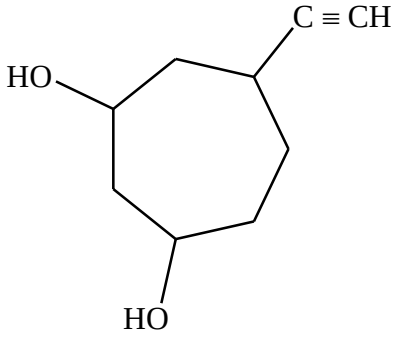
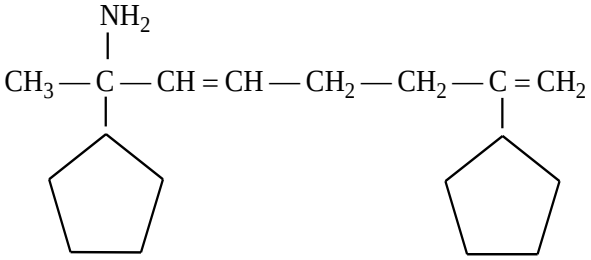
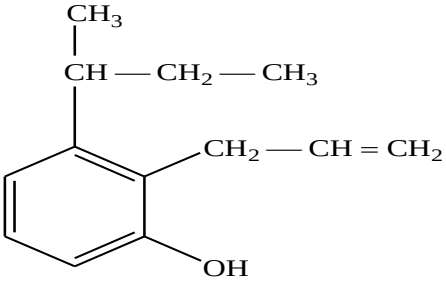
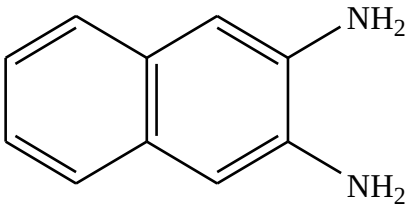
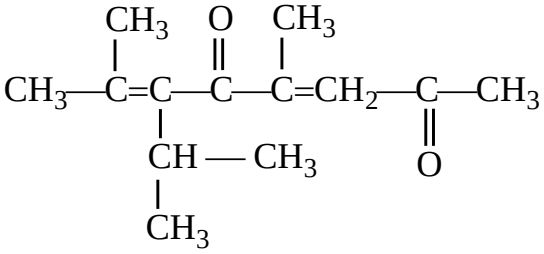
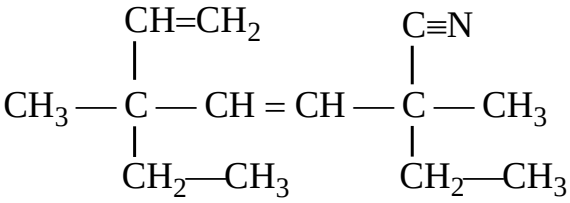
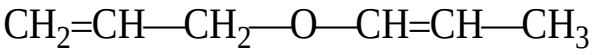
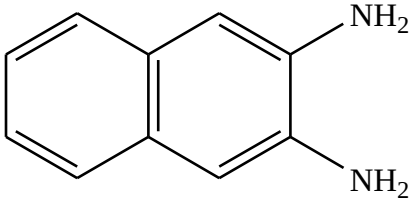
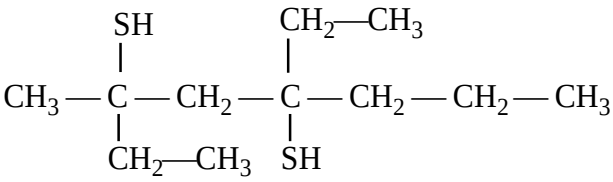
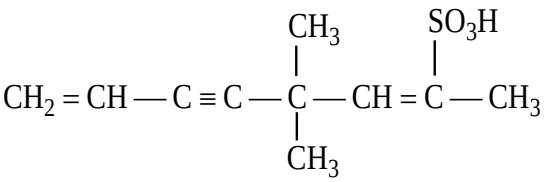
7) aromatic thiol.

4. The formula reflecting the belonging of the compound to the class of thiols is as follows: R-SH. Draw similarly the formulas corresponding to the following compounds:

1) dialkyl sulfide;
2) dialkyl disulfide;
3) alkylsulfonic acid;
4) dialkyl sulfoxide;
5) dialkylsulfone.

5. Name the following hydrocarbons according to the systematic nomenclature:

1 	2 
3 	4 
5 	6 
7 	8 

9 	10 
11 	12 
13 	14 
15 	16 
17 	18 
19 	20 

6. Write the structural formulas of the isomers of the following compounds:

1) C_3H_7OH;
2) $C_4H_8O_2$;
3) $C_6H_{12}O$;
4) $C_5H_{13}N$
5) C_4H_8O;
6) $C_6H_{15}N$
7) $C_6H_{12}O_2$;
8) $C_5H_{11}OH$;
9) $C_5H_{10}O$;
10) C_4H_9OH;
11) $C_5H_{11}NO_2$;
12) $C_5H_{10}O_2$.

Name them.

7. Write the structural formulas of all isomeric polyfunctional derivatives of hydrocarbons of the following compositions and name them according to the systematic nomenclature:

1) $C_4H_8(OH)_2$;
2) $C_4H_8(COOH)_2$;
3) $C_4H_{12}N_2$;
4) $C_5H_{12}S_2$;
5) $C_4H_{11}(OH)_3$;
6) $C_5H_{10}(NO_2)_2$.

8. Draw the structural formulas of all alkyl bromides of composition C_4H_9Br. Name the compound according to international nomenclature. Specify the primary, secondary and tertiary alkyl halides.

9. Write the structural formulas of all isomeric aromatic amines with the formula C_7H_9N and name them

10. Write the structural formulas of six secondary amines of composition $C_5H_{13}N$. Name according to rational and international nomenclature.

ACTIVITY №7

Topic:

ACIDITY AND BASICITY OF ORGANIC COMPOUNDS

Purpose of the lesson:

To form knowledge of the acid-base properties of organic compounds in accordance with the theories of Bronstod and Lewis, quantitative and qualitative assessment of these properties; the ability to conduct qualitative reactions on the acidic and basic properties of organic compounds.

Issues for discussion

1. Bronsted-Lowry protolytic theory of acidity and basicity of organic compounds.
2. Lewis electronic theory of acidity and basicity.
3. Classification of organic acids.
4. Quantitative and qualitative characteristics of acidic and basic properties of organic compounds.
5. Acidity. Factors affecting the severity of the acidic properties of organic compounds.
6. Basicity. Factors affecting the severity of the main properties of organic compounds. Amphoteric.
7. Hydrogen bond as a specific manifestation of acid-base properties. Hydrogen bonds in the structure of biopolymers.

Theoretical part

The acidic and basic properties of organic compounds are closely related to the structure and reactivity. However, the well-known theory of electrolytic dissociation in inorganic chemistry is inapplicable to them. To assess the acidity and basicity of organic compounds, two theories are of greatest importance - the Bronsted theory (protolytic) and the Lewis theory (electronic).

Bronsted acids (protic acids) are neutral molecules or ions capable of donating a proton (proton donors).

Bronsted bases are neutral molecules or ions that can accept a proton (proton acceptors).

The course of many biochemical reactions is associated with the transfer of H^+ between the O, N, S atoms. An important role in biochemical processes is played by acid or basic catalysis, carried out with the participation of the corresponding groups of enzymes.

Acidity and basicity are not absolute, but relative properties of compounds: acidic properties are found only in the presence of bases, basic properties - only in the presence of acids. The acid and base in an acid-base pair are interconnected: the stronger (weaker) the acid, the weaker (stronger) the conjugate base. Acidity is usually defined in relation to water as a base. It is quantified by the constant K_a or

pK_a (pK_a = - lgK_a): the larger the value of K_a and the smaller pK_a, the stronger the acid.

Depending on the nature of the element with which the proton is bound, i.e. Based on the structure of the acid site, Brönsted organic acids are divided into four main types:

O-H - acids: carboxylic acids, phenols, alcohols;

S-H - acids: thiols;

N-H - acids: amines, amides, imides;

C-H - acids: hydrocarbons and their derivatives.

With the exception of carboxylic acids, most organic compounds have rather weak acid properties (pK_a >15), which are usually not detectable by indicators. A comparative analysis of the strength of acids is carried out by comparing the stability (stability) of the corresponding conjugated bases (anions). The more stable the anion, the stronger the conjugate acid. The stability of the anion is determined by the degree of delocalization of the negative charge. For Bronsted acids containing the same aliphatic or the same aromatic radicals, the stability of their anions, and hence the acidity, depends on the electronegativity (EN) and the polarizability of the atoms in the acid center.

Increased anion stability and acid strength:

CH-acids < NH-acids < OH-acids < SH-acids.

The more EO, the stronger the acidic properties, the more stable the anion. For example:

$C_2H_5OH \leftrightarrow C_2H_5O^- + H^+$ pK = 15.8

$C_2H_5NH_2 \leftrightarrow C_2H_5NH^- + H^+$ pK = 30

EO (O) > EO (N), oxygen holds the electron more firmly and is less accessible to the proton, i.e. $C_2H_5O^-$ is more stable than $C_2H_5NH^-$, therefore, the acidic properties of C_2H_5OH are more pronounced than those of $C_2H_5NH_2$.

The larger the radius of the atom, the stronger the acid and the more stable the anion. For example, the radius of a sulfur atom is greater than the radius of an oxygen atom, so thiols are stronger acids than alcohols:

$C_2H_5OH \leftrightarrow C_2H_5O^- + H^+$ pK = 15.8

$C_2H_5SH \leftrightarrow C_2H_5S^- + H^+$ pK = 10.5

With the same nature of the atom in the acid center, the acidity is greatly influenced by the structure of the radical associated with it. In aliphatic acids and alcohols, when passing from the first to subsequent homologues, an increase in the length of the hydrocarbon radical and its branching leads to a decrease in acidity.

The acidity of alcohols decreases in the following sequence:

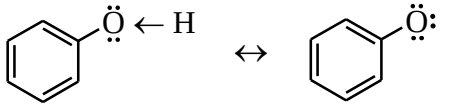
$CH_3—OH$	$CH_3—CH_2—OH$	$CH_3—\underset{\displaystyle OH}{\underset{\vert}{CH}}—CH_3$	$CH_3—\underset{\displaystyle OH}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}}—CH_3$
метанол pK = 15,2	этанол pK = 15,8	пропанол-2 pK = 16,9	2-метилпропанол-2 pK = 19,2
Methanol	**ethanol**	**propanol-2**	**2-methylpropanol-2**

Substituents introduced into aliphatic and aromatic radicals affect the acidity of compounds: electron-withdrawing substituents (EA) contribute to the delocalization of the negative charge, stabilize anions and thereby increase acidity; electron-donating substituents (ED), on the contrary, lower it. For example:

$CH_3—CH_2—OH \leftrightarrow CH_3—CH_2—O^- + H^+$ pK = 15,8

$CBr_3—CH_2—OH \leftrightarrow CBr_3—CH_2—O^- + H^+$ pK = 12,4

$CF_3—CH_2—OH \leftrightarrow CF_3—CH_2—O^- + H^+$ pK = 11,4



pK = 10,0

кислотные свойства увеличиваются

влияет эффект сопряжения

the pairing effect is affected **acidic properties increase**

According to the theory of Gilbert Lewis, the acidic and basic properties of compounds are determined by their ability to accept or donate an electron pair to form a bond.

Lewis acid is an electron pair acceptor; it participates in heterolytic reactions as an electrophilic reagent. For example: halides (BF3, AlCl3, FeCl3, etc.), metal cations, proton.

The Lewis base is an electron pair donor; it participates in heterolytic reactions as a nucleophilic reagent. For example: amines, alcohols, ethers, etc.

The advantage of the Lewis theory is its applicability to a wide range of organic reactions.

The experimental development of the Lewis theory led to the creation of the principle of hard and soft acids and bases (R. Pearson). According to the theory of hard and soft acids and bases (HMCA), Lewis acids and bases are divided into hard and soft.

Table 6

Hard and soft acids and bases

hard acids	**intermediate acids**	**soft acids**
H^+, Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, BF_3, $B(OR)_3$, AlR_3, $AlCl_3$, SO_3, $-RCO^+$, CO_2, RSO_2^+	Cu^{2+}, Fe^{2+}, Zn^{2+}, SO_2, R_3C^+, $C_6H_5^+$, NO^+	Ag^+, Cu^+, Hg^{2+}, RS^+, I^+, Br^+, Pb^{2+}, BH_3,
hard bases	**intermediate base**	**soft base**
H_2O, OH^-, RO^-, F^-, Cl^-, $RCOO^-$, NO_3^-, NH_3, RNH_2, H_2O, ROH, SO_4^{2-}, CO_3^{2-}, R_2O, NR_2^-, NH_2^-	Br^-, $C_6H_5NH_2$, NO_2^-, C_5H_5N	RS^-, RSH, I^-, H^-, R_3C^-, alkenes, C_6H_6, R_3P, $(RO)_3P$, CN^-

Rigid bases are donor particles with high electronegativity, low polarizability, and are difficult to oxidize. The term "rigid base" emphasizes that the compound holds its electrons firmly. Donor atoms in hard bases can be oxygen, nitrogen, fluorine, chlorine.

Soft bases are donor particles with low electronegativity, high polarizability, and rather easily oxidized. They weakly hold their valence electrons. Carbon, sulfur, and iodine atoms act as electron donors.

Hard acids are Lewis acids in which the acceptor atoms are small in size and therefore have a high positive charge, high electronegativity, and low polarizability. The lowest free molecular orbital of hard acids, to which donor electrons pass, has a low energy.

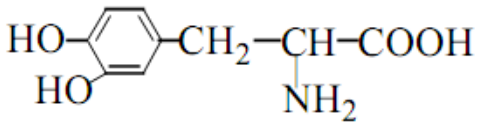
Soft acids are Lewis acids that contain acceptor atoms of large size, with a small positive charge, with low electronegativity and high polarizability. The lowest free molecular orbital of these compounds has a high energy. The essence of the principle of HICA is that hard acids preferentially react with hard bases, and soft acids with soft bases. This is expressed in a higher reaction rate and in the formation of more stable compounds, since the interaction between orbitals with similar energies is more efficient than between orbitals with different energies. Knowledge of this principle is useful as a general theoretical basis for various interactions of organic compounds.

EXERCISES

1. Arrange the groups of compounds in order of decreasing acidity and justify your answer:

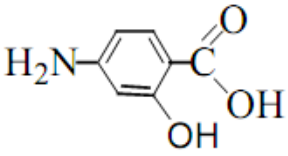
1) ethanol, 2-chloroethanol, 2,2-dichloroethanol;
2) phenol, n-nitrophenol, n-aminophenol;
3) ethanoic, ethanedioic, propanedioic acids;
4) ethanol, phenol, ethanoic acid;
5) ethanol, ethanethiol, propanol-2.

2. Qualitatively evaluate the strength of acid sites in molecules:



3,4–дигидроксифенилаланин

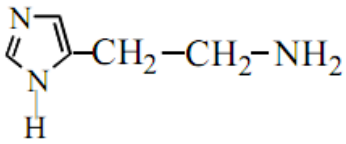
3,4-dihydroxyphenylalanine



n–аминосалициловая кислота

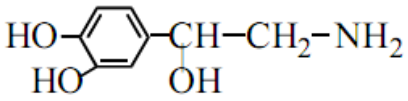
n-aminosalicylic acid

3. Divide the given compounds into groups of Lewis acids and bases:



гистамин

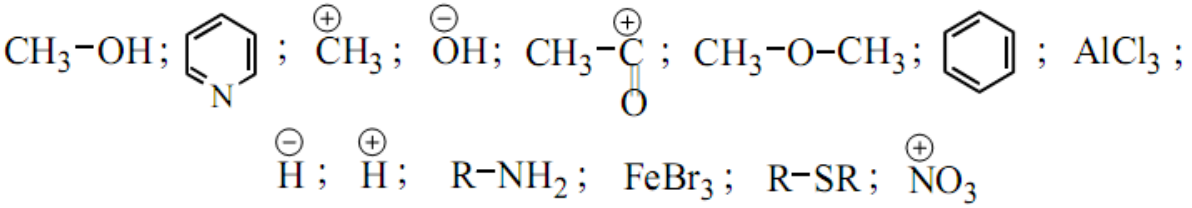
histamine



норадреналин

norepinephrine

4. Divide the above compounds into groups of Lewis acids and bases:



5. Compare the strength of the acid sites of propanol and propanethiol. Give reaction schemes confirming the difference in the acidic properties of these substances.

6. The strongest acid of the listed compounds is:
1) phenol;
2) glycerin;
3) ethanol;
4) acetic acid.

7. What substituents connected directly to the benzene ring of aniline enhance its basic properties:
1) -CH_3;
2) -NO_2;
3) -OH;
4) -COOH.

8. Which substituents directly connected to the benzene ring of phenol enhance its acidic properties:
1) -NO_2;
2) -SO_3H;
3) -CH_3;
4) -C_3H_7.

9. The strongest base of the listed compounds is:
1) CH_3-NH-CH_3;
2) $C_6H_5NH_2$;
3) CH_3NH_2;
4) NH_3.

10. The strongest acid of the listed compounds is:

1) CH_3-CH_2-SH;
2) CH_3-COOH;
3) C_6H_5OH;
4) Cl-CH_2-COOH.

11. The strongest acid of the listed compounds is:
1) butanol-1;
2) propanol-1;
3) ethylene glycol;
4) ethanol.

12. Set the correct sequence of decreasing acidic properties:
1) CH_3-CH_2-SH;
2) CH_3-COOH;
3) C_6H_5OH;
4) Cl-CH_2-COOH.

13. Set the correct sequence of decreasing acidic properties:
1) HO-CH_2-CH_2-OH;
2) C_6H_5-COOH;
3) C_6H_5-OH;
4) CH_3-CH_2-OH;
5) CH_3-COOH.

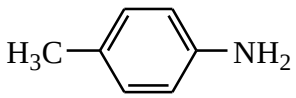
15. Give the names of the amines below and arrange them in order of increasing basic properties.

1) CH_3□NH_2

2) NH_3

3) CH_3□NH□CH_2□CH_3

4)



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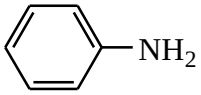

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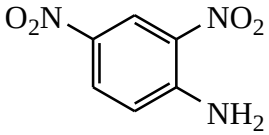

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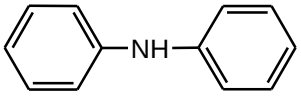

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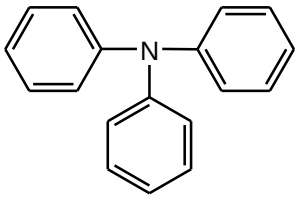


ACTIVITY №8

Topic:

NUCLEOPHILIC SUBSTITUTION AT A SATURATED CARBON ATOM

Purpose of the lesson:

To form knowledge of the reaction centers of alcohols, thiols, phenols and amines, predicting reactivity in nucleophilic substitution and elimination reactions; the ability to conduct qualitative and characteristic reactions for alcohols, phenols.

Issues for discussion

1. Reaction centers in the molecules of alcohols, thiols, amines, halogen derivatives of hydrocarbons, phenols.
2. Mechanism of nucleophilic substitution (SN) reactions at the sp3-hybridized carbon atom. SN_1 and SN_2 mechanisms.
3. Nucleophilic substitution of the hydroxyl group in alcohols. acid catalysis.
4. Competitive substitution reactions mono- and bimolecular reactions SN1, SN2 and elimination from alcohols.
5. Biologically important reactions of dehydration of hydroxyl-containing compounds.
6. Oxidation reactions of alcohols, thiols, phenols.

Theoretical part

Nucleophilic substitution at a saturated carbon atom is one of the most important synthetic organic reactions and is widely used for the synthesis of biologically active substances. Nucleophilic substitution reactions are most typical for saturated organic compounds containing the following functional groups: halogen, hydroxyl, thiol, amino group:

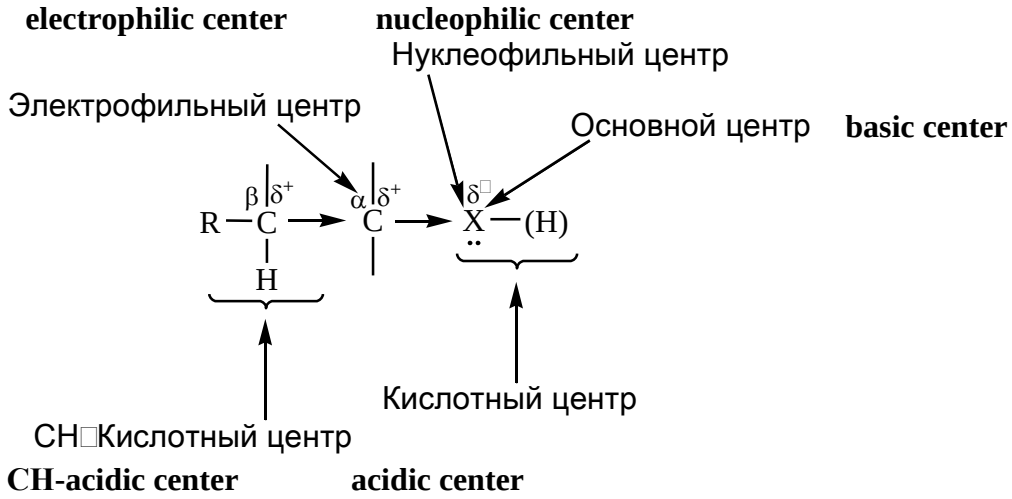
R-Hal (F, Cl, Br, I) - halogen derivatives

R-OH - alcohols

R-SH - thiols

R-NH - amines.

Schematically, the distribution of electron density in halogen derivatives, alcohols, thiols and amines of the aliphatic series, taking into account the transfer of the electronic influence of the electron-withdrawing heteroatom along the σ-bond, can be represented as follows:



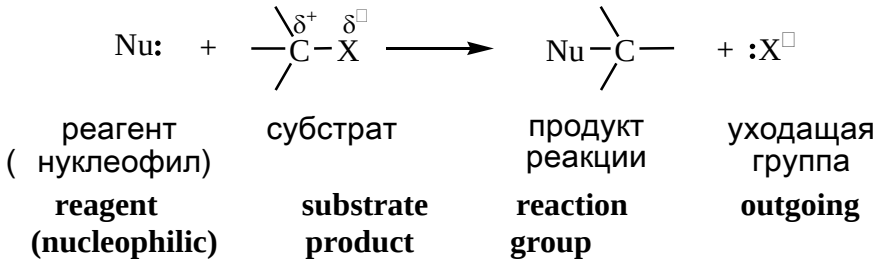
The saturated sp3-hybridized carbon atom is linked by a single σ-bond to the electroacceptor heteroatom (Hal, O, N, S) of the functional group. The heteroatom is more electronegative than carbon, and the electrons of the σ-bond are shifted towards it, and the C-X bond is polarized. The carbon atom becomes electron-deficient (electrophilic) and can be attacked by the nucleophile.

A shift in the electron density of neighboring bonds (i.e., the manifestation of the -I effect) leads to an increase in the mobility of the hydrogen atom at the β-carbon atom (an increase in acidity).

The presence of an electrophilic center in a molecule causes nucleophilic substitution reactions, and the presence of a CH-acid reaction center causes elimination, that is, competitive reactions SN and E occur in one molecule, but at different reaction centers.

NUCLEOPHILIC SUBSTITUTION REACTIONS

During the nucleophilic substitution reaction, a heterolytic cleavage of the C-X bond occurs, the bond electrons pass to the electronegative element X, and a new C-Nu bond is formed due to a pair of electrons of the nucleophilic reagent.



For a successful nucleophilic substitution reaction, the leaving group must be more stable and have lower energy than the attacking nucleophile.

It is important that the substituted, in other words, leaving group be more stable, poorer in energy than the attacking nucleophile, i.e. incoming group. Good leaving groups include halide ions (I- > Br- > Cl- > F-). Nucleophilic substitution in alcohols, thiols, and amines proceeds similarly, but these compounds contain

rather difficult-leaving groups (OH–, SH–, NH_2–) and these reactions usually proceed under acid catalysis conditions, while the difficult-leaving group is converted into easy-leaving CN.

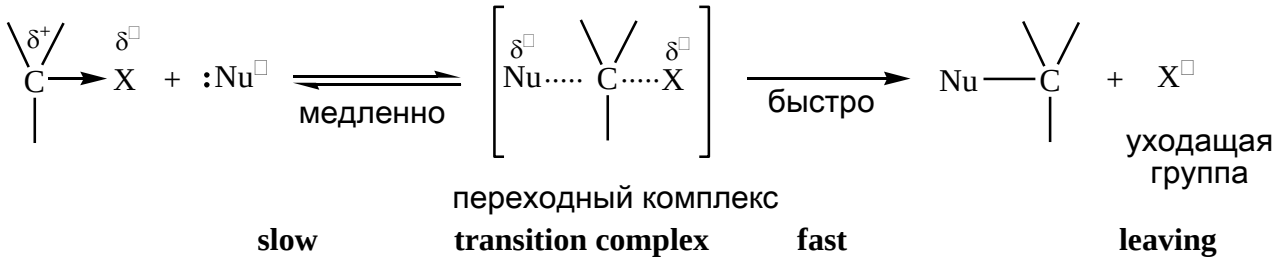
Nucleophilic substitution can proceed by two main mechanisms:

– bimolecular (associative);

- monomolecular (dissociative).

Bimolecular nucleophilic substitution of SN_2. With the bimolecular SN_2 mechanism, the attacking particle gradually displaces the leaving group, and the SN_2 reaction proceeds in one step.

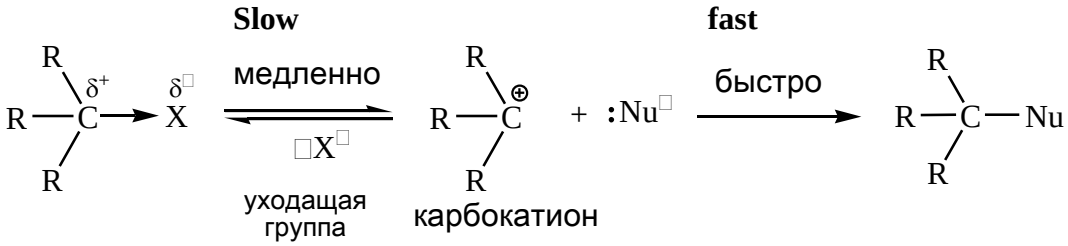
Mechanism of the nucleophilic substitution reaction



slow **transition complex** **fast** **leaving group**

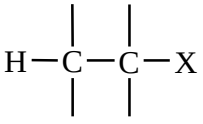
First, the nucleophilic particle Nu– attacks the carbon atom from the most favorable side (opposite to the leaving "attack from the rear" group). The rupture of the old C-X bond and the formation of a new C-Nu occurs synchronously, i.e., a transition state is formed (two molecules participate in this stage - a reagent and a substrate), the reaction rate depends on the concentration of both reagents. The SN2 reaction is characteristic of primary and secondary derivatives.

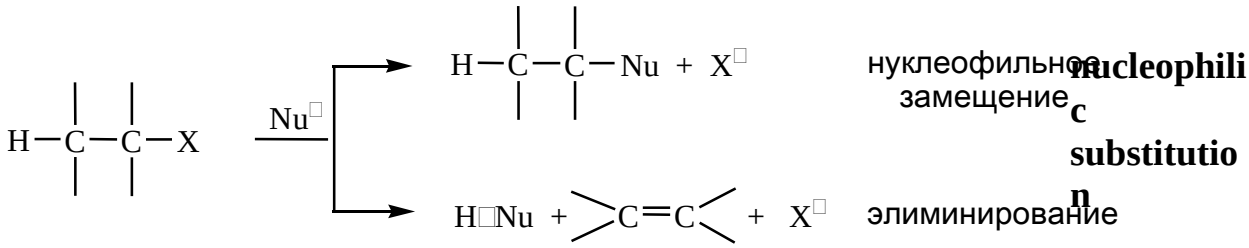
Monomolecular nucleophilic substitution of SN_1. The reaction of monomolecular nucleophilic substitution of SN_1 is not a synchronous process and consists of two main stages.



The first stage, which determines the rate of the process as a whole, involves only the substrate molecule, which dissociates relatively slowly (under the influence of the medium) to form a carbocation and a leaving group. Therefore, the reaction rate does not depend on the concentration of the nucleophile. In the subsequent step, the nucleophile rapidly attacks the carbocation to form the final product. The SN_1 reaction is typical for tertiary derivatives.

REMOVAL REACTIONS

SN processes are usually accompanied by elimination reactions (E). The elimination reaction consists in the elimination of 2 atoms or groups that make up one molecule. They compete with SN reactions and changing reaction conditions can lead to elimination reactions. The presence of a weak CH-acid center in monofunctional derivatives of hydrocarbons of the type:  , (where X is a halogen, OH, NR_3^+, etc. groups) predetermines the possibility of its attack by a base. Each nucleophile is also a base at the same time, and if its basic properties are significant, it can push out not only the leaving group, but also tear off a mobile proton from the β-carbon atom:



nucleophilic substitution

elimination

Elimination and substitution reactions proceed under the action of basic reagents and competition between them is possible. To direct the reaction along the elimination path, a low-polarity solvent and a high concentration of a strong base, for example, a concentrated alcoholic solution of alkali, are used.

Elimination reactions of monofunctional derivatives, like nucleophilic substitution reactions, can be both bimolecular (E_2) and monomolecular (E_1).

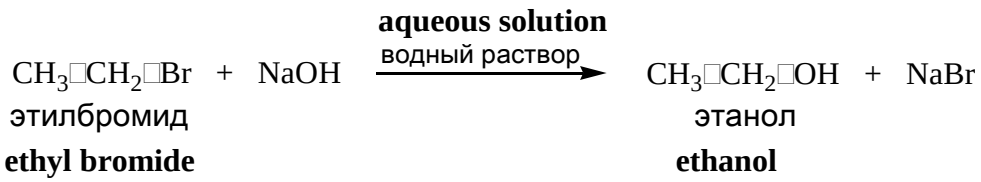
In elimination reactions, there is a preferential elimination of a proton from a carbon atom containing the minimum number of hydrogen atoms, that is, from the least hydrogenated carbon atom (**Zaitsev's rule)**.

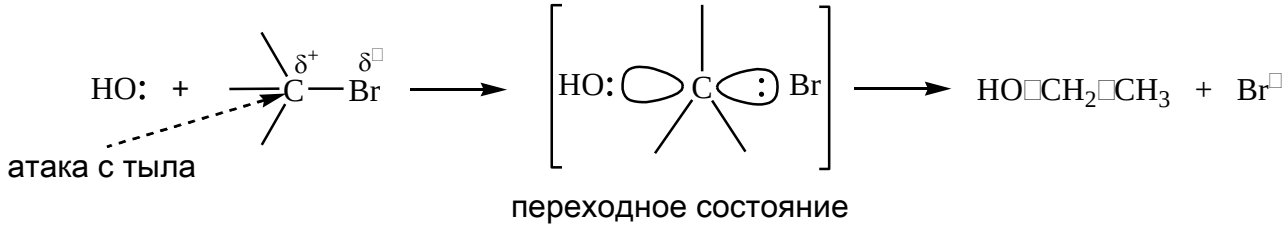
The Zaitsev rule obeys the elimination reactions proceeding according to the E_1 and E_2 mechanisms.

HALOGENIC HYDROCARBON DERIVATIVES

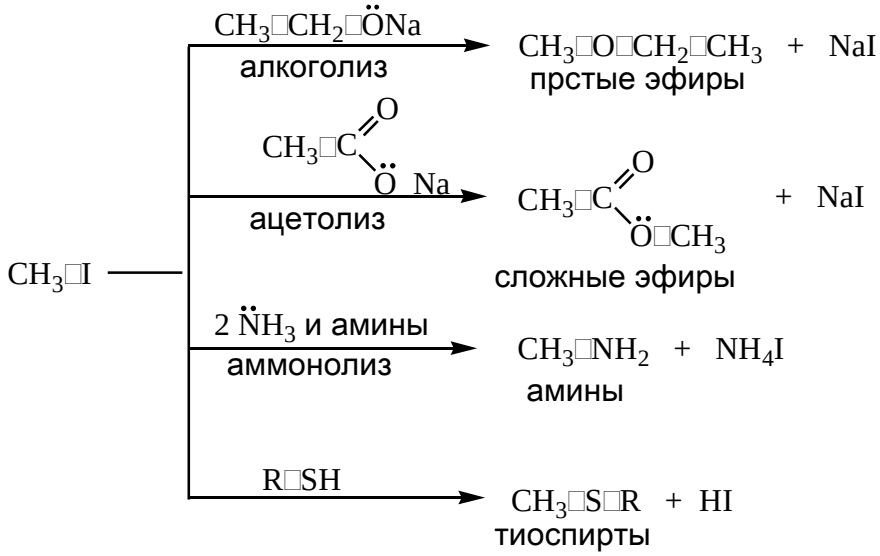
Halogen derivatives are a very reactive class of organic compounds. Based on them, you can go to almost almost all other classes: saturated and unsaturated hydrocarbons, alcohols, simple and complex ethers, amines….

Hydrolysis reaction. The substitution of halogen for hydroxyl proceeds under the influence of an aqueous solution of alkali, silver hydroxide or water (reversibly), and leads to the formation of alcohols:

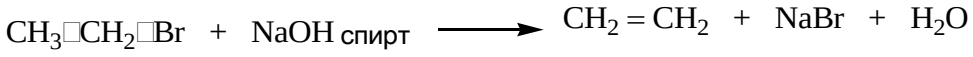




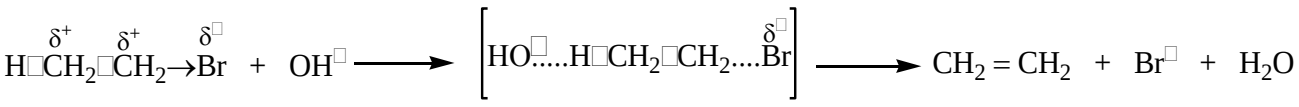
Nucleophiles in the S_N reactions of halogenated hydrocarbons can be not only water or hydroxide ion (HOH, :OH–), but also many other reagents: CN^- – cyanides, $:NO_2^-$ – nitriles, $:NO_2^-$ – nitriles, S^{2-} – sulfides, ammonia and amines (R-NH_2), salts of alcohols, carboxylic acids, …. These reactions follow the same patterns as the above hydrolysis reaction.



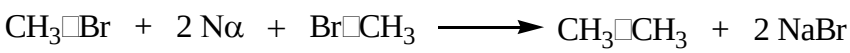
Dehydrohalogenation of haloalkanes. Elimination reactions, which are accompanied by the elimination of a halogen anion from the electrophilic center of haloalkanes, and a hydrogen proton from the neighboring β-carbon atom with the formation of a π-bond, are called elimination reactions. Reactions E proceed when halogen derivatives are exposed to strong bases in an alcoholic solution of alkali. Elimination reactions proceed according to the Zaitsev rule:



Mechanism:

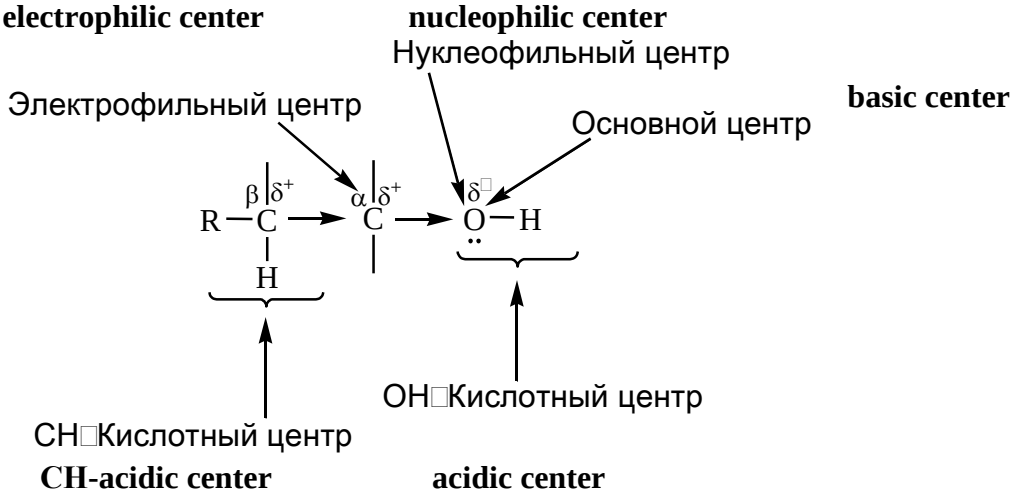


Wurtz reaction. Under the action of metallic sodium on haloalkyls, alkanes with a doubled number of carbon atoms are formed:

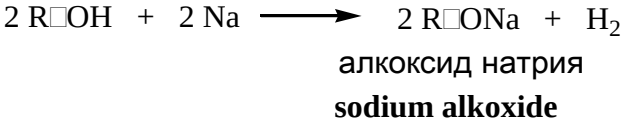


ALCOHOL

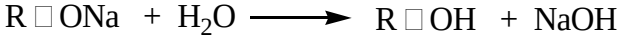
The properties of alcohols and phenols are largely determined by the properties of the hydroxyl group that is part of their molecules. Alcohols exhibit weak amphoteric properties: acidic due to the hydrogen atom of the hydroxyl group, basic - due to the lone pair of electrons of the oxygen atom. The following reaction centers can be distinguished in the alcohol molecule:



Reactions involving an OH-acid center. Alcohols are very weak OH-acids; they do not dissociate in water, but replace a hydrogen proton in reactions with active metals:



For the reaction to take place, anhydrous (absolute) alcohol is used, since in the presence of water, the reaction of hydrolysis of alkoxides occurs:

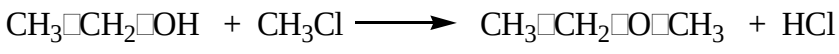


Reactions involving a nucleophilic center. Being rigid bases due to the low polarizability and high electronegativity of the oxygen atom, alcohols are weak nucleophiles. Nucleophilic substitution reactions in alcohols also proceed

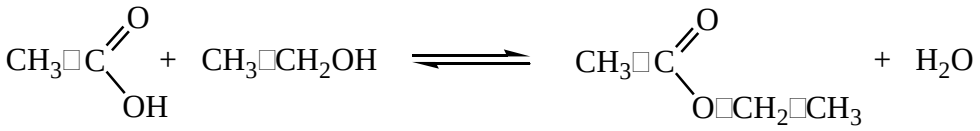
according to the nucleophilic substitution mechanism: according to the SN_2 mechanism in primary alcohols and according to the SN_1 mechanism in tertiary, sterically hindered alcohols. The hydroxyl group is an unstable, poorly leaving group, and therefore the reaction must be carried out in an acidic environment in order to convert the OH group into a good leaving group - a water molecule.

The reactions proceeding with the participation of the nucleophilic center include the reactions of alkylation, acylation of alcohols, and intermolecular dehydration.

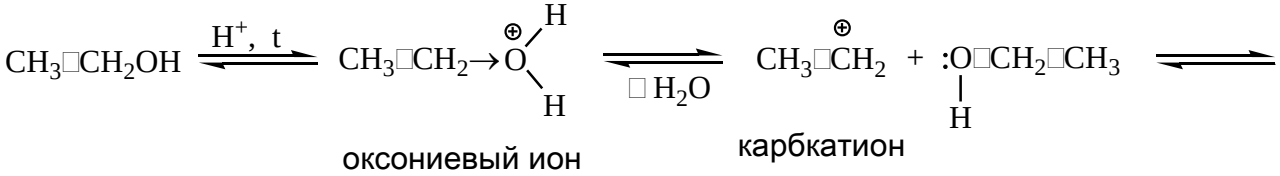
Alkylation of alcohols. Entering into this reaction, alcohols form ethers, the reaction proceeds slowly, however, the nucleophilicity of alcohols can be significantly increased by turning them into alkali metal alkoxides. Halogen derivatives, dialkyl sulfates, alkyl sulfonates are used as alkylating agents.

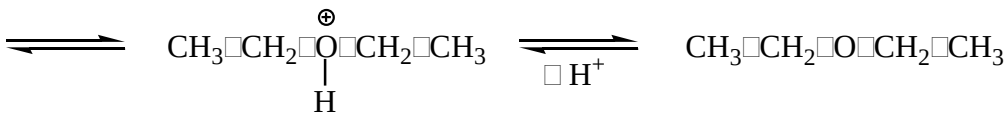


Acylation of alcohols. As a result of this reaction, alcohols form esters. Both oxygen-containing inorganic and organic acids and their functional derivatives can be used as acylating reagents.



intermolecular dehydration. Anhydrous alcohols, when heated in the presence of a small amount of concentrated sulfuric acid, undergo intermolecular dehydration to form dialkyl ethers. Essentially, this is the same SN reaction in which the role of the nucleophile is played by the second alcohol molecule. Nucleophilic properties are provided by the lone electron pair of the oxygen atom:

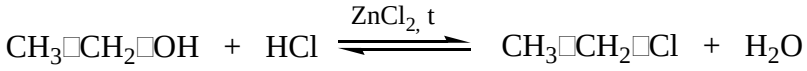




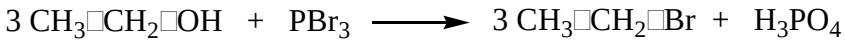
Reactions involving an electrophilic center. Many important reactions of alcohols are carried out by attacking the α-carbon atom (electrophilic center) with a nucleophile. As a result, the C-O bond is broken and the hydroxyl group is replaced by a halogen, an amino group, and others.

Reactions with hydrogen halides. The ease of entering into the S_N reaction in the class of alcohols increases from primary to tertiary alcohols. The reactivity of hydrohalic acids, acting as a catalyst and a source of nucleophile, decreases in the

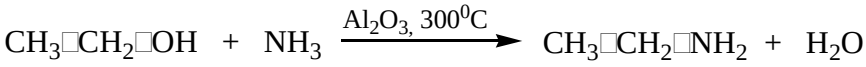
sequence HI>HBr>HCl, which is associated with a decrease in acid strength and a decrease in nucleophilicity when moving from iodide ion to chloride ion.



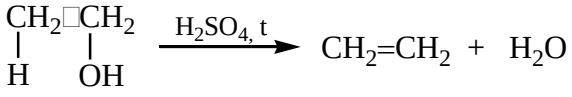
Reactions with halides of inorganic acids. Substitution of a hydroxyl group for a halogen atom is easier when using inorganic acid halides such as $SOCl_2$, PCl_5, PCl_3, PBr_5, PBr_3 and others:



Reactions with ammonia. When interacting with ammonia, the OH group of the alcohol is replaced by an amino group:



Reactions involving a CH-acid center. When alcohols are heated in the presence of mineral acids or Lewis acids, alkenes are formed as a result of intramolecular dehydration (β-elimination). In the case of secondary and tertiary alcohols, the elimination of water proceeds according to Zaitsev's empirical rule.

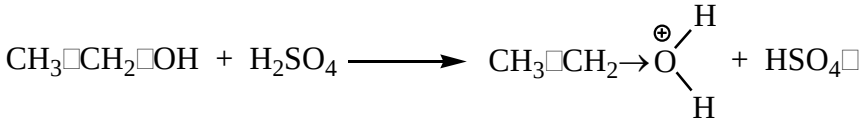


этанол — этен

Ethanol — ethene

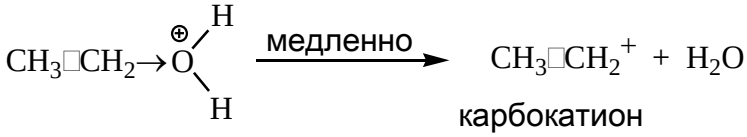
Reaction mechanism:

a) alcohol protonation



b) the formation of a carbocation

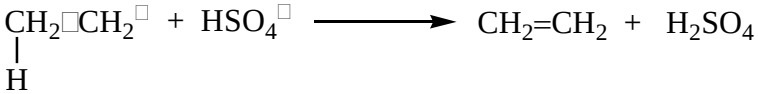
slow



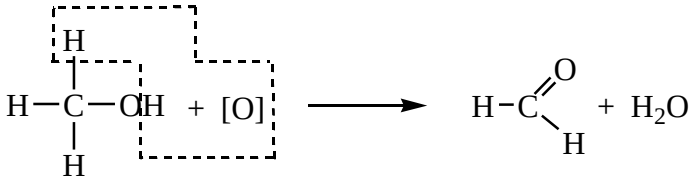
карбокатион

carbocation

c) the final stage of the reaction



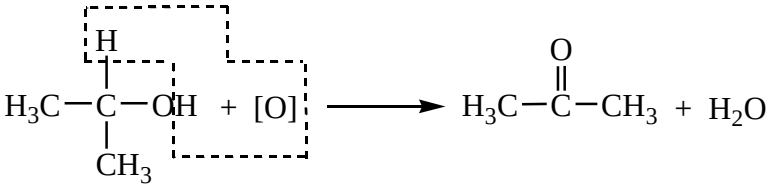
Oxidation reactions. Depending on the nature of the alcohol (primary, secondary, tertiary), as well as the reaction conditions, various products are formed. Primary alcohols are most easily oxidized, and aldehydes are formed:



метанол
methanol

метаналь
methanal

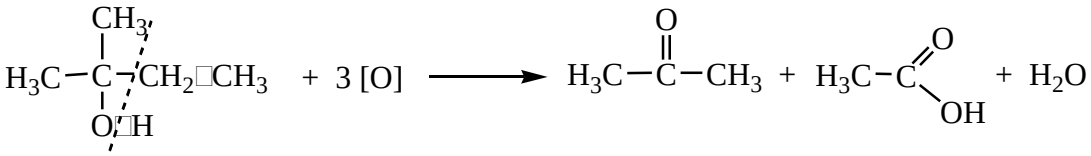
Ketones are formed from secondary alcohols during oxidation:



пропанол-2
propanol-2

ацетон
acetone

Tertiary alcohols are difficult to oxidize. Their oxidation is accompanied by the splitting of the hydrocarbon skeleton with the formation of a ketone and an acid:



изоамиловый спирт
iso amyl alcohol

ацетон
acetone

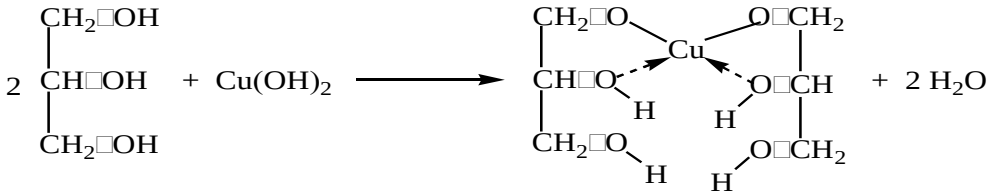
уксусная кислота
acetic acid

Properties of polyhydric alcohols

Polyhydric alcohols largely resemble monohydric alcohols in properties. The hydroxyl groups in them can be primary, secondary, tertiary, and one or more hydroxyl groups can enter into the reaction.

Polyhydric alcohols are more acidic than monohydric alcohols, which is a consequence of the presence of a larger number of hydroxyl groups and the negative inductive effect of one hydroxyl group in relation to another. The chemical proof of this is their interaction with the base.

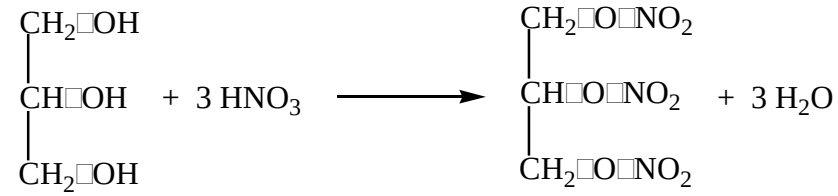
Polyhydric alcohols with hydroxides of some heavy metals in an alkaline medium form chelate compounds with a characteristic color. In particular, when interacting with copper (II) hydroxide, an intense blue coloration occurs.



хелат синего цвета
глицерат меди

This reaction can be used as a qualitative one for opening two or more hydroxyl groups (reaction for a diol fragment).

Esterification with nitric acid gives nitroesters. In particular, glycerol trinitrate is obtained from glycerol.

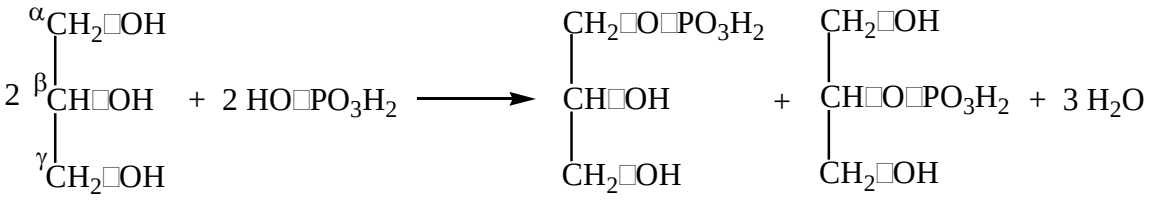


глицерин — тринитрат глицерина

glycerin — **trinitrate glycerin**

This compound is explosive and relatively poisonous, but in small concentrations (as a 1% solution in ethanol) it is a drug and is used as a vasodilator.

As a result of the action of phosphoric acid on glycerol, a mixture of α- and β-glycerophosphates is obtained.



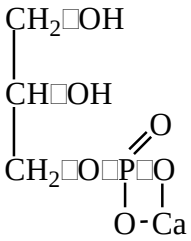
глицерин — α-глицерофосфат — β-глицерофосфат

Glycerin — **α-glycerophosphate** — **β-glycerophosphate**

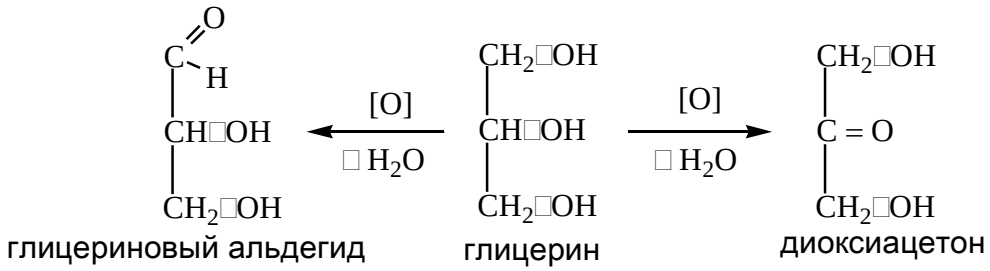
Glycerophosphates are structural elements of phospholipids that make up cell membranes.

When glycerol interacts with higher fatty acids, esters (fats, oils) are formed. The reaction of phosphoric acid with alcohols plays an important biological role, in particular, nucleic acids - esters of phosphoric acid and nucleosides.

In medicine, glycerol phosphoric acid is used in the form of calcium salt (calcium glycerophosphate) - a remedy for loss of strength and exhaustion of the nervous system



When the primary alcohol group of glycerol is oxidized, glyceraldehyde is formed, and when the secondary is oxidized, dihydroxyacetone is formed:



глицериновый альдегид — глицерин — диоксиацетон

Glycerin aldehyde — **glycerin** — **dioxyacetone**

The oxidation of glycerol to dihydroxyacetone and glyceraldehyde is a reversible biochemical transformation that binds lipids to carbohydrates.

PHENOLS

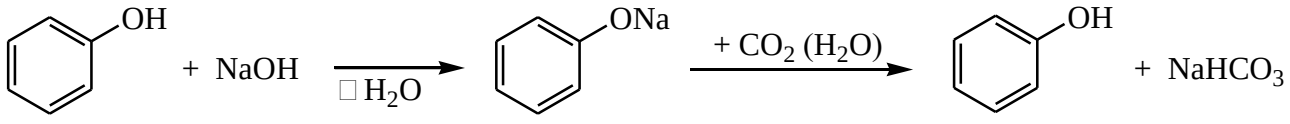
In aqueous solutions, phenols behave like weak acids; they dissociate to form phenolate ions:

At the same time, phenols are 2–4 orders of magnitude less basic than alkanols.

Phenols show high reactivity, showing two series of properties: phenolic hydroxyl and aromatic series.

Phenolic hydroxyl reactions. In phenol, due to the interaction of the lone pair of *p*-electrons of the oxygen atom with the 6-π-electron system of benzene, the electron density on the oxygen atom decreases. The O-H bond becomes more polar due to the shift of the electron density from the oxygen atom towards the benzene ring. Due to the M^+ hydroxyl group, a delocalized p, π-system of 8 electrons is formed (6 π-electrons of the benzene ring and 2 electrons from the oxygen atom).

acid properties. Since the aromatic cycle has an electron-withdrawing effect, the acidic properties of phenols are quite pronounced and, unlike alcohols of the aliphatic series, phenols are easily neutralized by alkalis with the formation of phenolates:



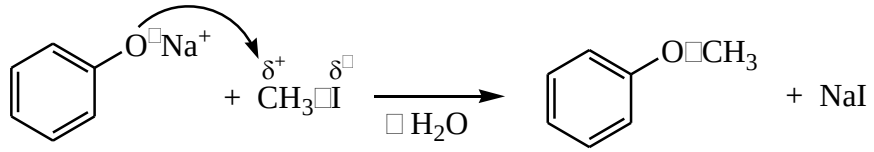
фенол — фенолят натрия

Phenol — **sodium phenolate**

In this case, the passage of carbon dioxide into the phenolate solution leads to the regeneration of phenol: carbonic acid, being stronger, displaces phenol from its salt.

Electrodonating substituents have little effect, while electron withdrawing substituents increase the acidic properties of phenol.

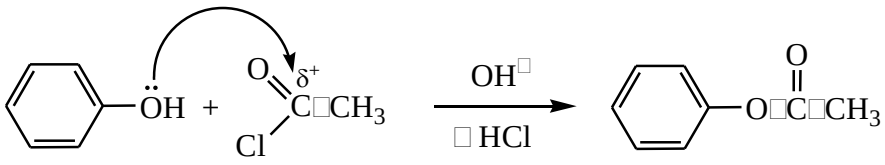
The formation of ethers. To obtain a simple ether, phenols are alkylated by the action of haloalkanes, alkyl sulfates, and the like. This is a common nucleophilic substitution reaction at a saturated carbon atom. Phenols are even weaker nucleophiles than alcohols due to the mesomeric effect. Therefore, it is not the phenols themselves that undergo alkylation, but the phenolates:



фенолят натрия — анизол (метилфениловый эфир)

sodium phenolate — **methylphenyl ether**

Acylation. Phenols do not interact with carboxylic acids due to the presence of p, π-conjugation between the lone electron pair of oxygen and the benzene ring, and as a result, a stronger C-O bond; they are acylated only by stronger acylating agents: anhydrides and acid halides in the presence of alkali by the mechanism of nucleophilic substitution:

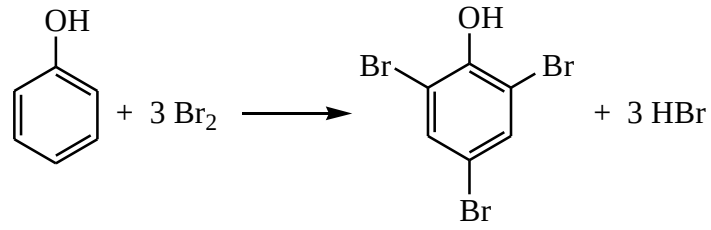


фенол — ацетилхлорид — фенилацетат

phenol — **acetyl chloride** — **phenyl acetate**

Reactions of phenols on the aromatic nucleus. The hydroxyl group in phenol is a type I orientant and a strong activator, that is, it facilitates electrophilic substitution reactions by directing the entry of the next substituent into the *ortho* and *para* positions.

Halogenation to the core. Phenol is easily brominated under normal conditions by the action of bromine water. In this case, the substitution goes to all (three) possible positions: there is a rapid discoloration of bromine water and the precipitation of a white precipitate:

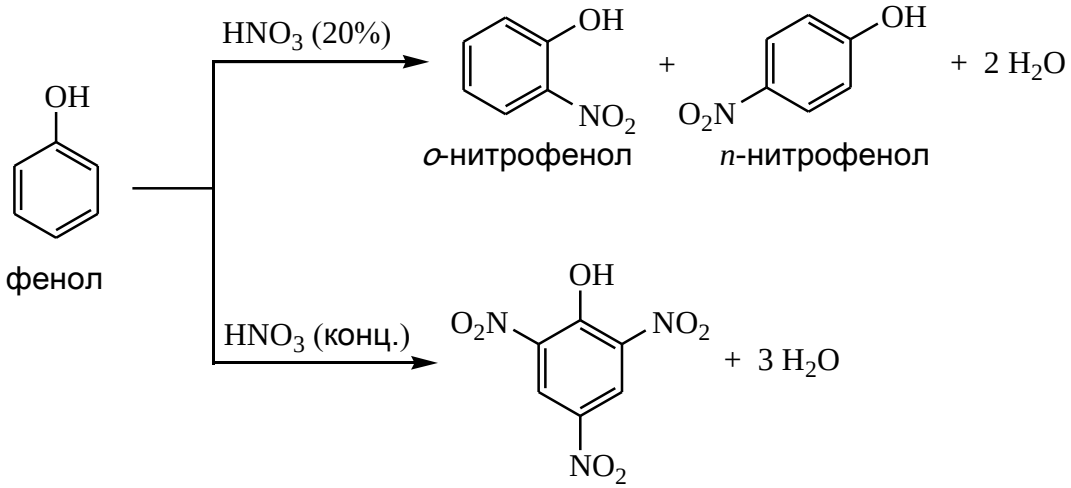


фенол — 2,4,6-трибромфенол

phenol — **2,4,6 tribromphenol**

Another qualitative reaction to phenols is its interaction with $FeCl_3$ (III)

Nitration. Phenol is easily nitrated with nitric acid:

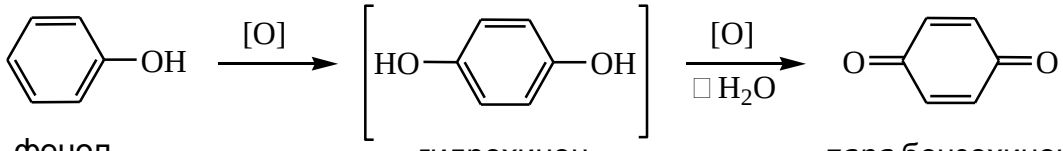


o-нитрофенол — *n*-нитрофенол

2,4,6-тринитрофенол (пикриновая кислота)

phenol — **2,4,6-trinitrophenol**

Oxidation. Phenols are easily oxidized due to the increased electron density in the nucleus. Strong oxidizers, such as persulfate in alkaline solution, bromates, oxidize phenol to *para*-benzoquinone, via the intermediate formation of hydroquinone:



фенол — гидрохинон — *пара*-бензохинон

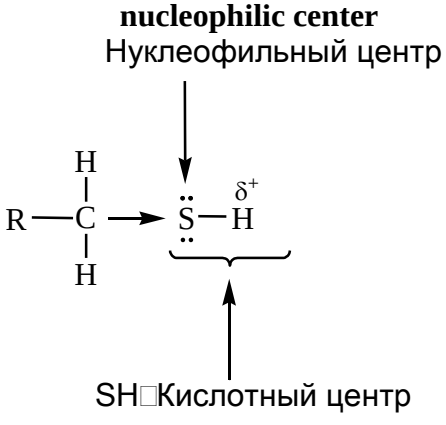
phenol — **hydroquinone** — ***para*-benzoquinone**

This process is reversible. In the body, similar redox processes are realized for ubiquinones that are part of the mitochondrial respiratory chain system.

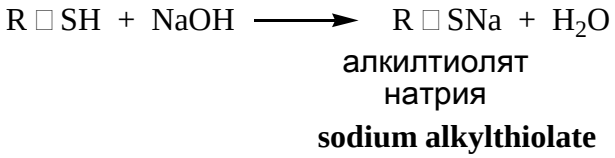
Quinoid groups are part of vitamin K, which promotes blood clotting.

THIOLS

Thiols lack an electrophilic reaction center, because the C-S bond is practically non-polar. For the same reason, thiols are not found (β-CH-acid center. Due to the high polarizability of the sulfur atom, thiols do not have the main reaction center, but there is a nucleophilic center on the sulfur atom. The acid reaction center in thiols is more active than in alcohols due to the greater polarizability sulfur atom.



Acid site reactions. Thiols exhibit stronger acidic properties, their anions are more stable than alcohols. The stability of the anions is ensured by the greater polarizability of the sulfur atom compared to the oxygen atom in alcohols. Therefore, thiols are converted into salts already when treated with an aqueous solution of alkali:

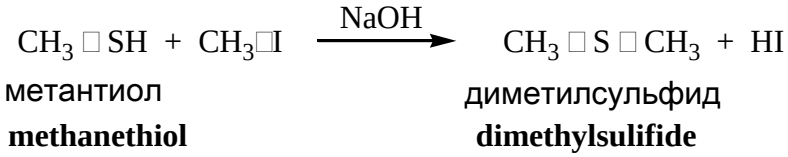


Heavy metals - mercury, lead, arsenic, cadmium, antimony, etc. can act as thiol poisons due to the ability to interact with thiol groups of enzymes or other biologically important SH-containing molecules and thereby inactivate them. Competitive complexation reactions with heavy metal ions underlie the use of heterofunctional thiols as antidotes for poisoning with heavy metal compounds.

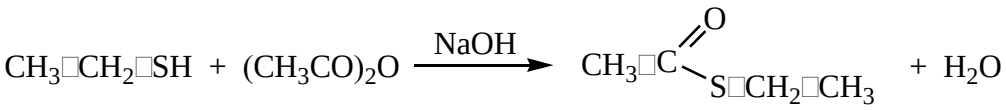
Reactions of the nucleophilic center. The nucleophilic properties of the heteroatom are more pronounced in thiols than in alcohols, because sulfur is a soft nucleophile and more actively reacts with a soft electrophile - a carbon atom in the composition of carboxylic acids, their functional derivatives, as well as aldehydes and ketones.

Thiols participate in S_N reactions as nucleophilic reagents. These reactions include alkylation and acylation.

Alkylation of thiols. The interaction of thiols with primary and secondary haloalkanes, active haloarenes, dialkyl sulfates or arenesulfates in the presence of bases proceeds with the formation of sulfides:

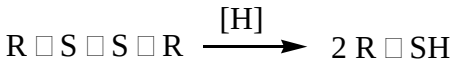


Acylation of thiols. In an alkaline environment, thiols react with acid chlorides and anhydrides of carboxylic acids, forming esters of S-thio acids:



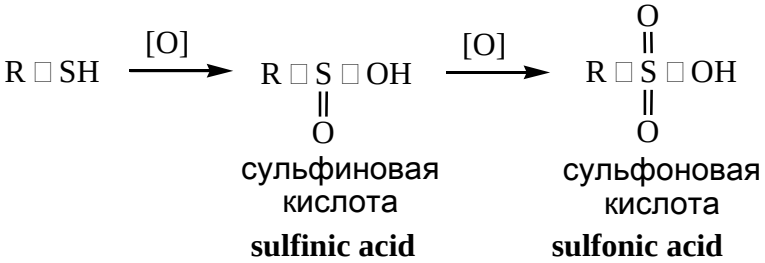
Thiol oxidation. Thiols under the action of even weak oxidizing agents (air oxygen, hydrogen peroxide, iodine, bromine, ...) are converted into disulfides.

In the body, the amino acid cysteine is converted into cystine during this oxidation. The S-S bond in disulfides is relatively weak, but it is about twice as strong as the O-O bond in organic peroxides. Many reducing agents (atomic hydrogen, sodium hydrosulfite, hydrides and complex metal hydrides) easily reduce disulfides to the corresponding thiols:



The thiol-disulfide interconversion plays an important role in biochemical processes, in particular, in the formation of the spatial structure of proteins.

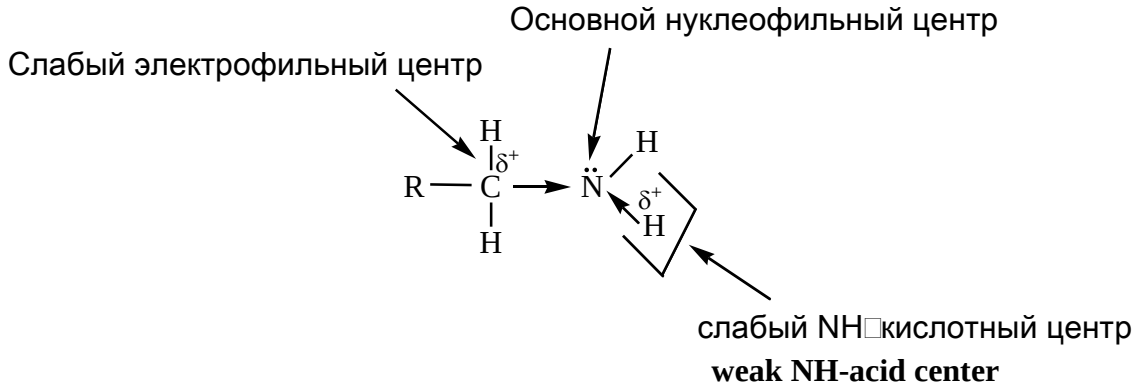
Oxidation of thiols with nitric acid, potassium permanganate, or peroxy acids leads to sulfonic acids; intermediate oxidation products are low-stable sulfinic acids:



AMINES

Amine molecules have strong basic and nucleophilic reaction centers on the nitrogen atom and weak acidic and electrophilic centers.

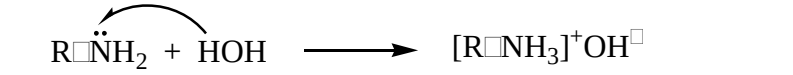
weak electrophilic center **basic nucleophilic center**



Amines practically do not exhibit acidic properties; they can only be detected in reactions with organomagnesium compounds.

Basic properties. Amines, like ammonia, exhibit basic properties, which is due to the presence in their molecules of a nitrogen atom with an unshared pair of electrons. Aliphatic amines are stronger bases than ammonia due to the electron-donating properties of alkyl radicals (positive inductive effect), which increase the electron density on the nitrogen atom in the amine, providing greater electron pair availability, and stabilize the resulting ammonium ion. The more radicals at nitrogen, the stronger their influence is expressed. Therefore, when moving from primary to tertiary amines, the basic properties increase.

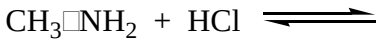
The strength of amines as bases is sufficient to pull a proton off water. Therefore, when dissolved in water, alkylamines form ionized alkyl-substituted ammonium hydroxides:



алкиламин — гидроксид алкиламмония

alkylammonium — **hydroxide alkylamine**

When interacting with acids, amines are converted into ammonium salts:



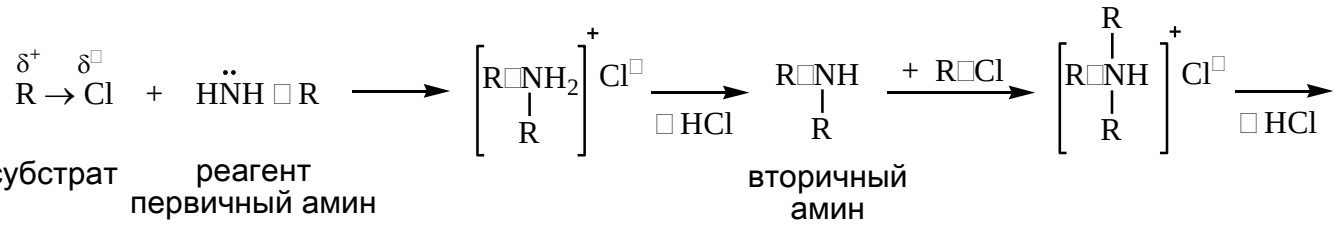
метиламин — хлорид метиламмония

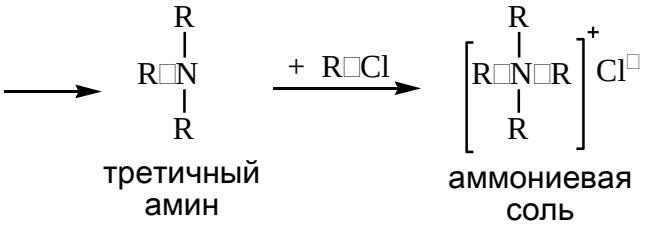
Methylamine — **methylammonium chloride**

nucleophilic properties. The nucleophilic properties of amines, like the basic ones, are due to the presence of a lone pair of electrons on the nitrogen atom. The nucleophilic properties of amines are manifested in the reactions of alkylation and acylation.

Alkylation. Amines, like ammonia, undergo alkylation with haloalkanes. Alkylation of ammonia leads to the formation of a primary amine, secondary amines are formed from primary amines, tertiary ones from secondary ones, and quaternary ammonium salts from tertiary ones.

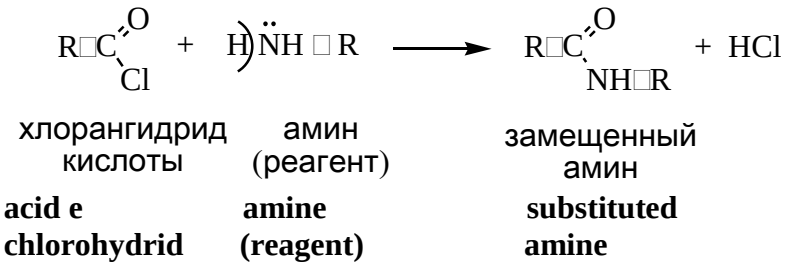
Substrate **primary reagent amine** **secondary amine**



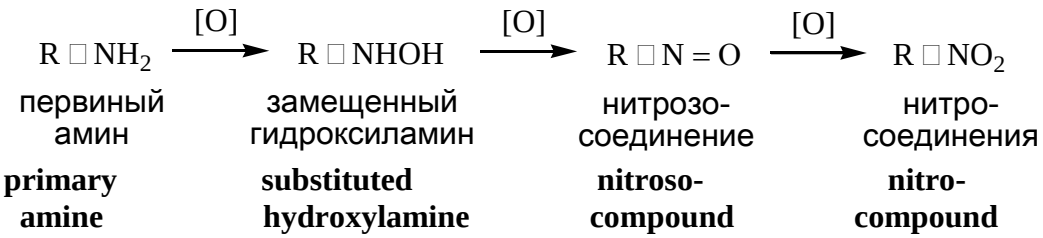


tertiary amine **ammonium salt**

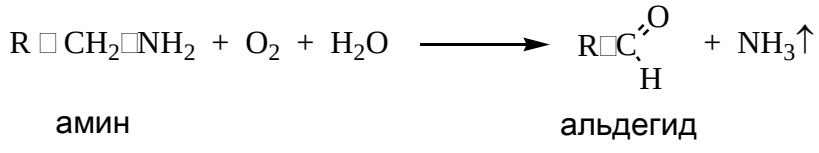
Acylation. Primary and secondary amines are easily acylated by carboxylic acids and their functional derivatives, forming mono- and disubstituted amides, respectively:



Oxidation of amines. Amines oxidize fairly easily. The final products in the oxidation of primary amines are nitro compounds, intermediate products are derivatives of hydroxylamine and nitroso compounds:

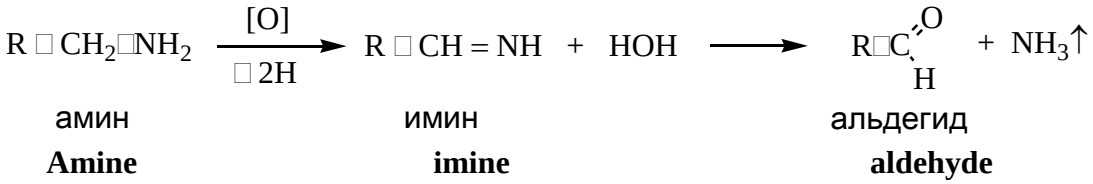


Oxidation of N-containing compounds in the human body is used to remove excess biogenic amines. The overall process is oxidative deamination:



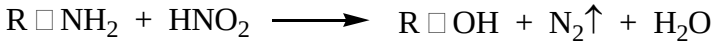
amine **aldehyde**

In this process, not the nitrogen atom is oxidized, but the neighboring carbon atom through the amine dehydrogenation step.



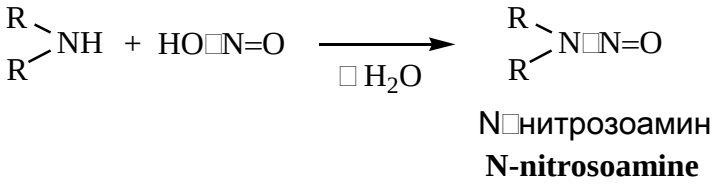
Reactions with nitrous acid. Amines of different types react differently with nitrous acid.

primary amines. These amines undergo deamination under the action of nitrous acid in aqueous solutions. Initially, they form diazonium salts, these salts are unstable and easily decompose in solutions to form a complex mixture of products, including alcohols:



The reaction is accompanied by the evolution of gas bubbles (N_2) and can be used to identify primary aliphatic amines.

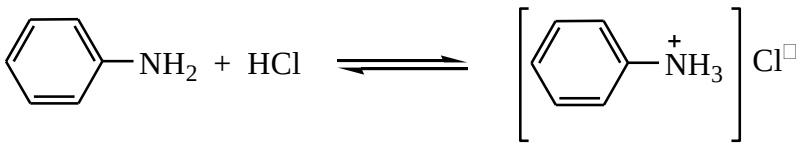
secondary amines. Aliphatic and aromatic secondary amines, when reacted with nitrous acid, form N-nitrosoamines, which are water-insoluble oily liquids or yellow solids.



Tertiary amines. At low or room temperature and in dilute solutions with nitrous acid, tertiary amines do not react.

Properties of aromatic amines

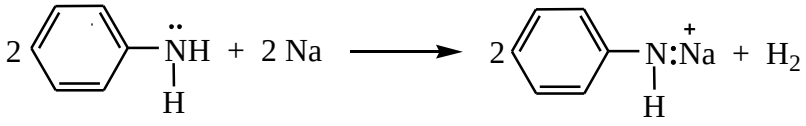
Acid-alkaline properties. The basicity of aromatic amines is significantly lower than that of aliphatic amines. This is explained by the fact that the lone pair of electrons of the nitrogen atom enters into p, π-conjugation with the electrons of the benzene ring. An aqueous solution of aniline does not change the color of the indicators. Aniline practically does not interact with weak acids and water and forms salts only with strong acids:



анилин
aniline

хлорид фениламмония
ammonium phenyl chloride

Under the action of stronger bases, aromatic amines are displaced from their salts. The acidic properties of aromatic amines are more pronounced than those of aliphatic ones. This is due to a decrease in the electron density on the nitrogen atom due to p, π-conjugation, which leads to an increase in the polarization of the N-H bond. However, the acidic properties of aromatic amines are very weak, and hydrogen can only be replaced by the action of alkali metals and amides:

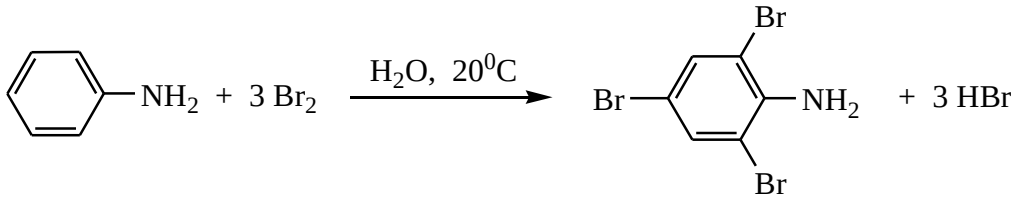


анилин
aniline

фениламид натрия
sodium phenyl amide

Ring reactions of aromatic amines. In aromatic amines, the amino group, due to the positive mesomeric effect, acts as a strong activator of the benzene ring in electrophilic substitution reactions. The -NH_2, -NHR, -NR_2 groups are strong substituents of the first kind and orient the electrophilic substituents both in the *ortho* and *para* positions of the benzene ring.

Halogenation. When aniline is treated with bromine water, a whitish-yellow precipitate of 2,4,6-tribromaniline rapidly precipitates. The activating effect of the amino group is so great that the reaction proceeds immediately in three positions:



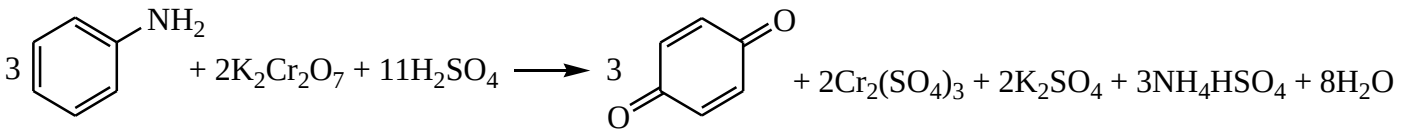
анилин
aniline

2,4,6-трибромanилин
2,4,6-tribromaniline

The reaction proceeds according to the S_{E2} mechanism. Bromine cation or protonated hypobromous acid acts as an electrophilic particle.

The bromination reaction is used to detect aniline, and the resulting tribromaniline is used in various syntheses.

Oxidation. Aniline oxidizes relatively easily to a variety of products. When oxidized with a chromium mixture and some other oxidizing agents, the so-called black aniline is formed, which is used for dyeing black fabrics, wood, and leather.



EXERCISES

1. Get isopropyl bromide from the following compounds (possible in several stages):

1) propane;
2) propene;
3) propanol;
4) isopropanol.

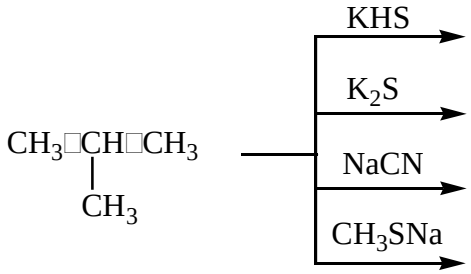
Specify reaction mechanisms.

2. Suggest reagents and reaction conditions for the following transformations:

1) 1-chloropropane → propene → 2-chloropropane;
2) butene-2 → 2,3-dibromobutane → butene-2.

Write the reactions in the form of diagrams, indicate their mechanisms.

3. Write down the following reactions in the form of diagrams. Specify the reagent and the direction of its attack. Name the reaction mechanisms. Write the name of the original compound and products.



4. What alcohols are formed as a result of alkaline hydrolysis:

1) 1-iodine-4-methylpentane;
2) 3-bromobutene-1;
3) 2,3-dibromobutane;
4) 2-chloropropene-1.

Name the resulting compounds.

5. Which of the following compounds reacts with propanol-2. Write reaction equations, indicate their mechanism (type), name the products.

1) $K_2Cr_2O_7$ (H^+);
2) CH_3COOH (H^+, t°);
3) KOH;
4) H_2SO_4 (t~180 °C);
5) H_2SO_4 (in the cold);
6) HBr;
7) Hg;

8) PCl5.

5. Determine for which of the alcohols butanol-1, butanol-2 and 2-methylbutanol-2 there is a reaction with hydrogen halides according to the S_{N1} or S_{N2} mechanism.

6. Give the reaction schemes for the dehydration of ethanol and 2-methylbutanol-2, indicate the type, mechanism and conditions necessary for these processes. Name the reaction products.

7. Write the equations of reactions that can occur between methyl alcohol and the following substances:

1) calcium;

2) hydrogen iodine;

3) copper oxide (II) when heated.

Specify the mechanism and conditions necessary for these processes.

8. Write the reaction equations between glycerol and the following substances:

1) sodium; 2) hydrogen bromide;

3) nitric acid; 4) copper (II) hydroxide.

Specify the mechanism and conditions necessary for these processes.

9. Write the reaction equations between the following compounds:

1) ethyl alcohol and propyl alcohol;

2) methyl alcohol and isopropyl alcohol;

3) butyl alcohol and isobutyl alcohol.

Name the ethers.

10. Name the following compounds:

Write reaction schemes for them with the following reagents:

1) $SOCl_2$;

2) NaOH (H_2O);

3) CH3COOH (H^+, t).

Indicate the mechanism (type) of reactions and name the products.

11. Write the equation for the reaction of diethylamine with acetic acid (aqueous solution), and then - the pyrolysis scheme of the resulting product. What class of compounds does the final product belong to?

12. The drug tetamon, used for vasospasm, is obtained by reacting triethylamine with ethyl iodide. Write down the equation for this reaction.

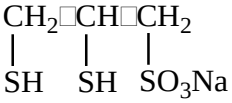
13. Write the reactions of isopropylamine with:

1) hydrobromic acid;

2) propanoic acid anhydride;
3) acetic acid (aqueous solution).

Name the products and indicate what properties the amine exhibits in these transformations.

14. Write the reaction equations for aniline with:
1) sodium nitrite in the presence of HCl at 0 ºC, then at room temperature;
2) bromine water;
3) ethanoic acid chloride.
Give the names of the products.
15. Write the reaction equations with which you can get from butylamine:
1) the corresponding propanoic acid amide;
2) secondary amine;
3) the corresponding alcohol.
Indicate the mechanism (type) of reactions. Name the products.
16. Unithiol (sodium 2,3-disulfanylpropanesulfonate)



used as an antidote for poisoning with arsenic and mercury salts. Explain the basis of its protective effect on the example of the interaction of unithiol with mercury(II) chloride.

17. Write the reactions of propane-2-thiol with:
1) KOH (H_2O);
2) $Pb(NO_3)_2$;
3) O_2 (air);
4) propanoic acid chloride.
Indicate what properties thiol exhibits in these interactions.

18. Complete the reaction equations, indicate the reaction mechanism:
1) $CH_3\text{-}Br + NH_3 \rightarrow$
2) $CH_3\text{-}CH_2\text{-}NH_2 + HNO_2 \xrightarrow{H^+}$
3) butanol-2 $\xrightarrow{t,\ H_2SO_{4(конц.)}}$
4) phenol + HNO_3 (conc.) $\xrightarrow{H_2SO_{4(конц.)}}$
5) $CH_3\text{-}CH_2\text{-}SH + NaOH \longrightarrow$
6) chloroethane + $NaOH \xrightarrow{t}$
7) 2-bromopropane + phenol $\xrightarrow{NaOH}$
8) trimethylamine + $HCl \longrightarrow$
9) iodomethane + $H_2 \longrightarrow$
10) aniline + $Br_2 \longrightarrow$
11) methylphenyl ether + $HBr \xrightarrow{t}$

19. Write the reaction equations that can be used to carry out the following transformations:

1) methane → chloromethane → methanol → methyl propyl ether → propanol-1 → chloropropane → n-hexane → benzene.

2) ethylene → ethanol → ethylene → ethylene glycol → copper glycolate.

3) $CH_2{=}CH_2 \rightarrow CH_3CH_2OH \rightarrow CH_3CH_2Br \rightarrow CH_3CH_2CN \rightarrow CH_3CH_2COOH$.

4) $C_2H_6 \xrightarrow{Cl_2, h\upsilon} X_1 \xrightarrow{спиртр-pKOH} X_2 \xrightarrow{O_2, Ag} X_3 \xrightarrow{H_2O, H^+} X_4 \xrightarrow{Cu(OH)_2} X_5$.

5) $CH_4 \xrightarrow{Cl_2, h\upsilon \ \ 1моль} X_1 \xrightarrow{Na} X_2 \xrightarrow{Br_2, h\upsilon} X_3 \xrightarrow{спиртр-pKOH} X_4 \xrightarrow{Br_2} X_5 \xrightarrow{спиртр-pKOH} X_6 \xrightarrow{C, t} X_7 \xrightarrow{CH_3Cl\,(1моль)\,AlCl_3} X_8 \xrightarrow{Br_2, AlBr_3} X_9 \xrightarrow{Br_2, h\upsilon} X_{10} \xrightarrow{NaOH_{(водный)}} X_{11}$.

6) 1,2-dichloroethane $\xrightarrow{NH_3\ (избыток)} X_1 \xrightarrow{CH_3COOH} X_2 \xrightarrow{t^0} X_3$.

7) isopropylamine $\xrightarrow{HNO_2} X_1 \xrightarrow{PCl_5} X_2 \xrightarrow{KCN} X_3 \xrightarrow{H_2/Pt} X_4$.

8) $X_1 \xrightarrow{O_2, (Ag, t, p)}$ epoxyethane $\xrightarrow{HCl} X_2 \xrightarrow{Na_2S} X_3 \xrightarrow{2\,SOCl_2} X_4$.

20. Determine the structure of a substance of the composition $C_5H_{12}O$, which reacts with metallic sodium with the release of gas, when oxidized it gives a ketone of the composition $C_5H_{10}O$, and when dehydrated it forms 2-methylbutene-2. Write the reaction equations and name all substances.

21. Establish the structure of a substance of the composition $C_4H_{11}N$, if it is known that it reacts with hydrochloric acid and acetic acid chloride, and when it interacts with nitrous acid, gas bubbles are released. The test substance has optical activity.

22. Establish the structure of a compound of composition $C_4H_{10}S$, if it is known that it is oxidized by nitric acid to 2-methylpropane-2-sulfonic acid. What class of sulfur-containing compounds does it belong to? Write a reaction scheme.

Laboratory work №2
PROPERTIES OF ALCOHOLS, PHENOLS, AMINES

Goal of the work:

To form knowledge of the reaction centers of alcohols, phenols and amines; the ability to conduct qualitative and characteristic reactions for alcohols, phenols.

Reagents:

1.	Aniline	C_6H_5-NH_2	–
2.	Potassium bichromate	$K_2Cr_2O_7$	0,5H solution
3.	sodium hydroxide	NaOH	2H solution
4.	Hydroquinone	C_6H_4-$(OH)_2$	1% solution
5.	Glycerin	$C_3H_8O_3$	–
6.	metallic sodium	Na	–
7.	Pyrogallol	C_6H_3-$(OH)_3$	1% solution
8.	Pyrocatechin	C_6H_4-$(OH)_2$	1% solution

9.	Resorcinol	C_6H_4-$(OH)_2$	1% solution
10.	sulfuric acid	H_2SO_4	2H solution
11.	copper sulfate	$CuSO_4$	0,2H solution
12.	ethyl alcohol	CH_3–CH_2–OH	–
13.	Phenol	C_6H_5-OH	1% solution
14.	Phenolphthalein	$C_{20}H_{14}O_4$	1% спирт. раствор
15.	iron chloride (III)	$FeCl_3$	2% solution
16.	distilled water	H_2O	–

Equipment:

- scalpel
- tweezers
- spirit lamp - glass rod
- rubber stopper for a test tube
- stand with test tubes

Experience 1. Oxidation of ethyl alcohol

Pour 10 drops of ethyl alcohol into a dry test tube and place a small piece (about the size of a grain of rice) of metallic sodium.

Then add water to the resulting sodium alcoholate, and then add a few drops of phenolphthalein.

Process chemistry:

CH_3–CH_2–OH + Na $\rightarrow$

CH_3–CH_2–ONa + H_2O $\rightarrow$

Answer questions about experience:

1. What properties did ethanol show in the reaction with metallic sodium?
2. Why can sodium ethoxide hydrolyze with water?
3. Explain the reason for the presence of an alkaline medium in the test tube, detected using phenolphthalein.

Experience 2. Oxidation of ethyl alcohol

Place 10 drops of potassium bichromate solution, 8 drops of sulfuric acid and 15 drops of ethyl alcohol into a test tube. Heat the resulting orange solution over the flame of an alcohol lamp until the color changes to bluish-green, the color of chromium (III) salt.

Process chemistry:

CH_3–CH_2–OH + $K_2Cr_2O_7$ + H_2SO_4 $\xrightarrow{t}$

Answer questions about experience:

1. What is the product of oxidation of primary and secondary alcohols?
2. Will tertiary alcohol be oxidized under the conditions of this experiment?
3. Determine the odor released after heating.

Experience 3. Features of the properties of polyhydric alcohols

Take 3 test tubes in each, pour 20 drops of copper (II) sulfate and 5 drops of sodium hydroxide. In the second test tube, add 5 drops of glycerin to the precipitate of copper (II) hydroxide. Add 5 drops of ethyl alcohol to the third test tube. Shake all test tubes and heat to a boil.

Process chemistry:

$CuSO_4 + NaOH \rightarrow ..... \xrightarrow{t}$

$$\begin{array}{l} CH_2{-}OH \\ | \\ CH{-}OH \\ | \\ CH_2{-}OH \end{array} + Cu(OH)_2 \xrightarrow{t}$$

$CH_3{-}CH_2{-}OH + Cu(OH)_2 \xrightarrow{t}$

Answer questions about experience:

1. Compare the acidic properties of glycerin and ethanol and justify your answer.

2. What complex compound is formed during the interaction of glycerol with copper (II) hydroxide?

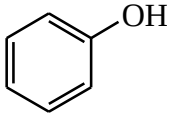
3. What structural fragment in a glycerol molecule dissolves copper hydroxide?

Experience 4. Qualitative reaction to phenols

Take 5 test tubes. Pour 3 drops of the solution into each: phenol in the first, pyrocatechol in the second, resorcinol in the third, hydroquinone in the fourth, pyrogallol in the fifth.

Then add 1 drop of iron (III) chloride solution to each tube. In all tubes, color changes are observed. Record the results of the experiment in the table.

Process chemistry:



$+ FeCl_3 \rightarrow$

Answer questions about experience:

1. Why is this reaction of high quality for the detection of phenolic compounds?

2. What reaction center is involved in this reaction?

№	Name of phenol	Structure of	Staining with $FeCl_3$
1.			
2.			
3.			
4.			
5.			

QUESTIONS FOR PROTECTION OF LABORATORY WORK 2.

1. Acidity and basicity of organic compounds.
2. Bronsted-Lowry theories.
3. Lewis theory.
4. Factors that determine the strength of the acidic properties of organic compounds.
5. Factors affecting the strength of basic properties in organic compounds.
6. Comparative characteristics of the acid properties of alcohols, amines, thiols, phenols, carboxylic acids.
7. The role of the lone pair of electrons of heteroatoms in the manifestation of the basic properties of amines, ethers, thioethers, alcohols.
8. Acid-base properties of nitrogen-containing heterocycles (pyrrole, pyridine, imidazole, thiazole, thiophene, pyrimidine).
9. Describe hard, soft acids and hard and soft Lewis bases.
10. Explain the general mechanism of reactions of nucleophilic substitution of SN at the sp3-hybridized carbon atom; show the features of S_{N1} and S_{N2} reactions.
11. S_{N1} and S_{N2} mechanisms of nucleophilic substitution in the series of haloalkanes.
12. Show the formation of an intermolecular hydrogen bond using the example of ethyl alcohol. How does this phenomenon affect the boiling point of alcohol?
13. Chemical properties of monohydric alcohols: hydrogen substitution reactions of hydroxyl, substitution reactions of the hydroxyl group, hydrogen substitution reactions of the radical. The mechanism of these reactions.
14. Dehydration reactions of alcohols (intramolecular and intermolecular), their mechanism. Zaitsev's rule.
15. What compounds are obtained by the oxidation of primary and secondary alcohols?
16. Chemical properties of polyhydric alcohols: hydrogen hydroxyl substitution reactions, esterification reactions, chelating reactions. The mechanism of these reactions.
17. Chemical properties of phenols: reactions involving a hydroxyl group, reactions involving a benzene ring. The mechanism of these reactions.
18. S_{N1} and S_{N2} mechanisms of nucleophilic substitution in amines.
19. Chemical properties of aniline: reactions involving the amino group, reactions involving the benzene ring. The mechanism of these reactions.

ACTIVITY №9

Topic:

NUCLEOPHILIC REACTIONS OF CARBONYL COMPOUNDS

Purpose of the lesson:

To form knowledge of the reaction centers of aldehydes and ketones, depending on the electronic structure of the oxo group and the electronic effects of substituents, a step-by-step representation of nucleophilic addition reactions; the ability to conduct qualitative and characteristic reactions to aldehydes and ketones.

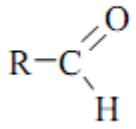
Issues for discussion

1. Reaction centers of aldehydes, ketones.
2. Reactions of nucleophilic addition. General reaction mechanism.
3. Accession of water, alcohols, amines. Formation of cyclic hemiacetals. Aldol addition reactions.
4. Reversibility of nucleophilic addition reactions.
5. Biological significance of acetalization reactions, aldol cleavage, interaction with amines.
6. Toxicity of aldehydes, the use of aldehydes as disinfectants and sterilization agents.
7. Reactions of oxidation and reduction of carbonyl compounds.
8. Qualitative reactions to the aldehyde group.
9. Acetone detection reactions.
10. Reaction centers in molecules of carboxylic acids.
11. Acid properties of mono-, dibasic, saturated, unsaturated, aromatic carboxylic acids.
12. General mechanism of the nucleophilic substitution reaction at the sp2-hybridized carbon atom of carboxylic acids and their functional derivatives.
13. Reactions of formation and hydrolysis of functional derivatives of carboxylic acids: anhydrides, halides, esters, amides.

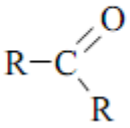
Theoretical part

Compounds containing a carbonyl group (>C=O), depending on the nature of the substituents associated with it, are divided into the following classes: aldehydes, ketones, carboxylic acids and their functional derivatives:

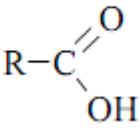
Aldehydes
Альдегиды



ketones
Кетоны



carboxylic acids
Карбоновые кислоты



For compounds containing a carbonyl group, the following types of reactions are characteristic:

– nucleophilic addition (A_N) for aldehydes and ketones;

– nucleophilic substitution (S_N) for carboxylic acids and their derivatives.

REACTIVITY OF ALDEHYDES AND KETONES

The carbon atom in the carbonyl group is in the sp2-hybrid state and forms three σ-bonds lying in the same plane, and one π-bond with oxygen due to the unhybridized p-orbital.

The oxygen atom is in the sp^2-hybrid state, its two pairs of electrons occupy the sp^2-hybrid orbitals. The high electronegativity of the oxygen atom contributes to the strong polarization of the bond between carbon and oxygen and the appearance of an electrophilic center on the carbon atom. The π-bond is less strong, it is easily cleaved and provides addition reactions. Thus, nucleophilic addition reactions proceed at the electrophilic center.

The ease of nucleophilic attack depends on the magnitude of the positive charge on the carbon atom, its spatial availability, and the acid-base properties of the medium.

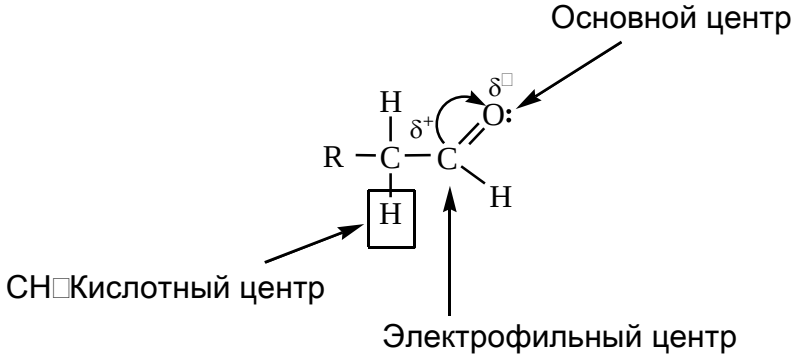
For ketones having two radicals with +I effect, the electrophilicity of the carbon atom is reduced, and the A_N reactions are slower than for aldehydes.

The spatial availability of carbonyl carbon decreases when hydrogen is replaced by more bulky organic radicals.

For these reasons, aldehydes are more reactive than ketones.

Reaction centers:

base center



CH-acid center **electrophilic center**

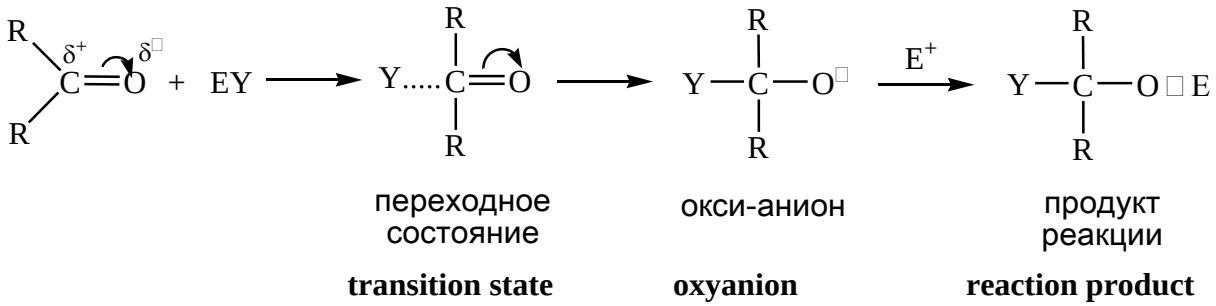
The presence of an electrophilic center determines the possibility of a nucleophilic attack; the main center is the site of acid attack. In addition, aldehydes and ketones contain a weak CH-acid center, the hydrogen atom of which has proton mobility and can be attacked by a base.

Nucleophilic addition reactions

The general scheme of the process includes 2 stages:

1 stage. Attack of the nucleophile on the carbonyl carbon from above or below the plane and the formation of a planar intermediate, which then passes into the oxy anion. This stage is limiting.

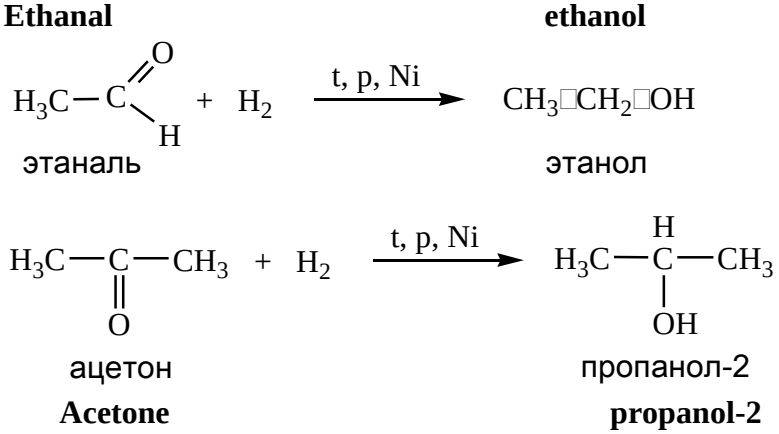
2nd stage. Stabilization of the oxy-anion due to the addition of an electrophile to oxygen, a fast stage.



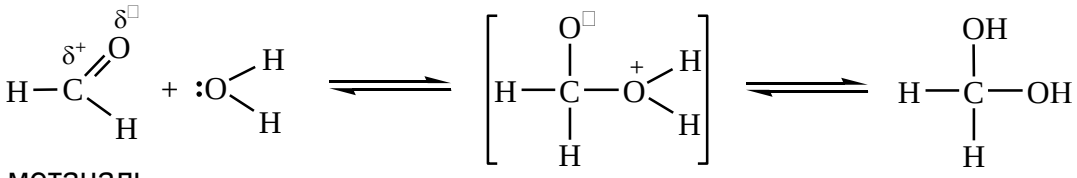
The process resembles the bimolecular nucleophilic substitution of S_{N2}, with the difference that the oxygen atom accepting the electron pair is not a leaving group here, but remains in the substrate molecule. According to the above mechanism, a number of important reactions of aldehydes and ketones are carried out.

Aldehydes and ketones add hydrogen (reduction), water, alcohols, thiols, hydrocyanic acid, sodium hydrosulfite, compounds of the NH2-X type. All addition reactions proceed rapidly under mild conditions; however, the resulting products are, as a rule, thermodynamically unstable. Therefore, the reactions proceed reversibly, and the content of addition products in the equilibrium mixture can be low.

Hydrogen addition reactions (hydrogenation). As a result of this reaction, primary alcohols are formed from aldehydes, and secondary alcohols from ketones.



Water addition reactions (hydration). Carbonyl compounds can add water, which acts as a nucleophilic reagent:

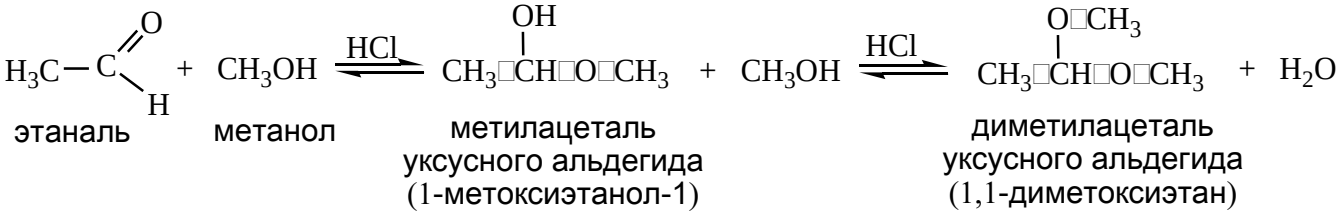


метаналь метандиол

methanal **methanediol**

Hydration products, which are geminal diols, cannot be isolated in the free state. They are dehydrotiated to give the parent compounds. However, trichloroacetic aldehyde hydrate is quite stable. Chloral hydrate is used in medicine as a sedative, hypnotic.

Reactions addition of alcohols (acetalization):

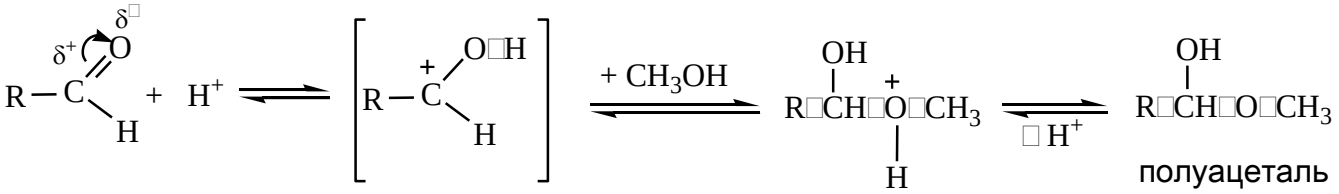


этаналь метанол метилацеталь уксусного альдегида (1-метоксиэтанол-1) диметилацеталь уксусного альдегида (1,1-диметоксиэтан)

ethanol **methanol** **methylacetal** **dimethylacetal**

When an aldehyde reacts with an alcohol, a hemiacetal is initially obtained, which is formed as a result of the addition of a nucleophilic reagent (alcohol) to the electrophilic center of the carbonyl group. The reaction is catalyzed by acids (usually hydrochloric) that activate the substrate by protonating the carbonyl group.

The reaction mechanism for the formation of hemiacetals:

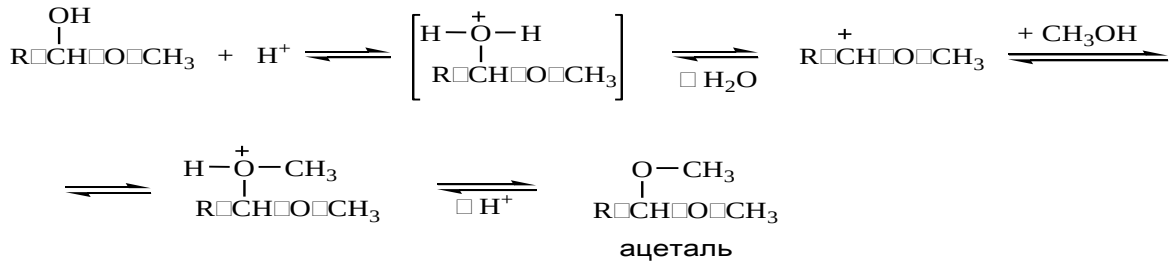


полуацеталь

Hemiacetal

Hemiacetals are unstable compounds that are almost impossible to isolate. When hemiacetals are treated with excess alcohol in an acidic medium, acetals can be obtained. Acetals are thermally stable compounds and are easy to isolate from the reaction mixture.

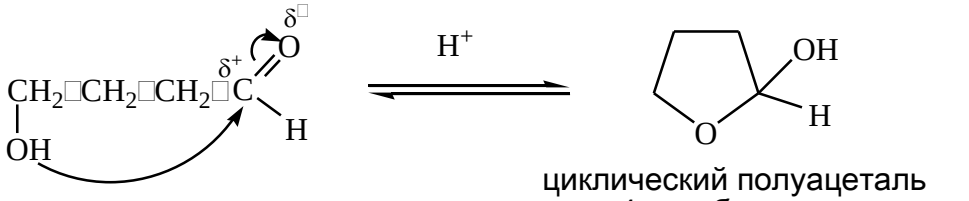
The reaction mechanism for the formation of acetals:



ацеталь

acetal

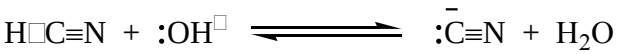
If the aldehyde and alcohol groups are in the same molecule, then due to the intramolecular reaction, a cyclic hemiacetal can be formed.

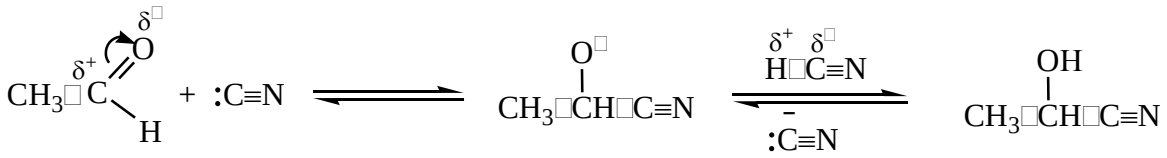


циклический полуацеталь
4-оксибутаналя

cyclic hemiacetal 4-oxybutanal

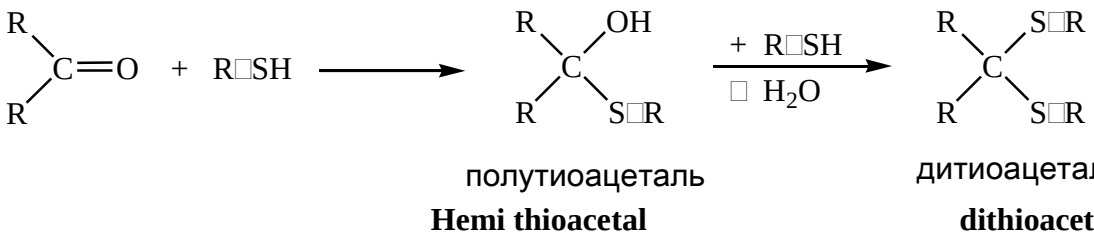
Reactions addition of hydrocyanic acid. Hydrocyanic acid, in the presence of traces of alkali, adds to aldehydes and ketones to form α-hydroxynitriles (cyanohydrins). Under the action of alkali, hydrogen cyanide is converted into a cyanide ion, which has a high nucleophilicity:





This reaction underlies specific methods for obtaining α-hydroxy- and α-amino acids, and is used to lengthen the carbon chain.

Thiol addition reactions. Thiols are more active than alcohols in reactions with aldehydes and ketones. They form the corresponding thioanalogues - hemithioacetals and dithioacetals:



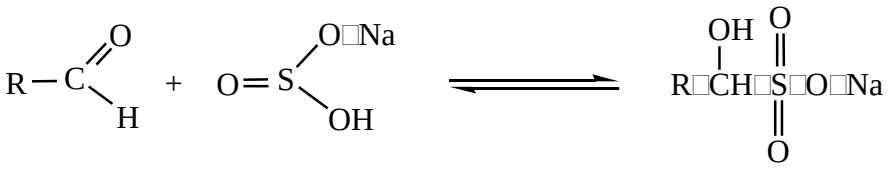
полутиоацеталь

Hemi thioacetal

дитиоацеталь

dithioacetal

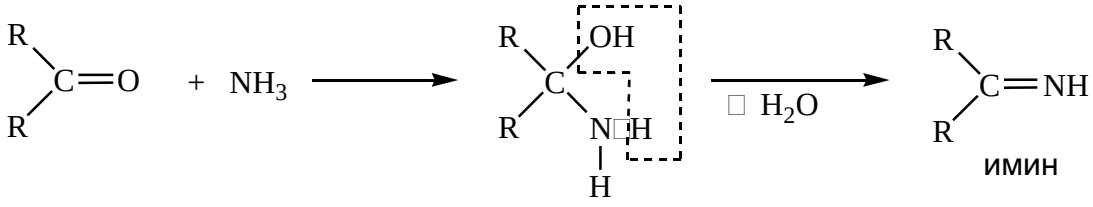
Addition reactions of sodium hydrosulfite. Aldehydes and ketones, when interacting with sodium hydrosulfite, form hydrosulfite derivatives:

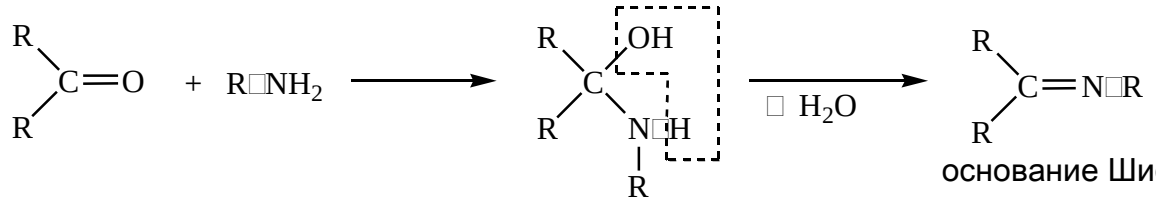


Most aldehydes and ketones enter into this reaction, with the exception of ketones with bulky substituents (due to steric hindrance). The reaction with sodium hydrosulfite is used for the qualitative determination of aldehydes and ketones, as well as for their isolation and purification.

Interaction with compounds of the general formula NH_2-X. Amines and other nitrogen-containing compounds of the general form NH_2-X react with aldehydes and ketones in two stages. First, nucleophilic addition products are formed, which then, due to instability, split off water.

imin





Schiff foundation

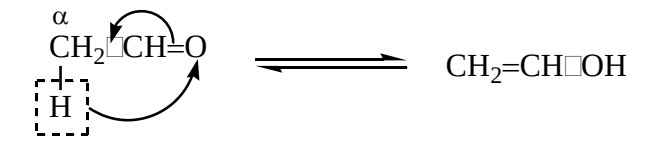
According to this scheme, not only ammonia, primary amines, but also hydrazine, substituted hydrazines, and hydroxylamine react with carbonyl compounds.

Reactions involving a CH-acid center

The presence of a weak CH-acid center in the aldehyde or ketone molecule leads to the fact that the α-hydrogen atoms of these carbonyl compounds have some proton mobility.

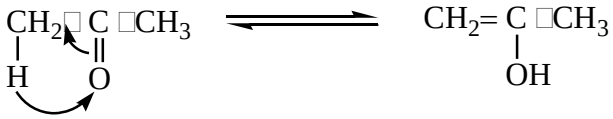
Enolization. The result of the proton mobility of the hydrogen atom in the α-position is the ability of carbonyl compounds to form enol forms due to the migration of a proton from the α-position to the oxygen atom of the carbonyl group. This phenomenon is called dynamic isomerism or tautomerism. In this case, keto-enol tautomerism is observed.

The process of transition from the ketone form to the enol form (enolization) is catalyzed by both bases and acids.



альдо-таутомер — енол-таутомер

aldo-tautomer — **enol-tautomer**



кето-таутомер — енол-таутомер

keto-tautomer — **enol-tautomer**

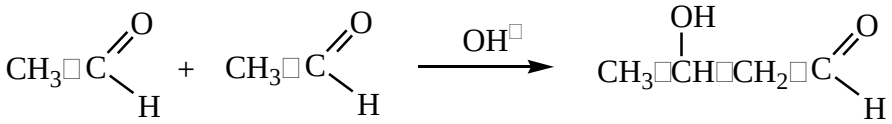
The phenomenon of keto-enol tautomerism explains many chemical properties of carbohydrates, hydroxy acids and oxo acids.

Enolization and the formation of enolate anions are the first steps in the reactions of carbonyl compounds occurring at the α-carbon atom. The most important of these are halogenation and aldol-crotonic condensation.

Aldol and croton condensation. Enol forms of aldehydes and ketones or enolate ions take part in the reaction of aldol condensation. Under the action of bases, the protonated hydrogen atom of the CH-acid center of aldehydes is split off with the formation of the corresponding carboanions, which act as nucleophiles. As a result of the interaction of the formed nucleophiles with the electrophilic center of aldehydes or ketones, condensation reactions occur.

The condensation reaction leads to an elongation of the carbon skeleton due to the emergence of a new carbon-carbon bond and is accompanied by the release of water or another low molecular weight substance.

So, aldehydes enter into an aldol condensation reaction in the presence of bases or acids.

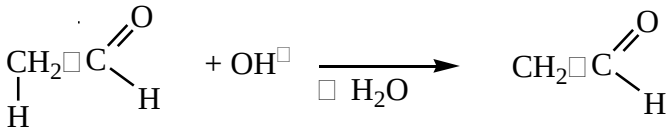


3-гидроксибутаналь

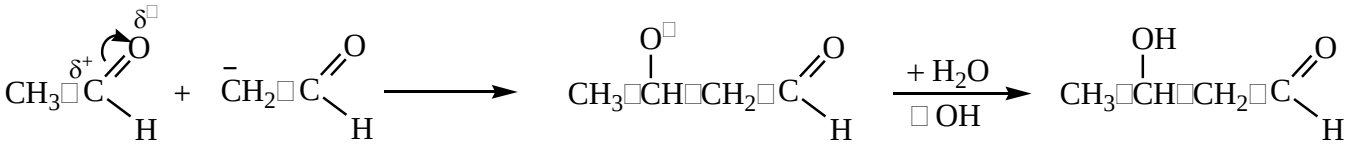
3-hydroxybutanal

In the presence of bases at the 1st stage of the reaction, an acid-base interaction occurs, therefore, 2 molecules of various aldehydes, ketones can enter into the reaction:

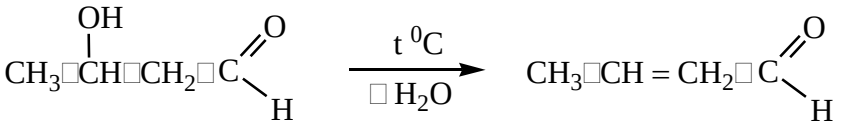
1st stage:



2nd stage:



The reaction of aldol condensation is often accompanied by further elimination of a water molecule with the formation of α, β-unsaturated carbonyl compounds (stable conjugated systems). This condensation is called croton condensation.

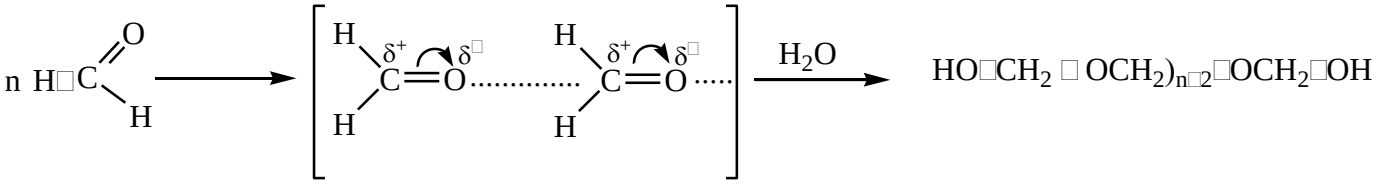


кротоновый альдегид
бутен-2-аль

croton aldehyde butene-2-al

Polymerization reactions.

Polymerization is typical mainly for aldehydes. The formation of polymers can be viewed as the result of a nucleophilic attack by an oxygen atom of one aldehyde molecule on the carbonyl carbon atom of another aldehyde molecule. So, when storing a 40% solution of formaldehyde, known as formalin, formaldehyde polymer - paraforms is formed in the form of a white precipitate.

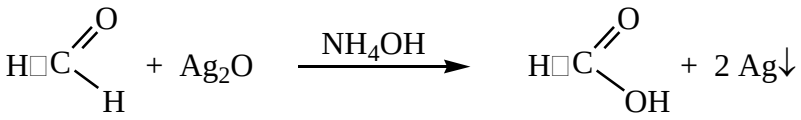


When heated with mineral acids, aldehyde polymers decompose into the starting products.

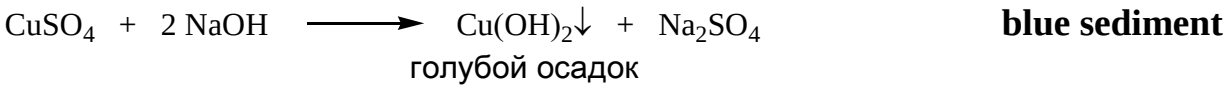
Oxidation reactions of aldehydes and ketones

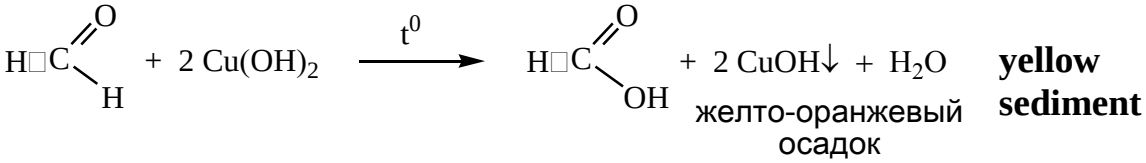
Aldehydes are very easily oxidized by such weak oxidizing agents as silver oxide, copper (II) hydroxide, and acids are formed. These reactions are qualitative for the discovery of aldehydes.

Silver mirror reaction:



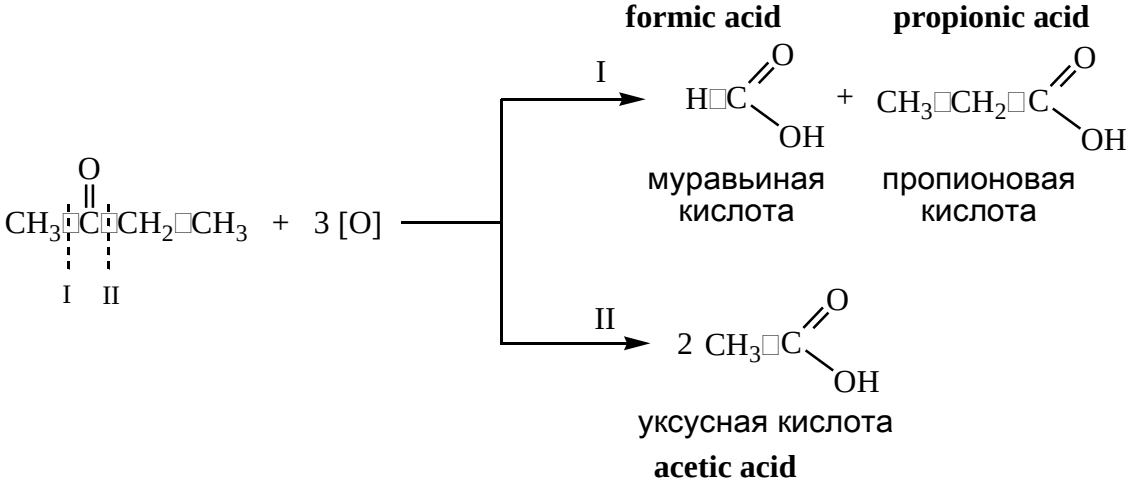
Copper mirror reaction (Trommer reaction):



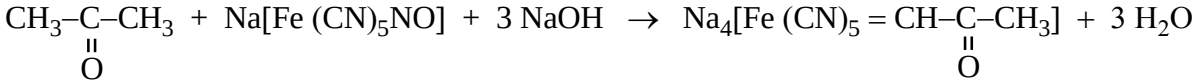


This reaction is used to discover glucose in the urine of diabetics, since it is an aldehyde of a polyhydric alcohol. In this regard, you should know that the Trommer reaction has a drawback: with an excess of copper (II) hydroxide and heating, it decomposes into black copper (II) oxide, which obscures the brick red or yellow-orange color, which makes it difficult to open glucose.

Ketones are much more difficult to oxidize and require harsher conditions for this. In this case, the chain breaks according to Popov's rule, resulting in the formation of two acids with fewer carbon atoms than the original ketone.



A qualitative reaction to acetone is the Legal test, that is, in the presence of ketones, sodium nitroprusside (sodium nitrosopentacyanoferrate) in an alkaline medium forms a complex anion, colored red-violet:



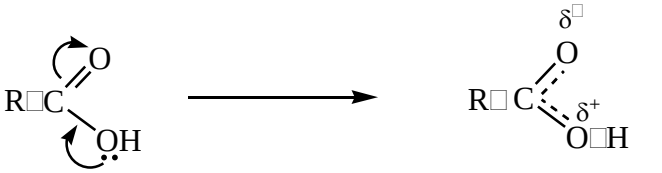
This method is used in the clinic as an express method for the detection of acetone in the urine of patients with diabetes mellitus.

REACTIVITY OF CARBOXY ACIDS

The chemical properties of carboxylic acids are determined by the structural features of the carboxyl group, which consists of carbonyl and hydroxyl groups that mutually influence each other.

The atoms of the carboxyl group (carboxyl carbon and both oxygen atoms) are in the state of sp^2 hybridization, the angle between the bonds is close to 120°, and the carboxyl group has a planar structure.

The carbonyl and hydroxyl groups in the carboxyl group have a strong influence on each other. The p-orbital of the lone electron pair of hydroxyl oxygen and two p-orbitals of the π-bond, located parallel and next to each other, overlap and form a single π-electron cloud covering all three atoms.



мезоформула

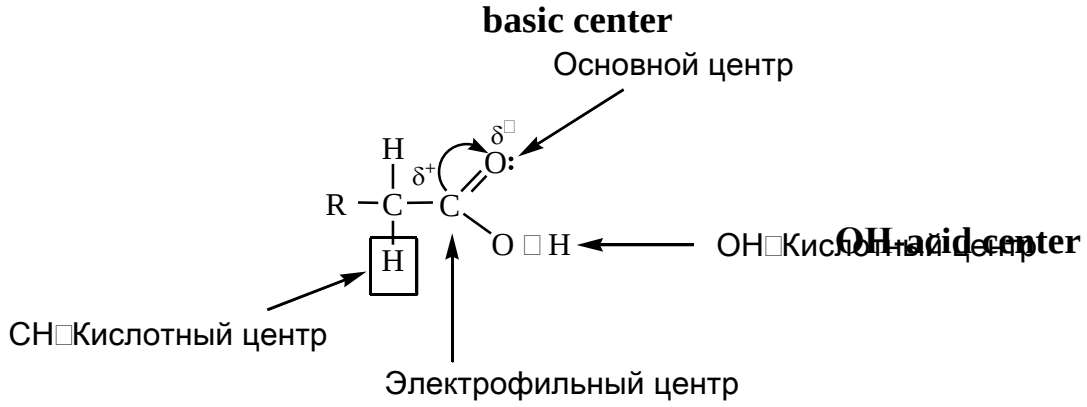
mesoformula

In the carboxyl group, the mesomeric effect of p, π-conjugation acts, changing the nature of both the hydroxyl and the carbonyl group. In the composition of the common π-electron cloud formed as a result of conjugation, the electron density is redistributed in the direction from hydroxyl oxygen to carbonyl. As a result, the decrease in O-H is much more polar compared to alcohols. That is, due to the p, π-conjugation in the carboxyl group, the acidity is greatly increased compared to alcohols.

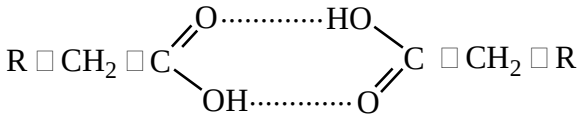
At the same time, in carboxylic acids, the partial positive charge on the carboxyl carbon atom is less than in oxo compounds; acids are less active in the perception of attack by a nucleophilic reagent, therefore, they are characterized by nucleophilic substitution reactions, and not addition, as for aldehydes and ketones.

The carboxyl group as a whole also affects the radical connected to it, causing a negative inductive effect, which occurs due to the influence of strongly electronegative oxygen atoms. The negative inductive effect of the COOH group leads, in particular, to an increase in the mobility of α-hydrogen atoms at the carbon atom adjacent to the carboxyl group.

Taking into account the above features of the composition and structure of the carboxyl group, the following reaction centers can be distinguished:



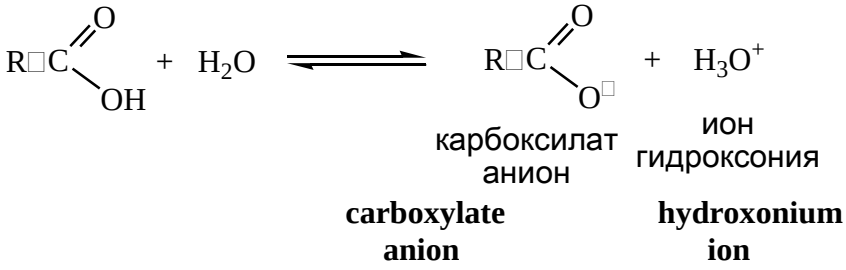
The carboxyl group contains acidic and basic centers, so carboxylic acids are able to form intermolecular hydrogen bonds and exist in the form of dimers.



Reactions involving carboxylic acids proceed in the following main directions: hydrogen substitution reactions in the carboxyl group (acidic properties); nucleophilic substitution reactions; decarboxylation reactions; reactions at the α-carbon atom.

Acid properties

Ionization (dissociation) of an acid in an aqueous solution leads to the formation of a carboxylate anion and a hydrated proton.



Carboxylic acids are one of the strongest organic acids. The strength of carboxylic acids is determined by the nature of the substituent on the carboxyl group.

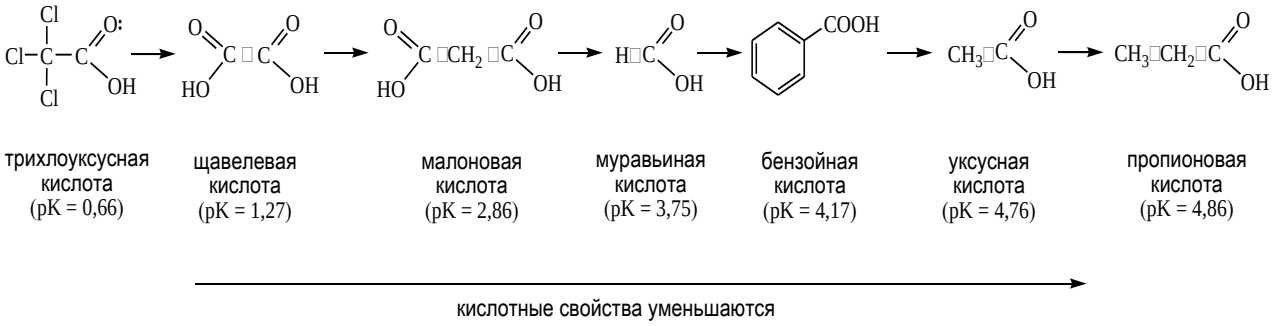
Donor groups increase the strength of the oxygen-hydrogen bond and destabilize the carboxylate anion, which leads to an increase in the strength of acids. So, formic acid is stronger than acetic acid, because. the alkyl substituent is an electron donor. As the length of the radical increases, the acidic properties decrease.

Acceptor groups reduce the electron density of the oxygen-hydrogen bond and stabilize the carboxylate anion, which leads to a decrease in the strength of acids.

Aromatic acids are stronger than aliphatic ones due to the participation of the COOH group in p, π conjugation with the electrons of the benzene ring.

Dicarboxylic acids exhibit stronger acidic properties than monocarboxylic acids (one -COOH group is an electron acceptor relative to the other).

Thus, the acidity of carboxylic acids depends on the nature of the radical. Electron-withdrawing substituents in the carboxylic acid radical increase the acidic properties, while electron-donating substituents decrease it.



acidic properties are reduced

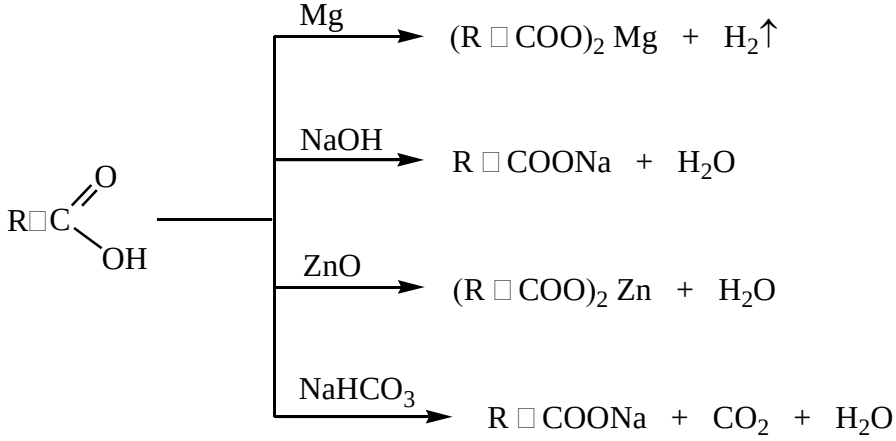
Carboxylic acids are rather weak compared to inorganic acids, but like inorganic acids they react:

with metals standing in the electrochemical series of voltages up to hydrogen;

with bases (neutralization reaction);

with basic and amphoteric oxides;

with salts formed by weaker and volatile acids, both inorganic and organic.

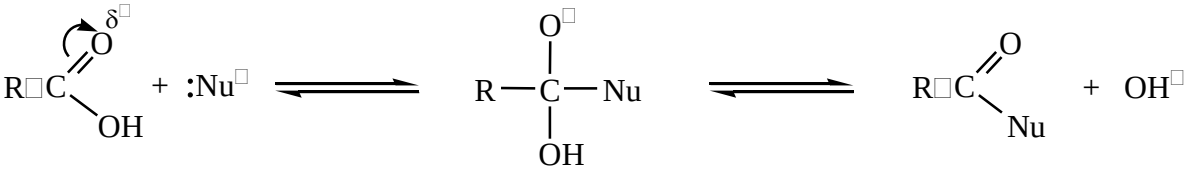


Nucleophilic substitution reactions

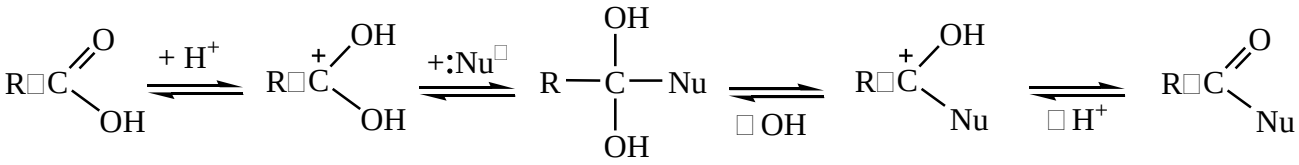
The main type of reactions of carboxylic acids is interaction with nucleophiles with the formation of functional derivatives: acid halides, anhydrides, esters, amides, etc.

The electrophilic carbon atom in the carboxyl group is attacked by nucleophilic reagents, which leads to the substitution of the OH group for other substituents by the nucleophilic substitution mechanism.

The scheme of the mechanism of such reactions includes the formation of an oxyanion, as a result of the nucleophilic attack of a carboxylic acid, and the stabilization of the anion due to the elimination of the leaving group.

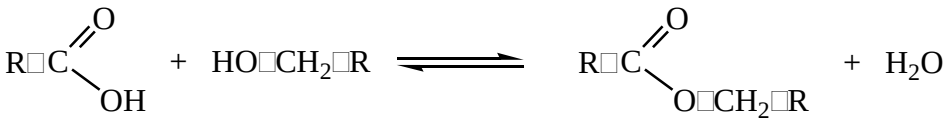


Due to the low electrophilicity of the carbonyl carbon, it is often necessary to use an acid catalyst. In the presence of a strong inorganic acid, the organic acid behaves like a base and is protonated. In this case, the positive charge on the carboxyl carbon increases, and the interaction with the nucleophile is facilitated. Thus, the role of the acid catalyst is to enhance the electrophilicity of the carboxylic acid. As a result, the mechanism of the acid-catalyzed reaction, compared with the mechanism of the non-catalyzed reaction, includes a preliminary protonation step and a final deprotonation step.



As a result of these reactions, functional derivatives of carboxylic acids are formed - esters, anhydrides, halides, amides, and others.

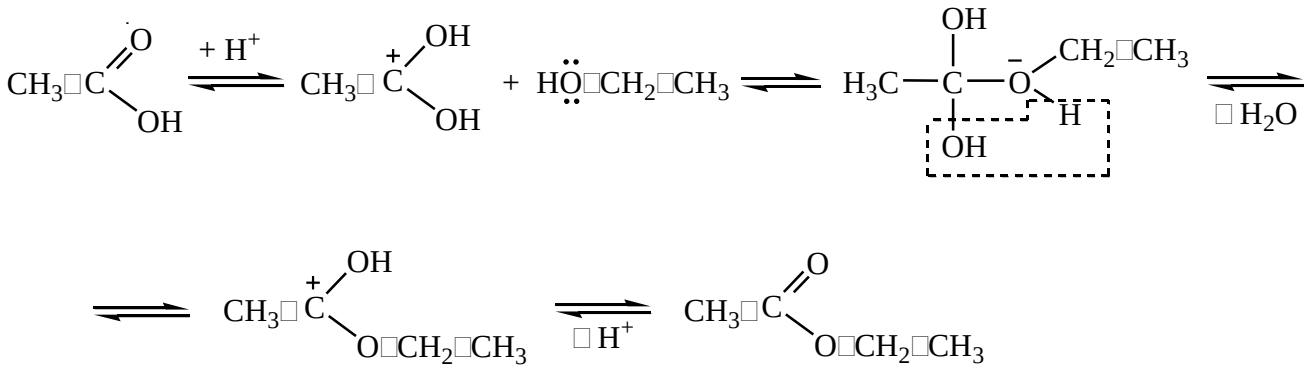
The formation of esters. When carboxylic acids interact with alcohols in the presence of strong mineral acid catalysts (H_2SO_4, HCl, ….), esters are formed, and the reaction itself is called the esterification reaction:



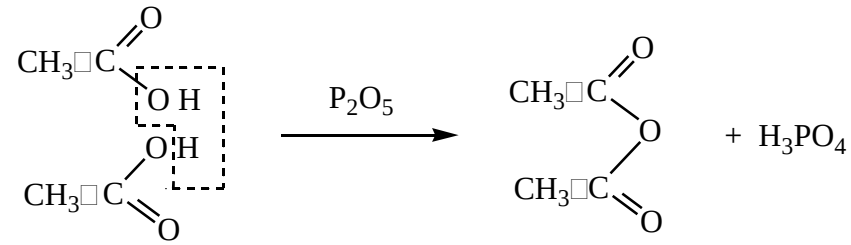
Water in this reaction is formed from the hydroxyl of a carboxylic acid and the hydrogen of an alcohol, which is also confirmed by the reaction mechanism - nucleophilic substitution, which proceeds through the stage of nucleophilic addition. The nucleophilic reagent is alcohol.

The esterification reaction proceeds slowly in the absence of catalysts due to the low ability of the carbonyl group in carboxylic acids to undergo nucleophilic

attack (due to the + M effect of the OH group, which reduces the effective positive charge on the carbon atom). A proton from a mineral acid greatly increases the positive charge on the carbon atom, which facilitates the nucleophilic attack of the alcohol, which results in the formation of an oxonium compound:



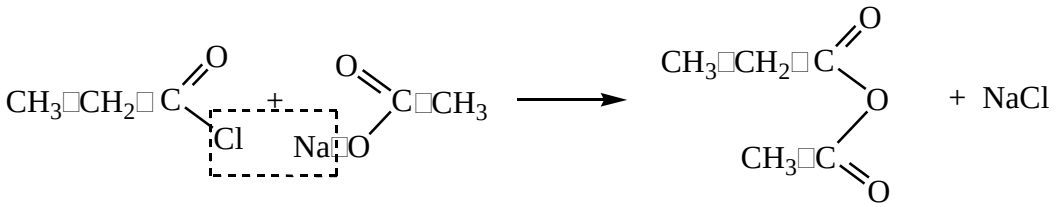
formation of anhydrides. Under the action of strong water-removing substances, such as phosphorus (V) oxide, carboxylic acids are converted into anhydrides. Anhydrides can be considered as the result of the elimination of a water molecule from two molecules of carboxylic acids:



уксусная кислота — уксусный ангидрид

acetic acid — **acetic anhydride**

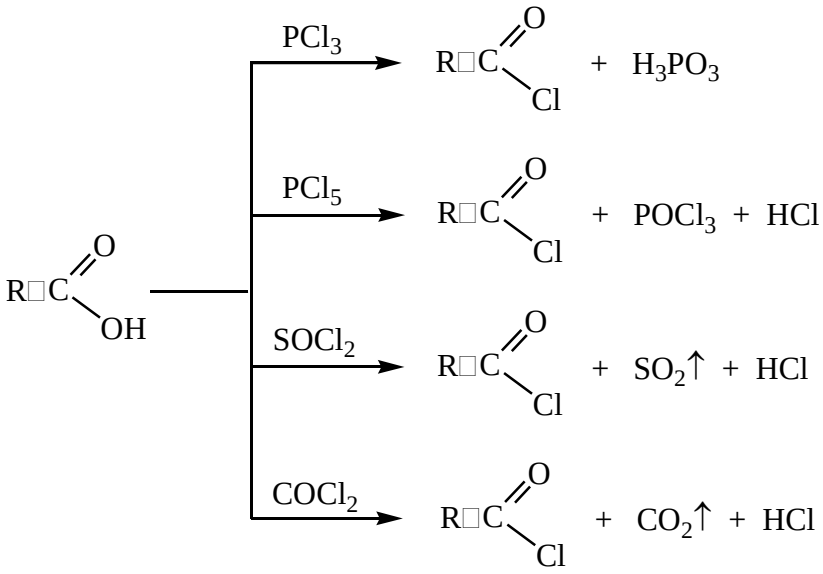
However, this method is rarely used. More often, an acid chloride is used for this purpose, which, with a salt of a carboxylic acid as a nucleophile, enters into a nucleophilic substitution reaction to form an anhydride.



пропионилхлорид — ацетат натрия — ангидрид уксусной и пропионовой кислот

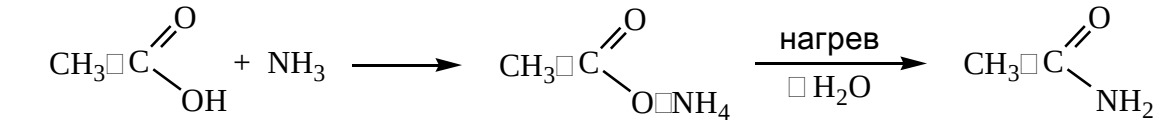
propionyl chloride — **sodium acetate** — **anhydride of acetic and propionic acids**

Formation of acid halides. When carboxylic acids react with phosphorus (III) or phosphorus (V) halides, phosphoryl chloride ($POCl_3$), phosgene ($COCl_2$), and also with thionyl chloride ($SOCl_2$), acid halides, otherwise called acyl halides, are formed. In this case, the OH group is replaced by a halogen. The more stable acid chlorides are most commonly obtained from the various acid halides.



The formation of amides. Amides can be obtained by reacting ammonia (NH_3) with carboxylic acids, esters, anhydrides and acid chlorides.

When acid and ammonia are mixed, an ammonium salt is first formed, which is then subjected to dry distillation:

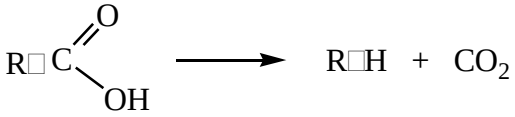


уксусная кислота — ацетат аммония — ацетамид

acetic acid — **ammonium acetate** — **acetamide**

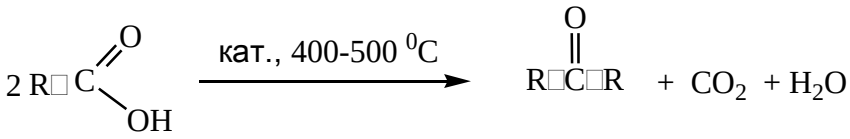
Decarboxylation reactions

In the process of decarboxylation, carboxylic acids split off carbon monoxide (IV) and turn into compounds of different classes, depending on the reaction conditions. Decarboxylation is carried out by heating in the presence of acids or bases. In this case, as a rule, the carboxyl group is replaced by a hydrogen atom:

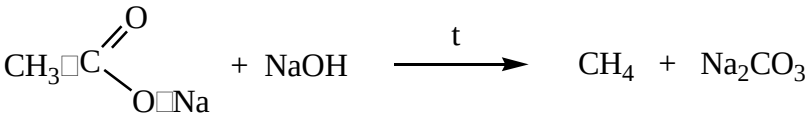


The enzymatic decarboxylation of keto, amino and hydroxy acids in the body is important.

Aliphatic acids, when their vapors are passed over oxides of thorium (IV) or manganese (IV), turn into ketones:



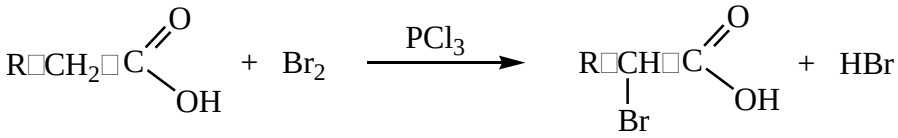
When sodium acetate is heated with alkali, methane is formed:



Decarboxylation of other saturated aliphatic acids in the presence of alkali is accompanied by the destruction of the hydrocarbon radical and does not lead to the corresponding alkane.

Reactions at the α-carbon atom

Aliphatic carboxylic acids are halogenated in the α-position with chlorine or bromine in the presence of a catalyst - red phosphorus or phosphorus halides (Gel-Volhard-Zelinsky reaction).



It is not the carboxylic acid itself that undergoes bromination, but the acid chloride formed from it. The acid chloride has stronger CH-acid properties than the carboxylic acid and more easily forms the enol form.

Other heterofunctional acids are synthesized from the resulting α-halogenated acids using nucleophilic substitution reactions.

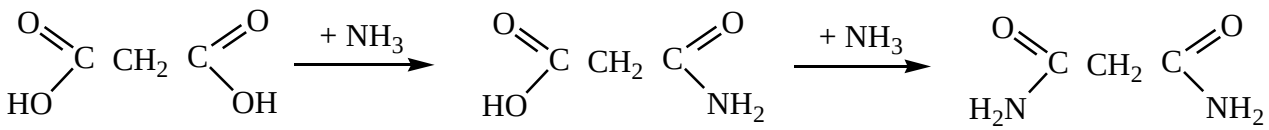
Dicarboxylic acids

The acidic properties of these acids, especially the first representatives, are much higher than those of monocarboxylic acids, due to the –I-effect of the carboxyl group. As the distance between carboxyl groups increases, the acidity of dicarboxylic acids decreases.

Dicarboxylic acids are capable of forming two types of functional derivatives: incomplete, i.e. on one carboxyl group, and complete - on both carboxyl groups.

The chemical properties of dicarboxylic acids are basically similar to those of monocarboxylic acids. They give all the reactions characteristic of the carboxyl group.

Dicarboxylic acids form incomplete and complete amides:

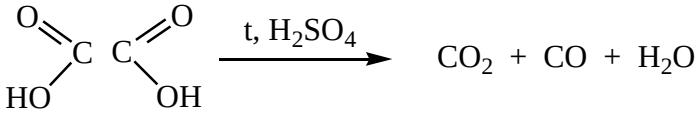


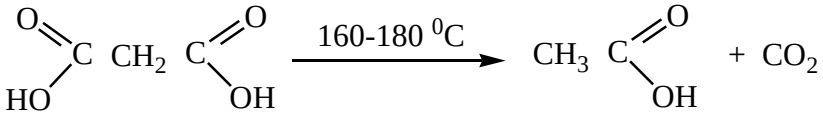
малоновая кислота — неполный амид — полный амид

malonic acid — incomplete amide — full amide

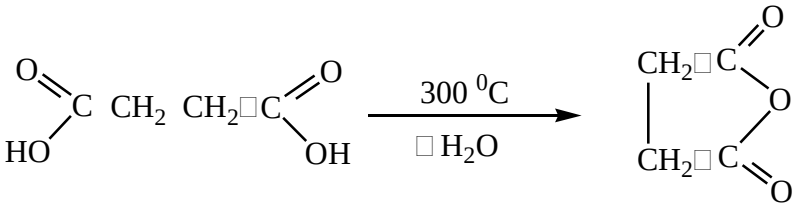
The specific properties of dicarboxylic acids, due to the presence of two carboxyl groups in the molecule, are manifested primarily in their tendency to decarboxylation reactions.

When heated, oxalic and malonic acids decarboxylate.





A dicarboxylic acid with a sufficiently long chain can be bent in the form of a claw, while the carboxyl groups will be closely spaced, which is already characteristic of succinic and glutaric acids. Therefore, when these acids are heated, an intramolecular acylation reaction occurs, accompanied by dehydration, with the formation of stable five- and six-membered cyclic anhydrides.



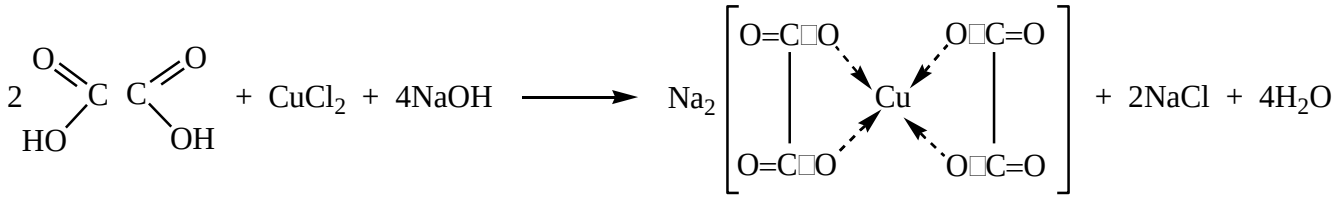
янтарная кислота

succinic acid

янтарный ангидрид

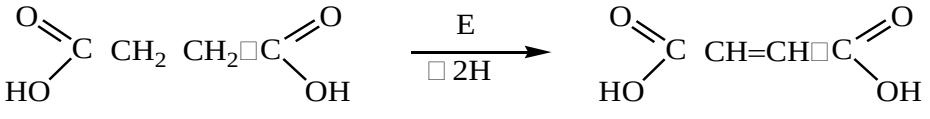
succinic anhydride

Dicarboxylic acids are bidentate ligands, forming strong chelate complexes:



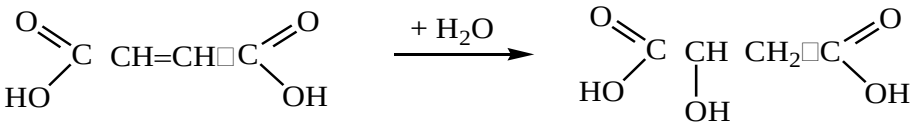
Fumaric - butenedioic, is a dicarboxylic unsaturated acid, common in nature. Participates in the cycle of tricarboxylic acids, being an intermediate link. It is obtained in the body from amber and then, when hydrated, forms malic.

succinic acid **fumaric acid**



янтарная кислота

фумаровая кислота

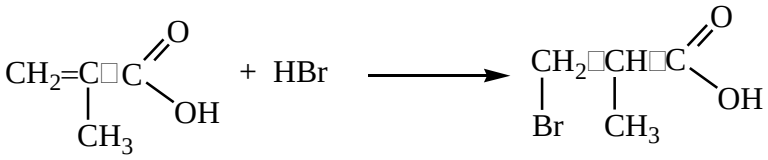


яблочная кислота

malic acid

Unsaturated carboxylic acids

For unsaturated carboxylic acids, electrophilic addition reactions are characteristic. The effect of the -COOH group is that the addition to the carbon atom in the α and β position occurs against the Markovnikov rule. The reason is the shift in electron density due to π-π conjugation:



метилпропеновая кислота

methylpropenic acid

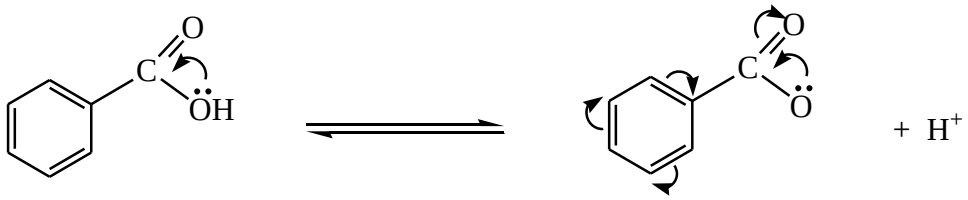
3-бром-2-метилпропановая кислота

2-bromo-2-methylpropanoic acid

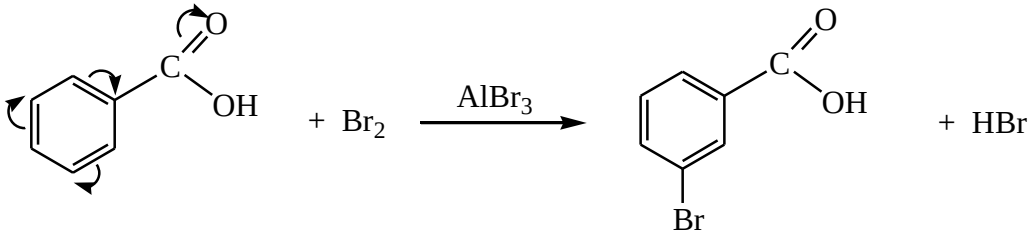
Polyacrylates, polymethacrylates are used for prosthetics in dental practice.

Aromatic acids

Aromatic acids have greater acidic properties than aliphatic ones due to the participation of the COOH group in p–π conjugation with the electrons of the benzene ring:



Aromatic acids are characterized by electrophilic substitution reactions in the benzene ring. The carboxyl group acts as a substituent of the second kind, orienting further substitution to the meta position and hindering the reaction:



бензойная кислота

benzoic acid

3-бромбензойная кислота

3-brombenzoic acid

EXERCISES

1. Give the equations of reactions that occur when ethanal interacts with:

1) KCN (H_2O);
2) $NaHSO_3$;
3) CH_3OH (H^+).

Specify the names of the classes of compounds to which the reaction products belong.

2. Give the reaction equations and name the products that are formed during the interaction of propanone with:

1) $C_2H_5NH_2$;
2) $C_6H_5NHNH_2$;
3) NH_2OH.

3. Write the schemes of aldol condensation of the following carbonyl compounds:

1) ethanal;
2) propanone.

What will happen to the aldols if the temperature is raised? Write diagrams of relevant processes.

4. Give reaction schemes with which you can distinguish:

1) propanal and propanone;
2) benzaldehyde and acetophenone.

5. Write the reaction schemes of Cannizzaro using an example:

1) benzaldehyde;
2) methanal.

Explain why aldol condensation is impossible for these compounds?

6. How does benzaldehyde react with the following substances:

1) NaOH;
2) H_2SO_4;
3) $C_6H_5NH_2$?

Make equations for the corresponding reactions, indicate their mechanism. Name the products.

7. What happens when the following oxo compounds are heated in an aqueous solution of alkali:

1) propanal;
2) 2-methylpropanal;
3) 2,2-dimethylpropanal?

Write the schemes of the occurring reactions. What explains the difference in the behavior of these compounds?

8. Give the reaction equations by which you can get from butanal:

1) aldol;

2) methylimine;

3) acetal using ethanol;

4) the corresponding alcohol.

9. Which of the following aldehydes are capable of entering into the Cannizzaro reaction?

1) ant;

2) acetic;

3) phenylacetic;

4) trimethylacetic.

Write the equations for the corresponding reactions.

10. Draw the structures and compare the stability of the enol forms of the following carbonyl compounds:

1) propanal;

2) pentane-2,4-dione;

3) cyclohexa-2,4-dienone.

Which of these compounds exists exclusively in the enol form? Give her name.

11. Write the schemes for the formation of a cyclic hemiacetal using 4-hydroxypentanal as an example. What type of tautomerism illustrates this reversible process?

12. Write the reaction equations and name the products that are formed during the interaction of benzoic acid with the following reagents:

1) $SOCl_2$;

2) CH_3OH (H^+, t);

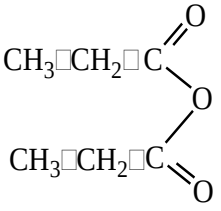
3) C_2H_5ONa;

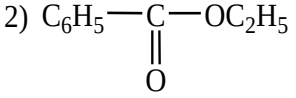
4) $(CH_3)_2NH$ (H_2O);

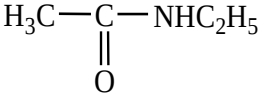
5) KOH (H_2O).

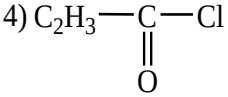
Indicate what properties the carboxylic acid exhibits in each interaction.

13. Determine which functional derivatives of carboxylic acids include compounds whose formulas are given below. Suggest schemes for their synthesis from the corresponding acids.

1) 

2) 

3) 

4) 

14. Write reaction schemes, indicate their mechanisms (types) and name the products that are formed during the interaction:

1) propanoic acid with sodium hydroxide;
2) butanoic acid anhydride with ethanol;
3) acetic acid chloride with methylamine;
4) ethyl propionate with water (in the presence of NaOH).

15. Write the reaction equations and name the products that are formed during the interaction of acetic anhydride with the following reagents:

1) H_2O;
2) C_2H_5OH (H^+, t);
3) $CH_3CH_2NH_2$.

By what mechanism do these reactions proceed?

16. Give the reactions by which propanoic acid chloride can be obtained:

1) propanoic acid anhydride;
2) propanoic acid;
3) phenylpropanoate;
4) propanoic acid methylamide;
5) sodium propanoate.

17. Suggest schemes for obtaining the following compounds from butanoic acid amide:

1) butanoic acid;
2) sodium butanoate;
3) butanoic acid chloride;
4) ethyl butanoate.

Give the equations of the corresponding reactions.

18. Write the reaction equations between the following compounds:

1) ethyl alcohol and acetic acid;
2) methyl alcohol and butyric acid;
3) butyl alcohol and propionic acid.

19. How can propionic acid be obtained from bromoethane?

20. Write the reaction equation corresponding to the schemes below. Name the reaction products:

1) $CH_2{=}CH{-}C(=O)H \xrightarrow{C_2H_5OH\,/\,H^+} X_1 \xrightarrow{KMnO_2,\ H_2O} X_2 \xrightarrow{H_2O\,/\,H^+} X_3.$

2) $C_2H_6 \xrightarrow{Cl_2,\ h\upsilon} X_1 \xrightarrow{Mg\ (эфир)} X_2 \xrightarrow{CH_2O,\ H^+} X_3 \xrightarrow{CuO,\ t} X_4 \xrightarrow{[Ag(NH_3)_2]OH} X_5 \xrightarrow{HCl} X_6 \xrightarrow{Cl_2,\ h\upsilon} X_7 \xrightarrow{NH_3\ (изб.)} X_8.$

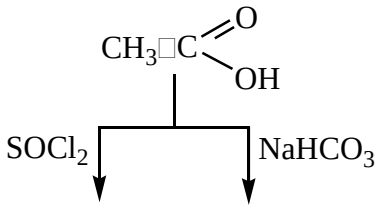
3) $CaC_2 \xrightarrow{H_2O} X_1 \xrightarrow{H_2O,\ Hg^{2+}} X_2 \xrightarrow{[Ag(NH_3)_2]OH} X_3 \xrightarrow{HCl} X_4 \xrightarrow{C_2H_5OH,\ H^+} X_5.$

4) $CH_3{-}C{\equiv}CH \xrightarrow{H_2O,\ H^+,\ Hg^{2+}} X_1 \xrightarrow{H_2,\ Ni} X_2 \xrightarrow{HBr} X_3 \xrightarrow{Mg\ (эфир)} X_4 \xrightarrow{CO_2,\ H^+} X_5 \xrightarrow{NH_3,\ H_2O} X_6 \xrightarrow{HCl} X_7 \xrightarrow{Cl_2,\ h\nu} X_8.$

5) $C_3H_8 \xrightarrow{Br_2,\ h\nu} X_1 \xrightarrow{Mg\ (эфир)} X_2 \xrightarrow{CH_2O,\ H^+} X_3 \xrightarrow{K_2Cr_2O_7,\ H_2SO_4} X_4 \xrightarrow{PCl_5} X_5 \xrightarrow{C_2H_5OH} X_6 \xrightarrow{NaOH} X_7.$

6) $CH_2Br{-}CH_2Br \xrightarrow{2\ KOH\ (C_2H_5OH)} X_1 \xrightarrow{H_2O,\ H^+,\ Hg^{2+}} X_2 \xrightarrow{HCN\ (KCN)} X_3 \xrightarrow{2\ H_2O,\ H^+} X_4 \xrightarrow{H_2SO_4,\ t} X_5 \xrightarrow{HBr} X_6.$

7)



$X_1 + X_2 \longrightarrow X_3 \xrightarrow{CH_3OH} X_4 \xrightarrow{H_2O\ /\ H^+} X_5 \xrightarrow{CH_3NH_2} X_6 \xrightarrow{t} X_7.$

Laboratory work № 3.
PROPERTIES OF ALDEHYDES, KETONES, CARBOXIC ACIDS

Goal of the work:

To form knowledge of the dependence of the reactivity of aldehydes, ketones and carboxylic acids on the electronic and spatial structure; to master the skills of performing qualitative reactions on aldehydes and ketones (acetone).

Reagents:

	sodium acetate	CH_3COONa	crystalline
1.	acetone	$CH_3–CO–CH_3$	–
2.	benzoic acid	C_6H_5-COOH	5% solution
3.	sodium hydroxide	NaOH	2H solution
4.	sodium nitroprusside	$Na_2[Fe(CN)_5NO]$	0,5H solution
5.	Lugol's solution	I_2 / KI	–
6.	sulfuric acid	H_2SO_4	2 H solution
7.	hydrochloric acid	HCl	2H solution
8.	acetic acid	CH_3COOH	2H solution
9.	calcium chloride	$CaCl_2$	0,5H solution
10.	oxalic acid	HOOC–COOH	5% solution
11.	ethanol	$CH_3–CH_2–OH$	–
12.	distilled water	H_2O	–

Equipment:

- alcohol lamp
- porcelain cup
- glass rod
- stand with test tubes
- universal indicator paper

Experience 1. Color reaction for acetone with sodium nitroprusside

The color reaction with sodium nitroprusside (Legal's test) is widely used in clinical laboratory practice to detect acetone in the urine (in the diagnosis of diabetes mellitus).

Place 5 drops of sodium nitroprusside solution, 20 drops of water and 5 drops of acetone into a test tube. Shake and add 5 drops of sodium hydroxide solution.

Divide the resulting solution into two parts. Add 5 drops of acetic acid solution to one of the test tubes.

Process chemistry:

$$CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + Na[Fe(CN)_5NO] + NaOH \rightarrow$$

Answer questions about experience:

1. Why is this method used in the clinic?

2. How does the pH of the medium affect the interaction of acetone with sodium nitroprusside?

Experience 2. Iodoform reaction to acetone

The iodoform test or the Lieben test is very sensitive and allows you to open acetone in aqueous solutions at its content of 0.04%.

Place 3 drops of a solution of iodine in potassium iodide (Lugol's solution) into a test tube and add sodium hydroxide solution drop by drop until the brown color of iodine disappears. Add 1 drop of acetone to the discolored solution, shake. A yellowish-white precipitate with a characteristic odor of iodoform falls out.

Process chemistry:

$$I_2 + NaOH \leftrightarrow$$

$$CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + HIO \rightarrow$$

$$CI_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + NaOH \rightarrow$$

Answer questions about experience:

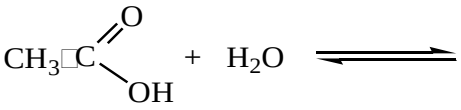
1. The presence of what structural fragments of the acetone molecule determines the positive "iodoform test"?

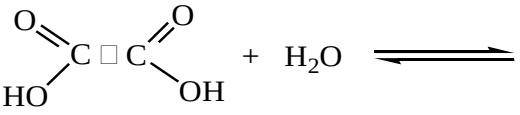
2. Can iodoform test be used as a qualitative test for acetone?

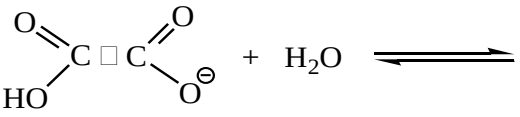
Experience 3. Dissociation of carboxylic acids

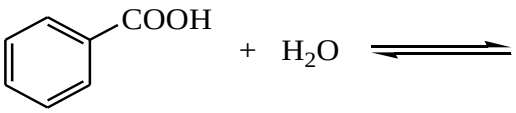
On a strip of universal indicator paper, apply a drop of solutions of acetic, oxalic and benzoic acids. Compare the resulting color with the scale of the universal indicator and record the approximate pH value. Qualitatively assess the strength of these acid-slots.

Process chemistry:









Answer questions about experience:

1. At what reaction center do carboxylic acids react with water and what is their solubility in water?

2. Arrange acetic, oxalic and benzoic acids in order of increasing acidic properties.

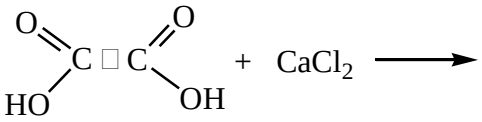
3. Why do the analyzed carboxylic acids have different acidic properties and how to determine this in practice?

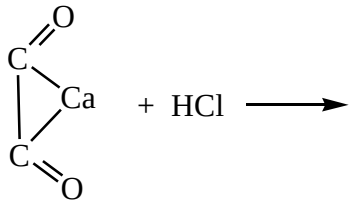
<u>Experiment 4. Discovery of the oxalate anion</u>

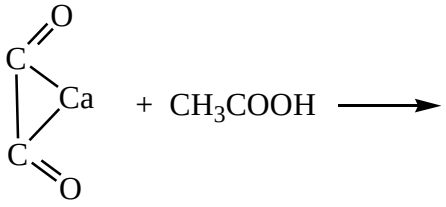
Take two test tubes and in each of them place 10 drops of oxalic acid solution and 5 drops of calcium chloride solution until a white precipitate of calcium oxalate forms.

Then add 5 drops of hydrochloric acid to the precipitate in the first test tube, and 5 drops of acetic acid to the precipitate in the second test tube.

Process chemistry:







Answer questions about experience:

1. At what reaction center does oxalic acid react with CaCl2?

2. What conclusion can be drawn about the strength of acids based on the results of the interaction of calcium oxalate with HCl and with CH3COOH?

3. Is it possible to detect oxalic acid by reaction with CaCl2?

QUESTIONS FOR PROTECTION OF LABORATORY WORK 3.

1. Electronic structure of the carbonyl group. Reaction centers in carbonyl-containing compounds (aldehydes and ketones).

2. General mechanism of the nucleophilic addition reaction (AN).

3. Examples of nucleophilic addition reactions: addition of water; reduction of aldehydes and ketones; acetalization reaction (addition of alcohols); addition of hydrocyanic acid, thiols, sodium hydrosulfite; interaction of aldehydes and ketones with amines.

4. Reactions involving the CH-acid center in carbonyl compounds.

5. Aldol and cratonic condensation reactions.

6. Oxidation reactions of aldehydes and ketones.

7. Disproportionation reactions (dismutation reaction, Cannizzaro).

8. Differences in the reactivity of aldehydes and ketones.

9. Spatial and electronic structure of the carboxyl group. Reaction centers in carboxylic acid molecules.

10. Acid-base properties of carboxylic acids, OH- and CH-acidity. Salt formation reactions.

11. General mechanism of nucleophilic substitution (SN) reactions at sp2-hybridized carbon atom.

12. Ways to increase the reactivity of carboxylic acids in SN-reactions.

13. Examples of nucleophilic substitution reactions: the formation of esters,

anhydrides, acid halides, amides.

14. The mechanism of the esterification reaction.

15. Decarboxylation reactions.

16. Reactions at the α-carbon atom.

17. Dibasic carboxylic acids: decarboxylation reactions and formation of cyclic anhydrides.

18. Unsaturated carboxylic acids.

19. Aromatic carboxylic acids.

ACTIVITY № 10

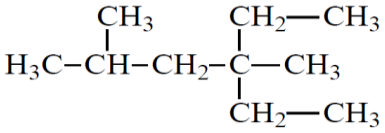
CONTROL WORK №2

Purpose of the lesson:

Assess the assimilation by students of the program material on the topic "Hydrocarbons" and the ability to use the knowledge gained to solve practical problems.

Exemplary test ticket 1.

1. Give a name according to the international nomenclature to the compound:



2. Write the formulas of substances in the molecules of which the hydroxyl group is an electron-withdrawing substituent:

1) glycerin
2) phenol
3) ethylene glycol
4) 2-aminoethanol-1.

Write formulas.

3. Give the equation for chlorination of 2-methylpropane and indicate the reaction mechanism

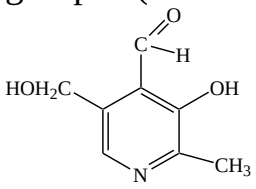
4. Give the formula of the compound corresponding to the following name: 2,5,5-trimethylheptene-3

5. A nucleophile is a particle that:

1) attaches a proton
2) attacks a positively charged carbon atom
3) supplies a pair of electrons to form a chemical bond
4) supplies a free orbital for the formation of a chemical bond

6. Write the equations for the reactions of benzene and ethylbenzene with chlorine under ultraviolet irradiation

7. Indicate the type and sign of the electronic effects of substituents in the molecule of pyridoxal, a vitamin of group B (vitamin B6).



7. Educational, methodological and information support of the discipline

7.1. List of basic and additional literature

	Basic literature
.	Osipova, O. V. Bioorganic chemistry: a textbook / O. V. Osipova, A.V. Shustov. – 2nd ed. – Saratov: Scientific Book, 2019. – 367 p. – ISBN 978-5-9758-1886-7. – Text: electronic // Digital educational resource IPR SMART: [website]. – URL: https://www.iprbookshop.ru/81002.html (date of application: 02/13/2023). – Access mode: for authorization. users
.	Frank, L. A. Bioorganic chemistry: a textbook / L. A. Frank. – Krasnoyarsk: Siberian Federal University, 2018. – 174 p. – ISBN 978-5-7638-3875-6. – Text: electronic // Digital educational resource IPR SMART: [website]. – URL: https://www.iprbookshop.ru/84320.html (date of application: 02/13/2023). – Access mode: for authorization. users
	Additional literature
.	Kovalchukova, O. V. General and bioorganic chemistry. Organic chemistry: a textbook / O. V. Kovalchukova, O. V. Avramenko. – Moscow: Peoples' Friendship University of Russia, 2011. – 124 p. – ISBN 978-5-209-03563-3. – Text: electronic // Digital educational resource IPR SMART: [website]. – URL: https://www.iprbookshop.ru/11428.html (date of application: 02/13/2023). – Access mode: for authorization. users
.	Varlamov, A.V. Bioorganic chemistry: a methodological guide to laboratory work / A.V. Varlamov, E. A. Sorokina, E. V. Nikitina. – Moscow: Peoples' Friendship University of Russia, 2017. – 48 p. – ISBN 978-5-209-08043-5. – Text: electronic // Digital educational resource IPR SMART: [website]. – URL: https://www.iprbookshop.ru/90980.html (accessed: 02/13/2023). –Access mode: for authorization. users
.	Rzhechitskaya, L. E. Bioorganic chemistry: texts of lectures / L. E. Rzhechitskaya, M. A. Burmasova. – Kazan: Kazan National Research Technological University, 2017. – 88 p. – ISBN 978-5-7882-2241-7. – Text: electronic // Digital educational resource IPR SMART: [website]. – URL: https://www.iprbookshop.ru/100688.html (date of application: 02/13/2023). – Access mode: for authorization. users

7.2. List of resources of the Internet information and telecommunication network

http://window.edu.ru – **A single window of access to educational resources;**

http://fcior.edu.ru – **Federal Center for Information and Educational Resources;**

http://elibrary.ru – **Scientific electronic library**.

АБАЛМАСОВА Ольга Викторовна
БОСТАНОВА Фатима Аминовна

БИООРГАНИЧЕСКАЯ ХИМИЯ

Учебно-методическое пособие
для студентов I курса обучающихся по специальностям
31.05.01 «Лечебное дело»;
Часть I

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