NATIONAL UNIVERSITY OF CIVIL DEFENSE OF UKRAINE
Department of Special Chemistry and Chemical Technology

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LECTURE NOTES

from the discipline “ **Organic Chemistry** ”
for cadets and students preparing for their first (bachelor's)
Equally cover knowledge 16 "Chemical and bioengineering"
in specialty - 161 "Chemical technologies and engineering"
Educational Program – “Radiation and chemical protection”

The methodical development was discussed and praised at the meeting of the Department of Chemical Technologies

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Content

Lecture 1.

Basic Provisions Of The Theory Of The Structure Of Organic Compounds. Types Of Chemical Bond

Organic chemistry is the chemistry of carbon compounds. According to another widely used definition, organic chemistry is the chemistry of hydrocarbons and their derivatives.

Several reasons led to the manifestation of the above-mentioned properties by carbon. It has been proven that the C-C bond energy (bond strength) is comparable to the C-O bond strength. The Si-O bond is much stronger than the Si-Si bond.

Carbon can exhibit not one, but three types of hybridization of orbitals: in the case of sp3-hybridization, four hybrid orbitals with tetrahedral orientation are formed; with their help, covalent bonds are formed. In the case of sp2-hybridization, three hybrid orbitals oriented in the same plane are formed, and in combination with a non-hybrid orbital they form double multiple bonds; finally, with the help of sp-hybrid orbitals, which have a linear orientation, and non-hybrid orbitals, triple bonds between carbon atoms arise.

Now it is well known that carbon atoms are able to form single, double and triple bonds not only with each other, but also with other elements. Thus, the modern theory of the structure of molecules explains both the large number of organic compounds and the dependence of the properties of these compounds on their chemical structure. It fully confirms the main principles of the theory of chemical structure, developed by the outstanding Russian scientist A.M. Butlerov.

Basic provisions of the theory of the structure of organic compounds

1) atoms in molecules are connected to each other by chemical bonds according to their valence;

2) atoms in the molecules of organic substances are connected to each other in a certain sequence, which determines the chemical structure of the molecule

3) the properties of organic compounds depend not only on the number and nature of the atoms included in their composition, but also on the chemical structure of the molecules;

4) in molecules, there is a mutual influence of atoms both related and not directly related to each other

5) the chemical structure of a substance can be determined as a result of studying its chemical transformations and, conversely, its properties can be characterized by the structure of a substance.

An important consequence of the theory of structure: each organic compound must have one chemical formula that reflects its structure. Structural formulas are used to depict the structure of organic compounds.

BOND POLARITY

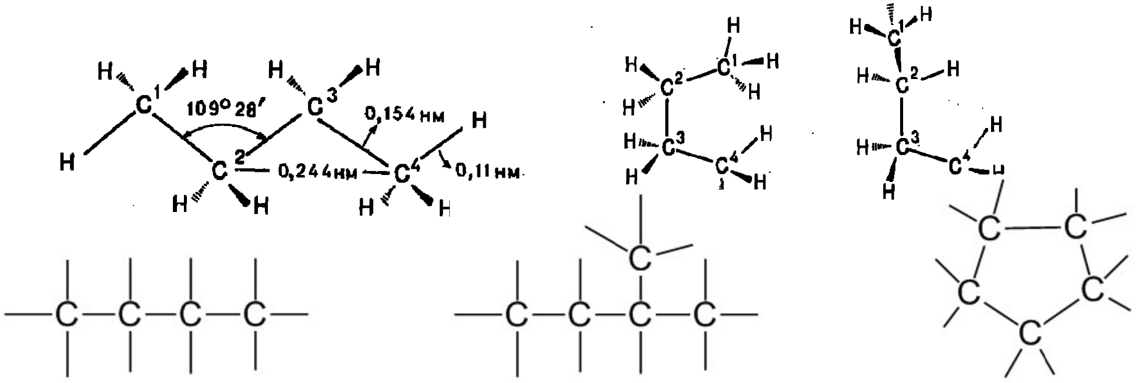
If two identical atoms are covalently bonded (for example, Cl2), then the electron density will be distributed evenly between both atoms.

If the atoms have different electronegativity (HCl), the bonding pair will be closer to the more electronegative atom, increasing the polarity of the covalent bond.

Pauling scale

K	Na	H	P	C	S	I	Br	Cl	N	O	F
0,8	0,9	2,1	2,1	2,5	2,5	2,5	2,8	3,0	3,0	3,5	4,0

The structure of the hydrocarbon chain:



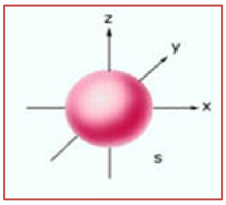
open unbranched chain

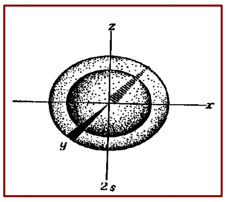
open branched chain

closed circuit

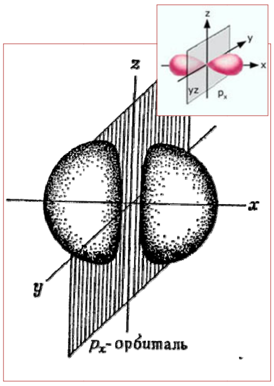
ATOMIC ORBITALS

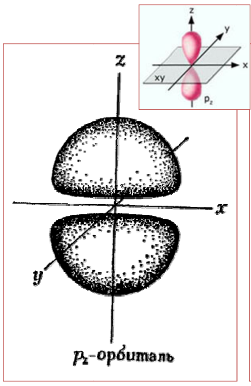
Comparison of 1s and 2s orbitals:

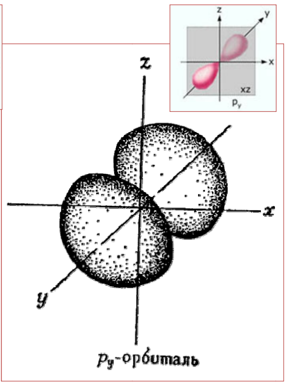




Three 2p-orbitals:





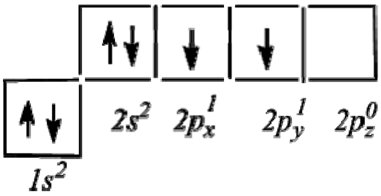


The nodal plane for the p-orbital is shaded.

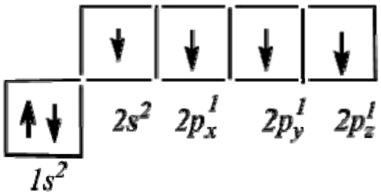
NODES - a place in space in which any property (or mathematical function) vanishes.

The three-dimensional equivalent of a node is called a nodal surface. In the case of an atom, the nodal surface is the place in space where the amplitude of the electron's wave function vanishes. The nucleus is part of the support surface for p-, d- and f-orbitals, but not for s-orbitals.

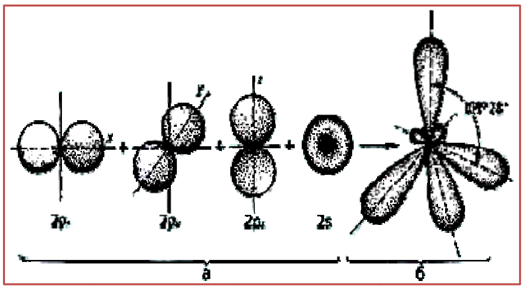
ELECTRONIC STRUCTURE OF THE CARBON ATOM

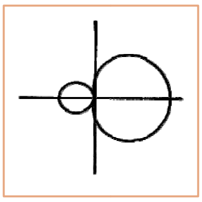


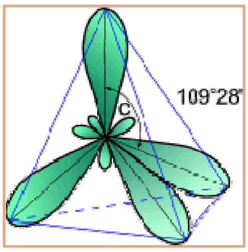
Basic state



Excited state





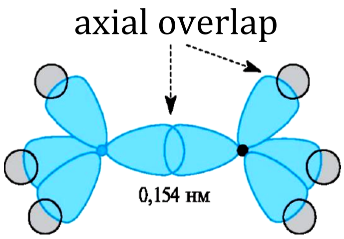


2sp^3-orbital

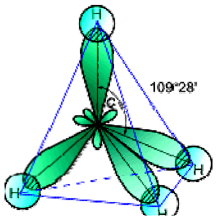
Model of the sp3-hybrid state of the electron shell of the carbon atom

The type of hybridization determines the orientation of hybrid AOs in space and, therefore, the geometry of molecules, that is, their spatial structure.

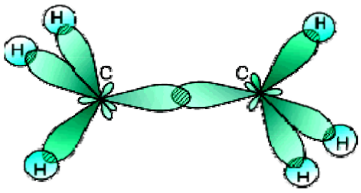
Sp3- hybridization. When mixing the four external AOs of an excited carbon atom - one 2s- and three 2p-orbitals - four equivalent sp3-hybrid orbitals arise. They have the shape of a volumetric "eight", one of the blades of which is much larger than the other.



Formation of σ-bonds in ethane by axial overlap of AO

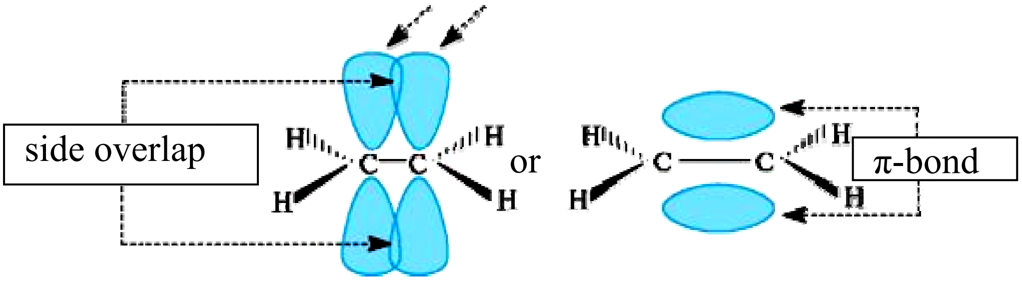


Scheme of the electronic structure of the methane molecule



Formation of an ethane molecule by overlapping of two hybrid electron clouds of carbon atoms

Sp2- hybridization. When mixing one 2s - and two 2p-ao of an excited carbon atom, three equivalent sp2 hybrid orbitals are formed, and the unhybridized 2p-ao remains. This state of carbon atom hybridization is typical for unsaturated hydrocarbons (alkenes), as well as for some functional groups, for example, carbonyl and carboxyl.

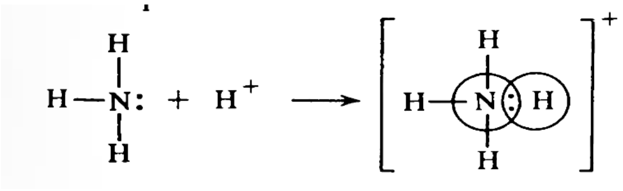


Formation of π-bonds in ethylene by lateral overlap of the AO district

Sp-hybridization. When mixing one 2s - and one 2p-orbitals of an excited carbon atom, two equivalent sp-hybrid aos are formed, and two p-aos remain unhybridized. This state of hybridization of the carbon atom is found in compounds having a triple bond, for example, in alkynes.

A coordination bond is a special case of a covalent bond. Such a connection occurs when one of the atoms has an unshared electron pair, and the other, on the contrary, is ready to accept it (has a free orbital or "electron vacancy"). It is two or more electrons short of an octet.

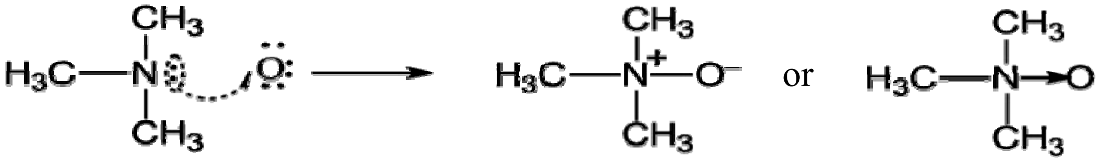
In this case, there is also a sharing of electrons, by transferring a pair of electrons to one of the atoms for common use. The other atom provides only its free orbital capable of accepting these electrons:



An atom that has an unshared pair of electrons and provides them for the formation of a new chemical bond is called a donor, and an atom that accepts them is an acceptor. Therefore, such a connection is often called a **donor-acceptor connection.**

A type of coordination bond is a **hemipolar bond.** This connection is also carried out due to an unshared pair of electrons of one of the atoms. But giving this pair to form a bond, the atom receives a positive charge. At the same time, another atom has a negative charge.

As a result, the new connection can be considered as a simultaneous manifestation of two types of connection - covalent (due to the shared electron pair) and ionic (due to the interaction of opposite charges). For example:



trimethylamine trimethylamine oxide

A hydrogen bond (H-bond) occurs between atoms that have a free electron pair (for example, oxygen, nitrogen, fluorine, etc.) and hydrogen, which is connected to another atom by a highly polar covalent bond (for example, , O-H). In this case, hydrogen has a fairly high proton mobility, as a result of which a bond of a special type (H - bond) occurs, the energy of which is only 12.5-21 kJ/mol. The emergence of such a connection, for example, between water molecules, can be depicted in the form of a diagram:

TYPES OF ORGANIC REACTIONS AND THEIR MECHANISMS

1. Addition reactions.

In this case, one new substance is formed from two (or more) molecules:

$$CH_2 = CH_2 + Br_2 \rightarrow CH_2Br–CH_2Br$$

2. Substitution reactions.

One atom (or group of atoms) is replaced in a molecule by another atom (or group of atoms), resulting in the formation of new compounds:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

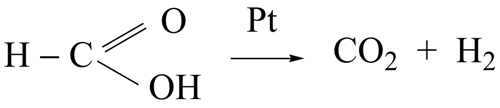
3. Cleavage reactions.

As a result of such a reaction, a new substance containing a multiple bond is formed:

$CH_3–CH_2Br + NaOH \rightarrow CH_2{=}CH_2 + NaBr + H_2O$
alcohol solution

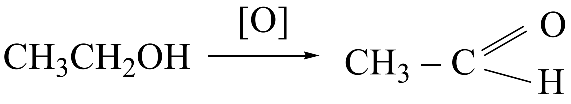
4. Decomposition reactions.

These reactions lead to the formation of new substances with a simpler structure as a result of the decomposition of the original compound into two or more:



5. Oxidation reactions.

When the original compound is oxidized by air oxygen in the presence of catalysts or oxidants, a new substance is formed:



6. Polymerization reactions.

As a result of the addition of a large number of simple substances (monomers) to each other, a new substance with a complex structure with a large molecular weight (polymers) is formed:

$$nCH_2{=}CH_2 \longrightarrow [–CH_2–CH_2–]_n$$

7. Condensation and polycondensation reactions.

A more complex substance is formed as a result of the connection of several molecules (sometimes - a large number), which proceeds with the separation of more simple substances (water, ammonia, etc.):

$$HO{-}CH_2{-}CH_2{-}\boxed{OH + H}O{-}CH_2{-}CH_2{-}OH \xrightarrow[-H_2O]{}$$

$$\longrightarrow HO{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}OH$$

$$nHO{-}CH_2{-}CH_2{-}OH \rightleftharpoons [{-}CH_2{-}CH_2{-}O{-}]_n + nH_2O$$

However, it is more convenient to classify organic reactions according to their mechanisms.

The mechanism of a chemical reaction is a path that leads to the breaking of an old chemical bond and the formation of a new one. At the same time, it is necessary to take into account the formation of not only the final products of the reaction, but also intermediate ones, as well as the effect of changing conditions on the course of the reaction. Depending on the nature of the attacking reagent and the nature of the bonds in the reacting molecule, the breaking of the σ-bond can proceed by two main mechanisms:

1. Heterolytic or ionic:

$$A{:}\boxed{B} + {:}C^- \longrightarrow \overset{-}{A{:}} + B{:}C \quad (S_N)$$ - nucleophilic substitution

$$A\boxed{{:}B} + {:}C^+ \longrightarrow A^+ + B{:}C \quad (S_E)$$ - electrophilic substitution

2. Homolytic or radical:

$$A{\cdot}\boxed{{\cdot}B} + {\cdot}C \longrightarrow A{\cdot} + B{:}C \quad (S_R)$$

Lecture 2 .

NOMENCLATURE OF ORGANIC COMPOUNDS

The nomenclature is recommended by IUPAC - International Union of Pure and Applied Chemistry.

The most common is the substitute nomenclature.

The very name of the nomenclature shows that some kind of base is distinguished in the compound, in which hydrogen atoms are replaced by other atoms or groups.

According to the rules of IUPAC, the name of an organic compound is constructed:

1) from the name of the main chain that forms the root of the word and the names of functions used as prefixes or suffixes (functional nomenclature).

2) the name of the compound consists of a word, the root of which is the name of the parent structure, and the names of substitutes are indicated by prefixes (prefixes) and suffixes (substitute nomenclature).

The names of the first 10 hydrocarbons and their radicals are given in the table:

Hydrocarbons			
Methane	CH_4	Hexane	C_6H_{14}
Ethan	C_2H_6	Heptane	C_7H_{16}
Propane	C_3H_8	Octane	C_8H_{18}
Butane	C_4H_{10}	Nonan	C_9H_{20}
Pentane	C_5H_{12}	Decan	$C_{10}H_{22}$
Одновалентні радикали			
Methyl	CH_3 -	Hexyl	C_6H_{13} -
Ethyl	C_2H_5 -	Heptyl	C_7H_{15} -
Propyl	C_3H_7 -	Octyl	C_8H_{17} -
Butyl	C_4H_9 -	Nonil	C_9H_{19} -
Pentyl (amyl)	C_5H_{11} -	Decil	$C_{10}H_{21}$ -

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

A functional group is an atom or a group of atoms of a hydrocarbon nature, which determine whether a compound belongs to a certain class with certain chemical properties (functions).

A characteristic group is a functional group associated with the family structure.

To construct the name, first of all, the type of characteristic group (if any) is determined.

When there are several characteristic groups in a compound, the oldest characteristic group is selected. The order of seniority is conditionally established for characteristic groups.

Then the ancestral structure is determined, which must necessarily include the oldest characteristic group.

To correctly construct the name, it is necessary to select the main chain and number the carbon atoms in it.

The numbering of carbon atoms in the main chain begins with the end of the chain closest to the oldest group.

If there are several such possibilities, then the numbering is carried out in such a way that either the multiple bond or another substituent present in the molecule receives the lowest number.

The basis of the name of the compound is the root of the word, which denotes a terminal hydrocarbon with the same number of atoms as the main chain.

The suffix characterizes the degree of saturation: -an, if there are no multiple bonds in the molecule, -en if there are double bonds, and -in for triple bonds, for example, pentane, pentene, pentyne.

If there are several multiple bonds in the molecule, then the number of such bonds is indicated in the suffix, for example: -diene, -triene, and after the suffix, the position of the multiple bond must be indicated in Arabic numerals (for example, butene-1, butene- 2, butadiene-1,3):

$CH_3\text{-}CH_2\text{-}CH{=}CH_2$	$CH_3\text{-}CH{=}CH\text{-}CH_3$	$CH_2{=}CH\text{-}CH{=}CH_2$
бутен-1	**бутен-2**	**бутадієн-1,3**

Next, the name of the oldest characteristic group in the molecule is added to the suffix, indicating its position with a number.

Other deputies are indicated by prefixes. At the same time, they are not listed in order of seniority, but alphabetically. The position of the substituent is indicated by a number before the prefix, for example: 3-methyl; 2-chloro, etc.

$CH_3–CH_2–CHCl–CH_3$ – 2-chlorobutane

If there are several identical substituents in the molecule, then their number is indicated by a word before the name of the corresponding group (for example, dimethyl-, trichloro-, etc.). All numbers in the names of molecules are separated from words by a hyphen, and from each other by commas.

Hydrocarbon radicals have their own names.

Limit hydrocarbon radicals:

$H_3C—$

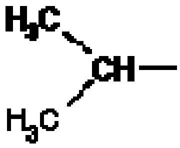
methyl

$H_3C—CH_2—$

ethyl

$H_3C—CH_2—CH_2—$

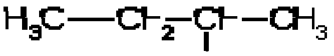
propyl



isopropyl

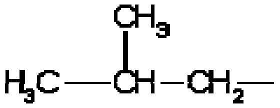
$H_3C—CH_2—CH_2—CH_2—$

butyl



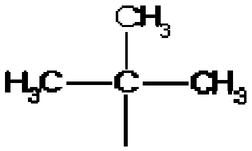
$H_3C—CH_2—CH—CH_3$

second-butyl



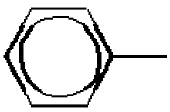
$H_3C—CH(CH_3)—CH_2—$

isobutyl

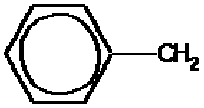


$H_3C—C(CH_3)—CH_3$

tert-butyl

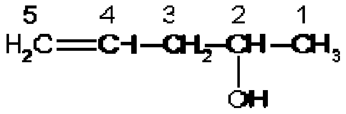


phenyl



benzyl

For example:



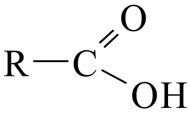
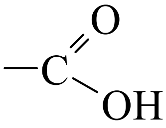
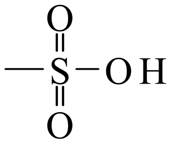
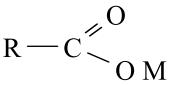
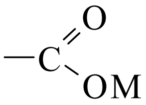
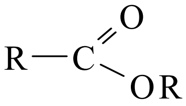
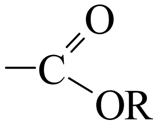
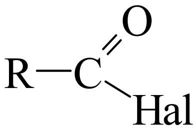
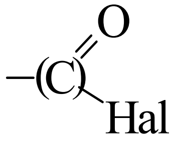
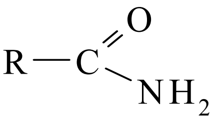
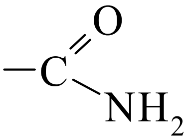
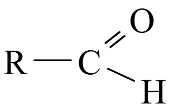
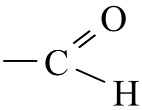
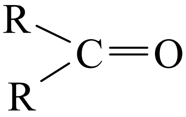
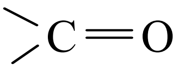
$H_2C=CH—CH_2—CH(OH)—CH_3$

penten-4-ol-2

The choice of chain is unambiguous, therefore, the root of the word is pent, followed by the suffix-en, which indicates the presence of a multiple connection; the numbering order provides the senior group (OH) with the lowest number. The full name of the compound ends with a suffix denoting the senior group (in this case, the suffix -ol indicates the presence of a hydroxyl group); the location of the double bond and the hydroxyl group is indicated by numbers.

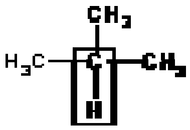
Table

The main functional groups are arranged in descending order of seniority

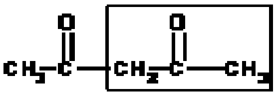
Compound class	General formula	Functional group	Marking	
			in the prefix	in the suffix
Carboxylic acids			карбокси-	-carbon acid
			–	- acid
Sulfonic acids	R–SO3H	 $-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-OH$	сульфо-	- sulfonate acid
Salts of acids			–	Metal… carboxylate
			–	Metal … ate
Complex ethers			R-окси-карбоніл	R… carboxylate
			–	R…ate
Halogen anhydrides			haloformyl-	-carbonyl halide
Amides			carbamoyl-	-carboxamide
			-	- amide
Nitriles	R–C≡N	–C≡N	cyano-	-carbonitrile
			–	-nitrile
Aldehydes			oxo-	- al
Ketones			оксо-	-on
Alcohols	R–OH	–OH	hydroxy-	-ol
Phenols	Ar–OH	–OH	phenoxy-	-ol
Amines	R–NH2	–NH2	amino-	-amine

Trivial nomenclature: is a collection of unsystematic historically formed names of organic compounds (for example: acetone, acetic acid, formaldehyde, etc.).

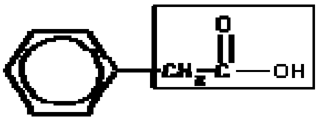
Rational nomenclature: the name of the simplest member of the homologous series is taken as the basis for the name of an organic compound. All other compounds are considered as derivatives of this compound, formed by replacing hydrogen atoms in it with hydrocarbon or other radicals. The method of such construction is illustrated by the following examples:



trimethylmethane



acetylacetone



phenylacetic acid

ISOMERY

Isomers are organic compounds with the same elemental composition.

All isomers are divided into two large classes - structural isomers and spatial isomers. Isomers corresponding to different structural formulas of organic compounds (with different order of connection of atoms) are called structural isomers. Spatial isomers have the same substituents on each carbon atom and differ only in their relative arrangement in space.

3 groups of structural isomers:

1) compounds containing different functional groups and belonging to different classes of organic compounds, for example:

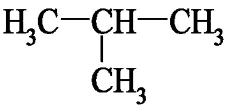
$CH_3\text{-}CH_2\text{-}NO_2$ — нітроетан

$HOOC\text{-}CH_2\text{-}NH_2$ — амінооцтова кислота (гліцин)

2) compounds that differ in carbon skeletons:

$CH_3\text{–}CH_2\text{–}CH_2\text{–}CH_3$ (C_4H_{10})

butane



$H_3C\text{—}CH(CH_3)\text{—}CH_3$

isobutane

2-methylpropane

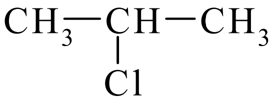
3) сполуки, що відрізняються положенням замісника або кратного зв'язку в молекулі:

$CH_2\text{=}CH\text{–}CH_2\text{–}CH_3$ — butene-1

$CH_3\text{–}CH\text{=}CH\text{–}CH_3$ — butene-2

(C_4H_8)

$CH_3–CH_2–CH_2–Cl$



$CH_3–CH(Cl)–CH_3$

(C_3H_7Cl)

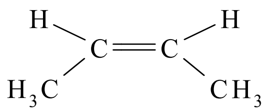
1-chloropropane 2-chloropropane

Spatial isomers (stereoisomers)

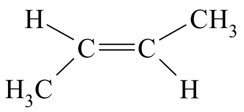
Stereoisomers can be divided into two types: geometric isomers and optical isomers.

Geometric isomerism is characteristic of compounds containing a double bond or a cycle.

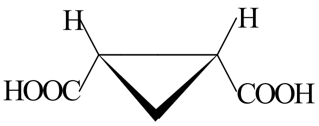
In such molecules, it is often possible to draw a conventional plane in such a way that the substituents of different carbon atoms can be on one side (cis-) or on different sides (trans-) from this plane.



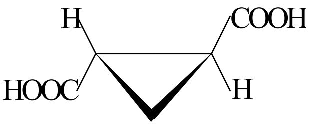
cis-butene-2



trans-butene-2



cis-1,2-cyclopropane dicarboxylic acid

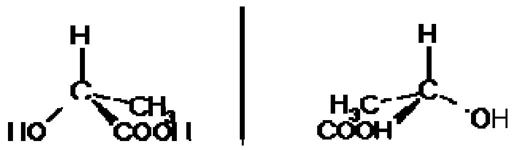


trans-1,2 cyclopropanedicarboxylic acid

Molecules whose mirror images are incompatible with each other are called **optical isomers.**

Molecules with an asymmetric center - a carbon atom connected to four different substituents - have this property.

For example, in the form of two optical isomers, there is a molecule of lactic acid CH_3-CH (OH) COOH, which contains one asymmetric center:



HOMOLOGOUS SERIES OF ORGANIC COMPOUNDS

Compounds similar in chemical properties, the composition of which differs from each other by the CH_2- group, are called homologues.

Homologs arranged in order of increasing relative molecular weight form a homologous series. The CH_2- group is called a homologous difference.

For example, a number of saturated hydrocarbons (alkanes).

Its simplest representative is CH_4 methane.

Homologues of methane are: ethane C_2H_6, propane C_3H_8, butane C_4H_{10}, pentane C_5H_{12}, hexane C_6H_{14}, heptane C_7H_{16}, etc.

The formula of any subsequent homolog can be obtained by adding to the formula of the preceding hydrocarbon the homologous difference.

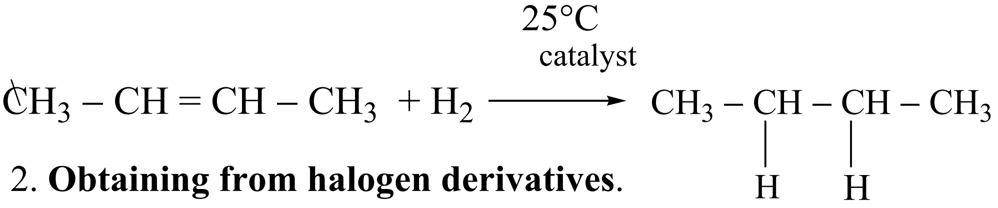
Lecture 3.

ALKANES

Alkanes are saturated hydrocarbons, the molecules of which consist of carbon and hydrogen atoms connected only by σ-bonds. Methane is the simplest representative of alkanes CH_4.

PREPARATION OF ALKANES

1. **Obtaining from unsaturated hydrocarbons**



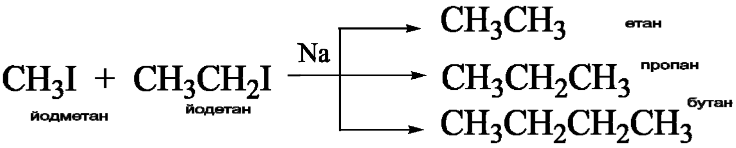
$$CH_3-CH=CH-CH_3 + H_2 \xrightarrow[\text{catalyst}]{25°C} CH_3-\underset{\displaystyle H}{\underset{|}{CH}}-\underset{\displaystyle H}{\underset{|}{CH}}-CH_3$$

2. **Obtaining from halogen derivatives**.

When haloalkanes interact with metallic sodium, alkanes with a doubled number of carbon atoms are obtained. This reaction was discovered by the French chemist S. A. Wurtz (1854) and named after him.

$$\underset{\text{iodomethane}}{2CH_3I} + 2Na \rightarrow \underset{\text{ethane}}{CH_3–CH_3} + 2NaI$$

If you take two different haloalkanes, you get a mixture different alkanes:



3. Obtaining from salts of carboxylic acids.

When fusing anhydrous salts of carboxylic acids with alkalis, alkanes are obtained, which contain one less carbon atom compared to the carbon chain of the original carboxylic acids.

$$CH_3COONa + NaOH \xrightarrow{t°} CH_4 + Na_2CO_3$$

4. **Direct synthesis from carbon and hydrogen.**

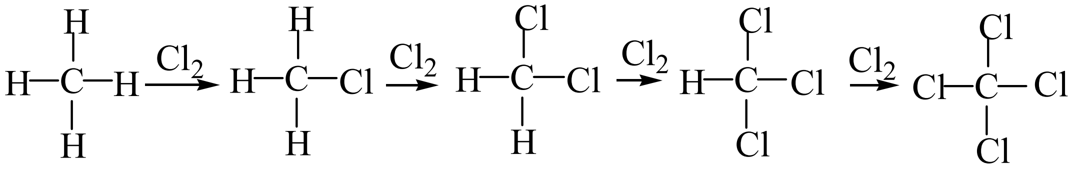
A significant amount of methane is formed in an electric arc burning in a hydrogen atmosphere.

$$C + 2H_2 \rightarrow CH_4$$

CHEMICAL PROPERTIES OF ALKANES

1. Free radical substitution reactions

Halogenation



methane chloromethane dichloromethane trichloromethane tetrachloromethane

Stages of the process:

1) Initiation

Under the action of a quantum of light, the halogen molecule disintegrates into radicals:

$$\mathrm{Cl : Cl} \xrightarrow{h\nu} \mathrm{2Cl^{\cdot}}$$

1) **Chain growth**

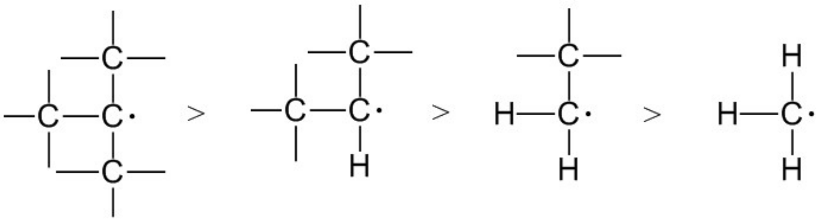
A halogen radical, approaching a hydrocarbon molecule, causes an increased movement of hydrogen in the C–H bond. This leads to the splitting off of a proton. A halogen radical combines with a proton to form a hydrohalogen (reaction a), and a new hydrocarbon radical (CH_3) appears in the reaction mixture, which attacks a new halogen molecule, forming a halogenated hydrocarbon (reaction b). The newly formed halogen radical attacks another alkane molecule, and all stages of the process are repeated (reactions c, d).

$$\mathrm{Cl^{\cdot} + H{:}CH_3 \rightarrow H{:}Cl + H_3C^{\cdot}} \qquad \text{(a)}$$
$$\mathrm{H_3C^{\cdot} + Cl{:}Cl \rightarrow H_3C{:}Cl + Cl^{\cdot}} \qquad \text{(b)}$$

$$\mathrm{H_3C{:}Cl + Cl^{\cdot} \rightarrow H_2CCl^{\cdot} + HCl} \qquad \text{(c)}$$

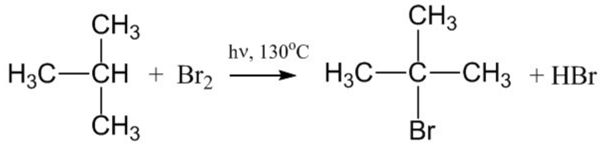
$$\mathrm{H_2CCl^{\cdot} + Cl{:}Cl \rightarrow H_2CCl_2 + Cl^{\cdot}} \qquad \text{(d)}$$

A free halogen atom attacks first of all the hydrogen atom of the tertiary carbon atom, then the secondary one, and lastly the primary one, that is, selectivity is manifested in the halogen attack.



tertiary radical > secondary radical > primary radical > methyl radical

The bromination reaction is more difficult than the chlorination reaction, requiring heating to 130 °C in addition to a quantum of light. The ratio of bromination reaction rates on tertiary, secondary and primary carbon atoms is 600:82:1, respectively. Accordingly, it can be stated that the **bromination reaction proceeds exclusively on the tertiary carbon atom.**



2-methylpropane 2-bromo-2-methylpropane

As the activity of the halogen decreases, the rate of the halogenation reaction also decreases: when iodine is used, the reaction practically does not proceed.

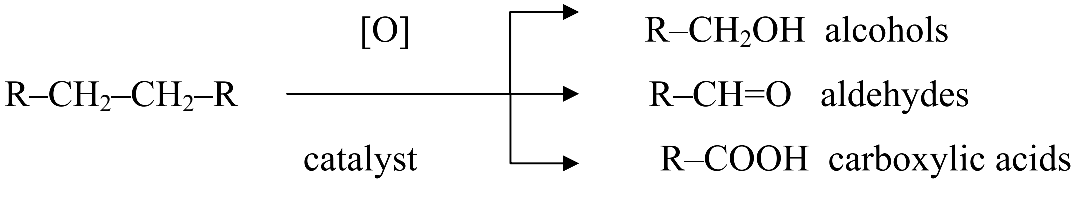
Fluorination of alkanes is practically impossible to carry out in a direct way, because the energy released during the reaction is enough to break C-C and C-H bonds, so the process proceeds with an explosion. Usually, fluorination is carried out with a mixture CoF_2 та F_2.

Nitration:

$$R\text{–}H + HNO_{3(dilute)} \rightarrow R\text{–}NO_2 + H_2O$$

Oxidation:

Oxidation with atomic oxygen occurs in stages, with the gradual formation of alcohols, aldehydes and carboxylic acids:



$R\text{–}CH_2\text{–}CH_2\text{–}R \xrightarrow[\text{catalyst}]{[O]}$ $R\text{–}CH_2OH$ alcohols; $R\text{–}CH{=}O$ aldehydes; $R\text{–}COOH$ carboxylic acids

If oxidation occurs in the presence of a stoichiometric norm or an excess of oxygen, alkanes decompose into carbon dioxide and water.

This reaction is characteristic of all classes of hydrocarbons:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 890\ \text{kJ/mol}$$

Under the conditions of the participation of a catalyst, such as nickel, at 1000 °C, the destruction of the alkane molecule with the formation of starting elements is possible:

$$CH_4 \xrightarrow{Ni, 1000°C} C + 2H_2$$

Heating to high temperatures in an oxygen-free environment leads to the detachment of hydrogen atoms with the formation of a triple bond –C≡C– :

$$2CH_4 \xrightarrow{1500°C} HC{\equiv}CH + 2H_2$$

Combustion of alkanes with the participation of a catalyst leads to partial oxidation with the formation of carbon monoxide and hydrogen:

$$CH_4 \xrightarrow{NiO,\ 700°C} CO + 3H_2$$

If alkanes are oxidized by air oxygen, which is not enough in the reaction mixture (less than the stoichiometric norm), carbon monoxide is also formed:

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2$$

This reaction is often realized in household stoves and fireplaces, if the oven door is tightly closed. This mode of burning gas or wood and the stove can lead to poisoning of people and their death.

Individual representatives. Alkanes make up the main part of oil. Oils contain slightly more alkanes with an even number of carbon atoms, which is explained by the formation of these hydrocarbons from fatty acids of animal origin through their decarboxylation (for example, palmitic and stearic acids are converted into pentadecane and heptadecane, respectively):

$$C_{15}H_{31}COOH \rightarrow C_{15}H_{32} + CO_2$$
$$C_{17}H_{35}COOH \rightarrow C_{17}H_{36} + CO_2$$

Usually, the content of alkanes in oils ranges from 20 to 50%. Some oils, so-called low-paraffin or non-paraffin, contain no more than 1-2% of these hydrocarbons, others can contain up to 80% of alkanes, and they are called paraffinic oils.

Methane CH4 is the simplest hydrocarbon, a colorless, odorless gas. Slightly soluble in water, lighter than air. When used in households and industry, an odorant with a specific "gas smell" is usually added to methane. Enrichment with odorants is done in order for a person to notice a gas leak in time.

As a result of the reaction of methane with water vapor, which flows over a Ni/Al_2O_3 catalyst at 800 – 900 °C or without a catalyst at 1400 – 1600 °C, the resulting synthesis gas can be used for the synthesis of methanol, hydrocarbons, acetic acid, acetaldehyde and other products.

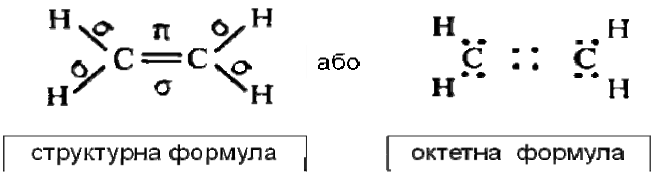
Methane is explosive at a concentration in the air of 5 % to 15 %.

Methane is the main component of natural (77 – 99 %), associated petroleum (31 – 90 %), mine and swamp gases (hence the other names of methane - swamp or mine gas).

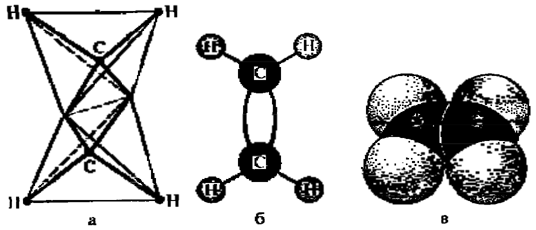
The MPC of methane in the air of the working area is 7000 mg/m^3.

Ethane C_2H_6, propane C_3H_8, butane C_4H_{10} - colorless gases (n.u.), odorless. Propane and butane are easily liquefied, which allows you to use them in everyday life as fuel (cylinder liquefied gas). Like methane, they are widely used in the chemical industry as a raw material for the production of ethylene, propylene, butadiene and other substances of important practical importance.

Lecture 4. ALKENES (OLEFINS)



Models of the spatial structure of the ethylene molecule:

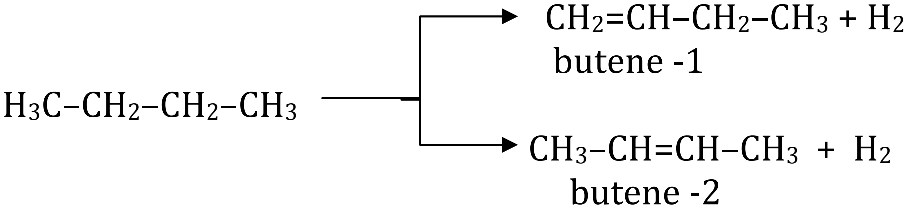


a – tetrahedral, b – ball-rod model, c – Brigleb model

PREPARATION OF ALKENES

1. Gaseous alkenes (ethylene, propylene, butylene) are isolated from oil refining gases (produced during thermal cracking). Cracking of alkanes contained in oil is an industrial way of obtaining ethylene hydrocarbons used for the production of polymers. A large number of alkenes are also formed during the pyrolysis of oil.

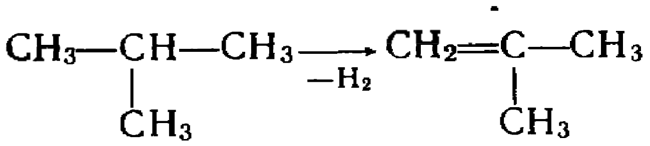
2. **Dehydrogenation of alkanes**. For example, butylene is obtained from n-butane at 560-620 °C in the presence of an aluminum-chromopotassium catalyst (K_2O-Cr_2O_3-Al_2O):



$$H_3C{-}CH_2{-}CH_2{-}CH_3 \rightarrow CH_2{=}CH{-}CH_2{-}CH_3 + H_2 \quad \text{butene -1}$$

$$H_3C{-}CH_2{-}CH_2{-}CH_3 \rightarrow CH_3{-}CH{=}CH{-}CH_3 + H_2 \quad \text{butene -2}$$

This process is even easier with isobutane:



$$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_3 \xrightarrow[-H_2]{} CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3$$

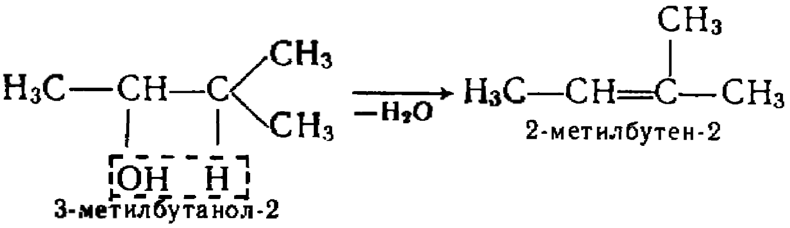
2-methylpropene-1

3. **Dehydration of alcohols** (catalysts – sulfuric or phosphoric acid, Al_2O_3, $ZnCl_2$, etc. (liquid phase method):

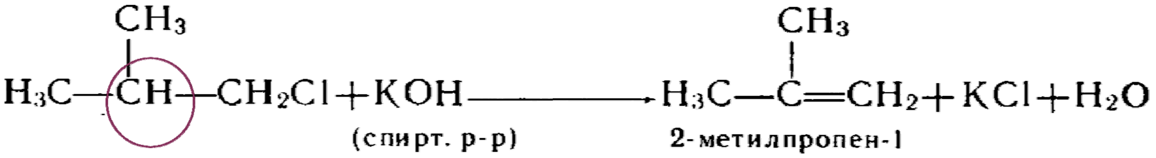
$$CH_3{-}CH_2OH + H_2SO_4 \xrightarrow{140°C,\ catalyst} CH_3{-}CH_2{-}O{-}SO_2OH + H_2O \xrightarrow{160\text{-}170°C} CH_2{=}CH_2 + H_2SO_4$$

ethanol ethyl sulfuric acid ethylene

During the dehydration of alcohols, the hydrogen atom is most easily separated from the least hydrogenated carbon atom, i.e. secondary or tertiary (the rule of A.M. Zaitsev):



4. **Dehydrohalogenation of haloalkyls** under the action of alcoholic or solid (crushed) potassium hydroxide:



$$H_3C{-}\overset{CH_3}{\overset{|}{CH}}{-}CH_2Cl + KOH \xrightarrow[\text{(спирт. р-р)}]{} H_3C{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2 + KCl + H_2O$$

2-метилпропен-1

According to rule A.M. Zaitsev hydrogen is split from the least hydrogenated carbon atom. The more stable the alkene is formed, the easier it is obtained in the dehydrohalogenation reaction.

According to stability, alkenes can be arranged in the following series:

$R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2 > RCH{=}CHR > RCH{=}CH_2 > CH_2{=}CH_2$

5. Dehalogenation of dihalogen derivatives with halogen atoms at neighboring carbon atoms (by the action of Zn or Mg):

$$R{-}CHCl{-}CH_2Cl + Zn \xrightarrow[t°]{\text{спирт}} R{-}CH{=}CH_2 + ZnCl_2$$

6. **Selective hydrogenation** in the presence of a palladium catalyst: $CH{\equiv}CH + H_2 \rightarrow CH_2{=}CH_2$

CHEMICAL PROPERTIES OF ALKENES

The chemical properties of alkenes are determined by the presence of a double bond in their structure, which consists of one σ- and one π-bond.

The π-bond is formed by the lateral overlapping of non-hybrid electron clouds of carbon. The lateral overlap has a much smaller area than the axial overlap of the σ-bond, so the π-bond is weaker than σ-bond. When approaching an alkene molecule of an electronegative element, the molecule is slightly deformed, which leads to the breaking of the π-bond. At the same time, uncompensated electrons (one from each of them) appear on carbon atoms that formed a double bond. Often, the breaking of the π-bond is associated with the action of catalysts:

1.Hydrogenation (addition of hydrogen).

Alkenes, adding hydrogen in the presence of catalysts (Pt or Pd) at normal temperature, turn into saturated or alkane hydrocarbons:

$$CH_2{=}CH_2 + H_2 \rightarrow CH_3{-}CH_3$$

2. Halogenation (addition of halogens).

Halogens are easily added to olefins. At the same time, vicinal halogen derivatives (halogens at neighboring carbon atoms) are formed:

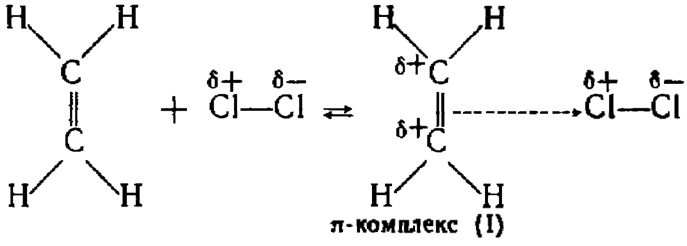
$CH_3{-}CH{=}CH_2 + Cl_2 \rightarrow CH_3{-}CHCl{-}CH_2Cl$

propene 1,2-dichloropropane

Alkene halogenation reaction mechanism:

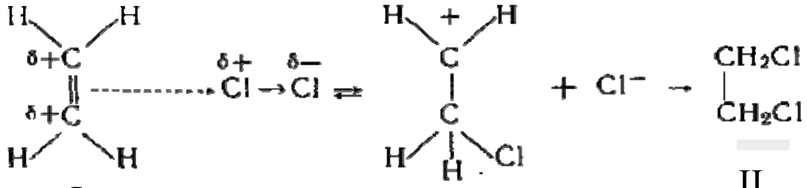
The addition of halogens, depending on the reaction conditions, can take place by either an ionic or a radical mechanism.

According to the ionic mechanism, under the influence of the π-electrons of the alkene, the polarization of the halogen molecule first occurs. The halogen molecule approaches the π-bond with its positive edge as a result of electrostatic (van der Waals) forces. At the same time, a π-complex is formed, which is a spatial associate of alkene and halogen molecules. This stage passes quickly.



The resulting π-complex (I) slowly rearranges into a halogen-containing carbonium ion. That is, at this stage: 1) the halogen molecule breaks down into ions; 2) the positively charged halogen ion is more strongly attracted by the π-bond; 3) the destruction of the π-bond and the attachment of a halogen ion to one of the carbon atoms, which were previously bound by a double bond; 4) the addition of a positive halogen ion causes the appearance of a positive charge on the C–C bond and the formation of a carbonium ion (carbcation). This stage is slow.

A negatively charged halogen ion associates quickly enough to a place in the alkene molecule that is positively charged, and, joining, compensates for this positive charge, forming the reaction product (II):



I

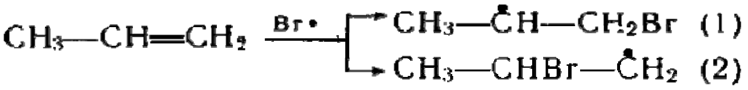
II

π-complex carbonium ion dichloroethane

Joining by the radical mechanism

Under the influence of light and elevated temperature or in the presence of peroxides, the halogen addition reaction can be radical:

$$Br_2 \xrightarrow{h\nu} 2Br\bullet \quad \text{(ініціювання реакції)}$$



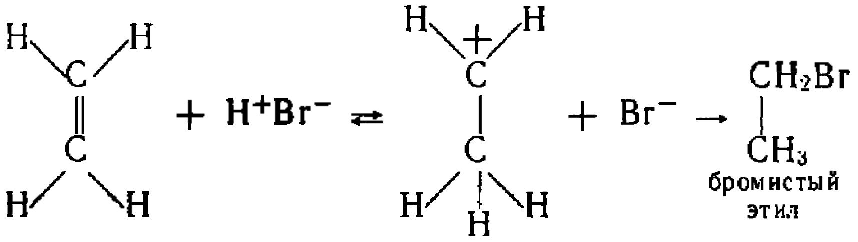
Joining by the radical mechanism proceeds through the formation of the most stable free radical. Radical (1) as a result of the combination of a free electron with the electrons of five C-H-bonds (recall that the hydrocarbon chain has a snake-like shape due to the angle between the –C–C– bonds of 109o, so the electron will be “hidden” under electron clouds of these five C–H bonds) will be more stable than radical (2). When it interacts with halogen, a dihalogen derivative is formed:

$$CH_3{-}\dot{C}H{-}CH_2Br + Br_2 \rightarrow CH_3{-}CHBr{-}CH_2Br + Br\bullet$$

Alkene halogenation reactions are widely used in industry.

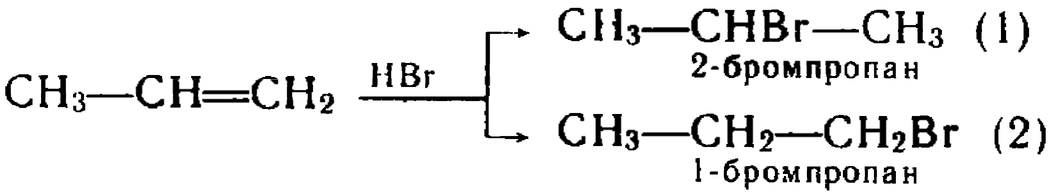
The reaction with bromine (bromine water) is used to detect unsaturated hydrocarbons (qualitative reaction).

3. **Hydrohalogenation** (addition of hydrogen halides) also occurs according to the ionic mechanism in 2 two stages:



$$CH_2=CH_2 + HBr \rightarrow CH_3\text{-}CH_2Br$$

In the case of unsymmetrical alkenes, the addition can proceed in different ways:



Markovnikov's rule: during the ionic addition of hydrogen halides to asymmetric olefins (under normal conditions), hydrogen is attached to the most hydrogenated (with the largest number of hydrogen atoms) carbon atom at the site of the double bond, and halogen - to the less hydrogenated.

Thus, the addition in the above reaction equation follows scheme (1).

4. Hydration (addition of water).

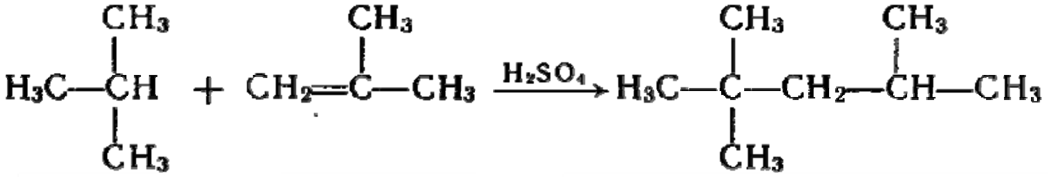
In the presence of catalysts (concentrated H_2SO_4, ZnCl, etc.), water is added to alkenes to form alcohols. The reaction proceeds according to Markovnikov's rule:

$$CH_3\text{—}CH{=}CH_2 + H\text{—}OH \xrightarrow{H_2SO_4} CH_3\text{—}CHOH\text{—}CH_3$$

$$CH_2{=}CH_2 + H_2O \xrightarrow[\text{кат.}]{\substack{H_3PO_4 \\ 280-320°C;\ \text{давл.}}} CH_3\text{—}CH_2OH$$

5. Alkylation of alkanes with alkenes.

Alkylation is a reaction by which various hydrocarbon radicals (alkyls) can be introduced into the molecules of many organic compounds.



$$H_3C-\underset{CH_3}{\overset{CH_3}{CH}} + CH_2{=}\overset{CH_3}{C}-CH_3 \xrightarrow{H_2SO_4} H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{CH}-CH_3$$

ізобутан ізобутен ізооктан (2,2 триметилпентан)

6. Polymerization reactions.

The reaction of polymerization of alkenes was first discovered by AM Butlerov. This reaction makes it possible to obtain various high-molecular compounds. example:

$$nCH_2{=}CH_2 \rightarrow [-CH_2-CH_2-]n$$

поліетилен

7. Oxidation reactions.

Alkenes are quite easily oxidized. The products formed in this case and their structure depend mainly on the nature of the starting alkenes and on the reaction conditions:

$$CH_2{=}CH_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

$$CH_2{=}CH_2 + 4KMnO_{4конц} \rightarrow 2CO_2 + 4MnO_2 + 4KOH$$

$$R-CH{=}CH-R + 2O_2 \rightarrow 2R-COOH$$

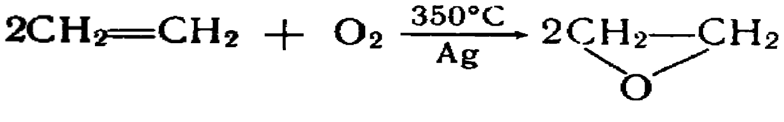
carboxylic acid

If a diluted aqueous solution of $KMnO_4$ acts on ethylene at ordinary temperature, it turns into a diatomic alcohol - ethylene glycol (Wagner reaction):

$$3CH_2{=}CH_2 + 2KMnO_4 + 4H_2O \rightarrow 3CH_2OH-CH_2OH + 2MnO_2 + 2KOH$$

етиленгліколь

When ethylene is oxidized by air oxygen in the presence of metallic silver, ethylene oxide is formed:

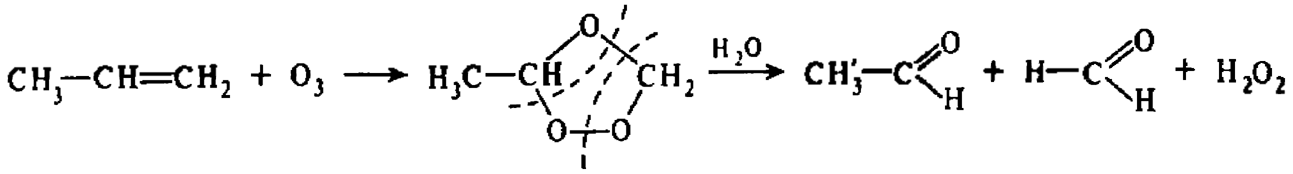


ethylene oxide

8. Ozonation reaction of alkenes.

This reaction refers to reactions of cleavage of alkenes.

As a result, a double bond is broken with the formation of ozonides, which upon hydrolysis form aldehydes or ketones (Harries reaction):



Ozonide vinegar aldehyde ant aldehyde

Ozonides are explosive substances, so they are usually not isolated in a free state, but decomposed with water in the presence of zinc, so that the aldehydes are oxidized by hydrogen peroxide.

Individual representatives

Ethylene (ethene) $CH_2 = CH_2$ is a colorless gas that burns in air with a smoky flame. It is widely used for the synthesis of various organic substances: ethyl alcohol, styrene, halogen derivatives, polyethylene, etc. Metals can be cut and welded with oxyethylene flame. Ethylene forms explosive mixtures with air.

Propylene (propene) $CH–CH = CH_2$ is a colorless gas.

It is released from the gases of oil refining. In laboratory conditions, it can be obtained by passing vapors of propyl or isopropyl alcohol over Al2Oz at 300-400 °C. Serves as a raw material for obtaining isopropylbenzene, acetone, phenol, glycerin, acrylonitrile, synthetic rubber, isopropyl alcohol, etc.

Butylenes (butene-1 and butene-2), isobutylene (2-methylpropene-1), C4H8 can be isolated from gases of cracking and pyrolysis of oil and its tailings, as well as from natural gases.

Butene-1 is used to obtain butadiene-1,3 and isooctane. **Butene-2** is used as a medium for polymerization of butadiene-1,3. **Isobutylene** produces isooctane and isoprene.

Alkenes are used as monomers for the production of high molecular compounds that are widely used in almost all industries.

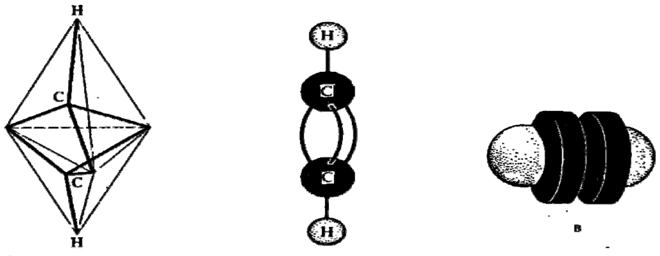
Lecture 5.

ALKYNES

$H-C\equiv C-H$ structural formula

$H:C{:}{:}{:}C:H$ electronic formula

Models of the spatial structure of the acetylene molecule:



a – tetrahedral, b – ball-rod model, c – Brigleb model

PREPARATION OF ALKYNES

1. When decomposing calcium carbide with water, which, in turn, is obtained by calcining a mixture of coal and quicklime in electric furnaces:

$$3C + CaO \xrightarrow{2500°C} CaC_2 + CO$$
$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$$

2. From dihalogen derivatives containing two halogen atoms at one carbon atom or two adjacent ones, by the action of an alcoholic alkali solution:

$$CH_3{-}CH_2{-}CHCl + 2KOH \rightarrow \underset{\text{пропін}}{CH_3{-}C{\equiv}CH} + 2KCl + 2H_2O$$

3. **From natural gas or oil hydrocarbons** during their thermal or electric cracking:

$$2CH_4 \xrightarrow{1500°C} C_2H_2 + 3H_2$$

or during the pyrolysis of a mixture of methane with its homologues:

$$C_2H_6 \xrightarrow{1200°C} C_2H_2 + 2H_2$$

4. Alkylation of metal derivatives of acetylene:

CHEMICAL PROPERTIES OF ALKYNES

1. 1. Hydrogenation (addition of hydrogen). In the presence of catalysts (Pt, Pd, Ni) there is a process of reduction of alkynes into alkenes and alkanes:

$$HC\equiv CH + H_2 \longrightarrow H_2C{=}CH_2 + H_2 \longrightarrow H_3C{-}CH_3$$

acetylene ethene ethane

2. 2. Halogenation of acetylene proceeds at a slower rate than the same reaction with ethylene:

$$HC\equiv CH + Br_2 \longrightarrow BrHC{=}CHBr + Br_2 \longrightarrow Br_2HC{-}CHBr_2$$

1,2-dibromoethane 1,1,2,2-tetrabromoethane

3. 3. Hydrohalogenation (addition of hydrogen halides).

$$HC\equiv CH + HCl \longrightarrow H_2C{=}CHCl + HCl \longrightarrow H_3C{-}CHCl_2$$

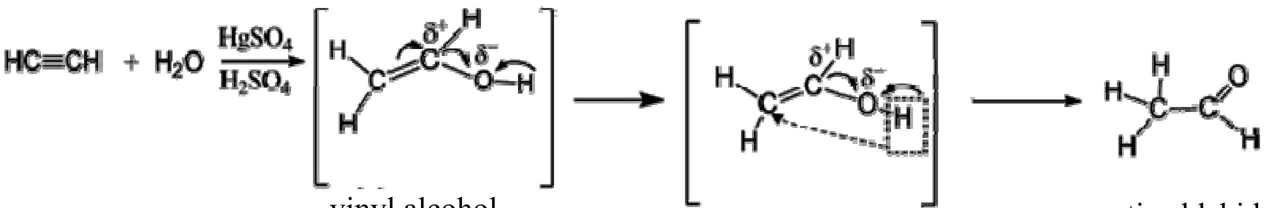
chloroethene
(vinyl chloride)

1,1 dichloroethane

This reaction is easier with olefins. The second hydrogen halide molecule is attached according to Markovnikov's rule.

4. Addition of water (reaction of M. G. Kucherov, 1881):

The catalyst for this reaction is mercury (II) salt. An unstable intermediate compound (vinyl alcohol) rearranges into acetaldehyde.



vinyl alcohol

acetic aldehide

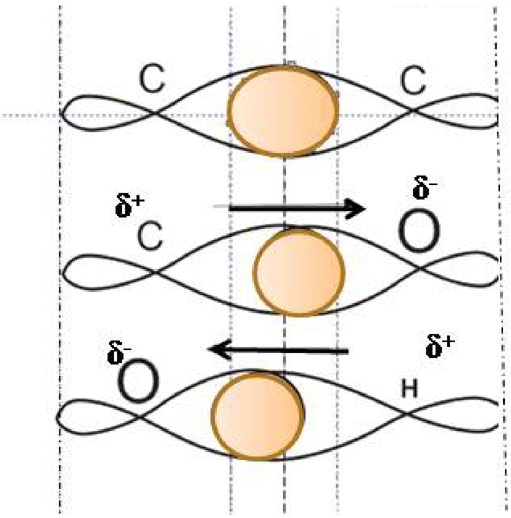
Reaction mechanism: dissociated water ions (H+ and OH–) provoke a (slight) deformation of the acetylene molecule, as a result of which one π-bond is broken and uncompensated electrons appear on the carbon atoms. These electrons are joined by hydrogen and the OH group. The result of such joining is the formation of an intermediate complex (vinyl alcohol) - a very unstable substance due to the fact that two functional groups are attached to one carbon atom: a double bond and an electronegative oxygen. The molecule tries to release the excess energy that appeared during the approach and attachment of the water molecule. This can happen in two ways: by restructuring the structure of the resulting molecule, or by its reaction with some reagent.

In our case, the structure of the molecule is rearranged. The diagram shows the redistribution of the electron density of O-H, C-O, C=C bonds. This is explained by the fact that oxygen is an electronegative element that attracts the electron density (the overlapping zone of electron clouds) of bonds formed with it. Therefore, a partial negative charge appears on oxygen, and a positive charge on other elements. The δ+ mark shows that the element has insufficient electron density.

In our case, oxygen attracts the electron density of the O-H bond and the C-O bond, as a result of which hydrogen acquires increased mobility, and a δ+ charge is formed on carbon. This positive charge can be compensated by a shift in the electron density of the C=C double bond, but this shift leads to the destruction of the second π-bond and the formation of uncompensated electrons on the two carbon atoms. These electrons cannot combine again into a π-bond, because part of the energy has already been spent during the breaking of this π-bond. Therefore, the only way out is to detach hydrogen from the OH group and attach it to another carbon atom. After hydrogen removal, there are uncompensated electrons on carbon and oxygen, which can combine to form a new π bond between carbon and oxygen. Thus, an aldehyde is formed from an unsaturated alcohol.

The processes of shifting the electron density of OH, C-O, C=C bonds are shown in the figure:

Overlapping zones of electron clouds of σ-bonds in the carbon chain

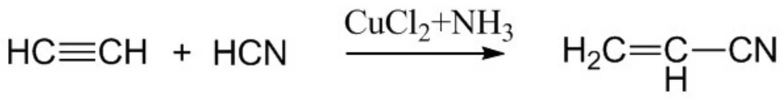


Non-polar C–C bond: cloud overlap zone in the middle

The electron density of the C–O bond (cloud overlap zone) shifts toward electronegative oxygen; a partial positive charge δ+ is formed on carbon.

The electron density of the O–H bond (cloud overlapping zone) shifts toward electronegative oxygen, and hydrogen acquires increased mobility.

5. **Addition of hydrocyanic acid**:

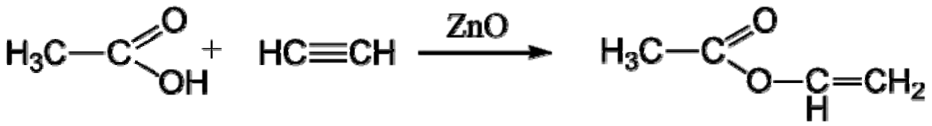


$$HC\equiv CH + HCN \xrightarrow{CuCl_2+NH_3} H_2C=\underset{H}{C}-CN$$

acrylonitrile

Acrylonitrile is a very important product, which as a monomer is used to obtain a synthetic fiber - nitron.

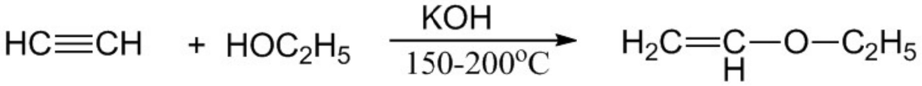
6. Addition of organic acids and alcohols:



acetic acid vinyl acetate

Ether - vinyl acetate is used as a monomer to obtain polyvinyl acetate.

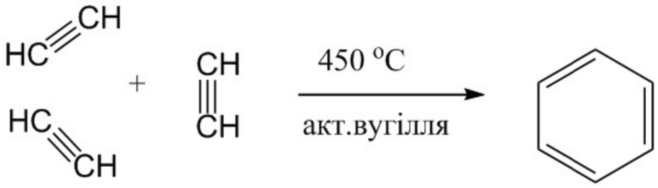
When acetylene interacts with alcohol, simple vinyl ethers are formed (AE Favorskyi):



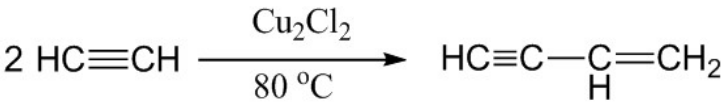
$$HC\equiv CH \quad + \; HOC_2H_5 \xrightarrow[150\text{-}200^{o}C]{KOH} H_2C=\underset{H}{C}-O-C_2H_5$$

ethylvinylether

7. Polymerization reactions. Acetylene hydrocarbons, depending on the reaction conditions, can form various polymerization products:



benzene



$$2\ HC\equiv CH \xrightarrow[80\ ^{o}C]{Cu_2Cl_2} HC\equiv C-\underset{H}{C}=CH_2$$

vinyl acetylene

Cyclooctatetraene

8. Substitution reactions. Hydrogen atoms in acetylene can be replaced by metal. This reaction is called a metalation reaction. As a result, metal derivatives of acetylene - acetylenides are formed.

This happens because the hydrogen atoms in the acetylene molecule have slightly acidic properties. This is explained by the fact that the electronegativity of the carbon atom depends on its valence state and varies in the series: C (sp) > C (sp^2) > C (sp^3)

Thus, hydrogen atoms in acetylene and its monoalkyl derivatives acquire some mobility in contrast to alkenes and alkanes:

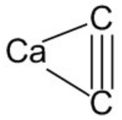
$$\overset{\delta+}{H}\rightarrow\overset{\delta-}{C}\equiv\overset{\delta-}{C}\leftarrow\overset{\delta+}{H}$$

Acetylene is a weaker "acid" than water, but stronger than ammonia. For example, when an ammonia solution of silver hydroxide acts on acetylene, silver acetylenide is formed:

$$HC\equiv CH + 2[Ag(NH_3)_2]OH \longrightarrow AgC\equiv CAg + 4NH_3 + 2H_2O$$

silver acetylenide

Calcium carbide can also be considered as a product of replacing two hydrogen atoms in acetylene with calcium:



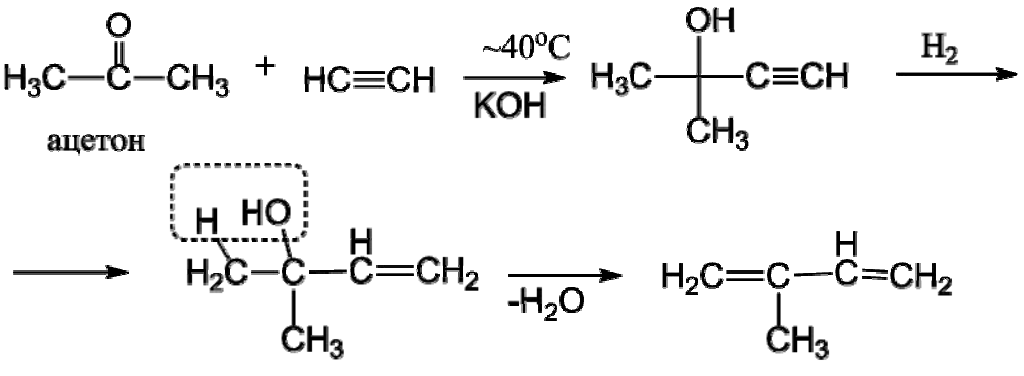
9. Oxidative polycondensation of acetylene can be explained by increased mobility of hydrogen atoms in its structure:

$$n\,HC\equiv CH \xrightarrow[CuCl_2]{O_2} \left[-C\equiv C-\right]_n + H_2O$$

carbine

Carbine is a high-molecular compound with exceptional heat resistance (it can withstand heating up to 2300°C). In this compound, carbon is in the state of sp-hybridization (in diamond - sp3, in graphite - sp^2).

10. Condensation reactions with carbonyl compounds. For example, isoprene can be obtained from acetylene and acetone (reaction of A.E. Favorsky):



isoprene

11. Oxidation reactions. Acetylene hydrocarbons are easily oxidized with partial or complete cleavage of the molecule by the triple bond (for example, under the action of $KMnO_4$ in a neutral environment):

$$3CH{\equiv}CH + 8KMnO_4 \rightarrow \underset{\text{potassium oxalate}}{3K_2C_2O_4} + 8MnO_2 + 2KOH + 2H_2O$$

$$R{-}C{\equiv}C{-}R' \xrightarrow{[O],\ H_2O} R{-}COOH + R'{-}COOH$$

Lecture 6.

ALKADIENES (DIOLEFINS)

Alkadienes are hydrocarbons that contain two double bonds in the hydrocarbon chain.

According to the systematic nomenclature, diene hydrocarbons are called the same as ethylene hydrocarbons, replacing the suffix -ene with -diene (two double bonds). The position of each double bond is indicated by a number. Numbering is done so that these numbers have a smaller serial number.

They distinguish:

- alkadienes with isolated bonds, that is, those that are located far from each other (through 2 or more σ-bonds)

$$H_3C–CH=CH–CH_2– CH_2– CH=CH–CH_3$$

octadiene-2,6

- alkadienes, in the structure of which one carbon atom forms two double bonds (cumulative):

$$H_3C–CH_2– CH= C=CH–CH_3$$

hexadiene – 3,4

- alkadienes, in which double bonds are located through one σ-bond (conjugate or conjugated bonds):

$$C_2H=CH–CH=CH_2$$

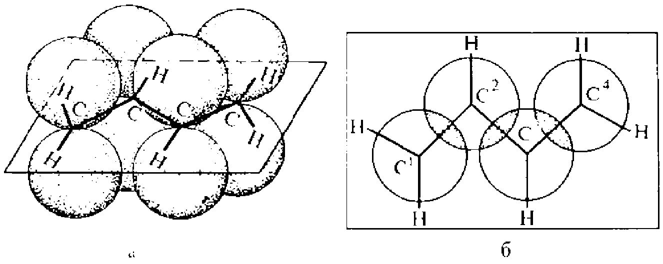
butadiene-1,3

divine

Divinyl is a very important substance for industry, therefore, the information on the production methods and chemical properties of divinyl and its homologue, isoprene, is considered below.

Double bonds are formed from one σ-bond and π-bond, as was already discussed in the lecture "Olefins". A feature of the structure of conjugated alkadienes is the presence of a number of bonds: π-σ-π. (=CH-CH=..) Considering that the π-bond is formed as a result of the lateral overlap of non-hybrid clouds (large, bulky), a partial overlap of these clouds (albeit very weak) over the σ-bond is observed. In this way, the so-called π-conjugation of electron clouds in divinyl is formed (Fig.).

The presence of π-conjugation in the molecule of conjugated alkadienes ensures not only the stability of their structure, but also increased chemical activity: in the case of the approach of an electronegative reagent, the alkadiene molecule is slightly deformed, resulting in the breaking of both double bonds and the formation of uncompensated electrons on all four carbon atoms in the conjugation zone.

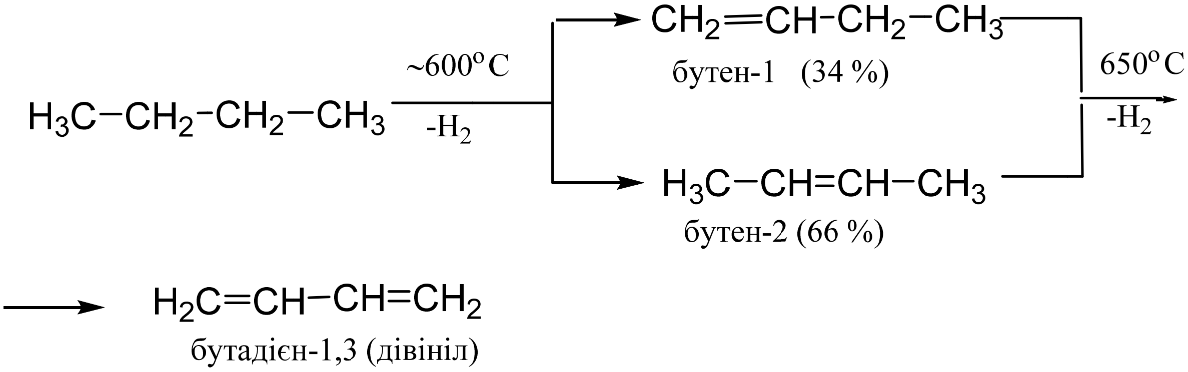


Formation of π-bonds in the 1,3-butadiene molecule
due to overlapping of 2p-orbitals:
a — side view; b — top view

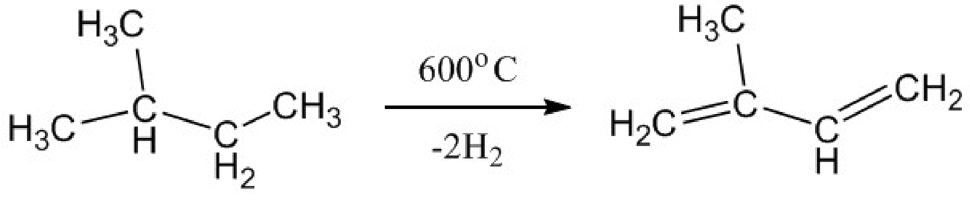
PREPARATION OF ALKADIENES

1. Divinyl and isoprene in small quantities can be isolated from the products of oil pyrolysis.

2. Dehydrogenation. The main industrial method of obtaining 1,3-butadiene (divinyl) is the dehydrogenation of n-butane or n-butylene over a chromium-aluminum (chromium oxide on aluminum oxide) catalyst:

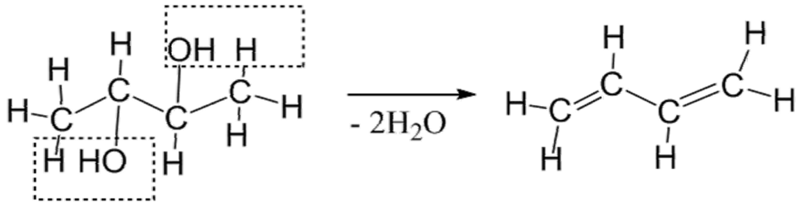


Isoprene is obtained by dehydrogenation of isopentane or isoamilenes (the pentane-pentene fraction of petroleum cracking gases):

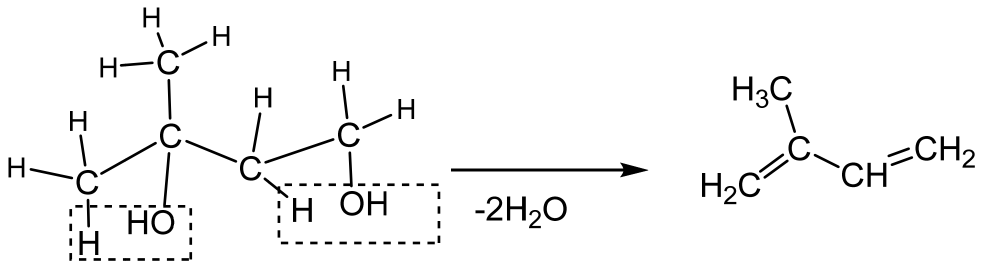


The production of isoprene is a more complicated process than the production of 1,3-butadiene, because different isomers can be obtained under dehydrogenation conditions.

3. Dehydration of glycols:

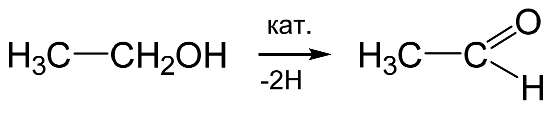


бутандіол-1,3 бутадієн-1,3



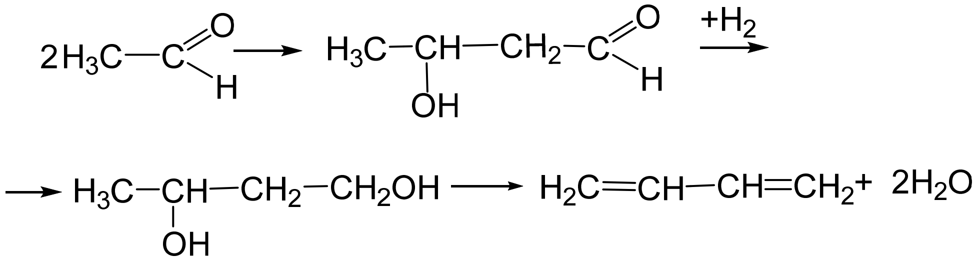
3-метилбутандіол-1,3 2-метилбутадієн-1,3 ізопрен

4. Lebedev's method is the basis of the industrial synthesis of divinyl. The process proceeds with the use of dehydrating-dehydrogenating catalysts (MgO-ZnO) at 450°C:



$$H_3C-CH_2OH \xrightarrow[-2H]{кат.} H_3C-C(=O)H$$

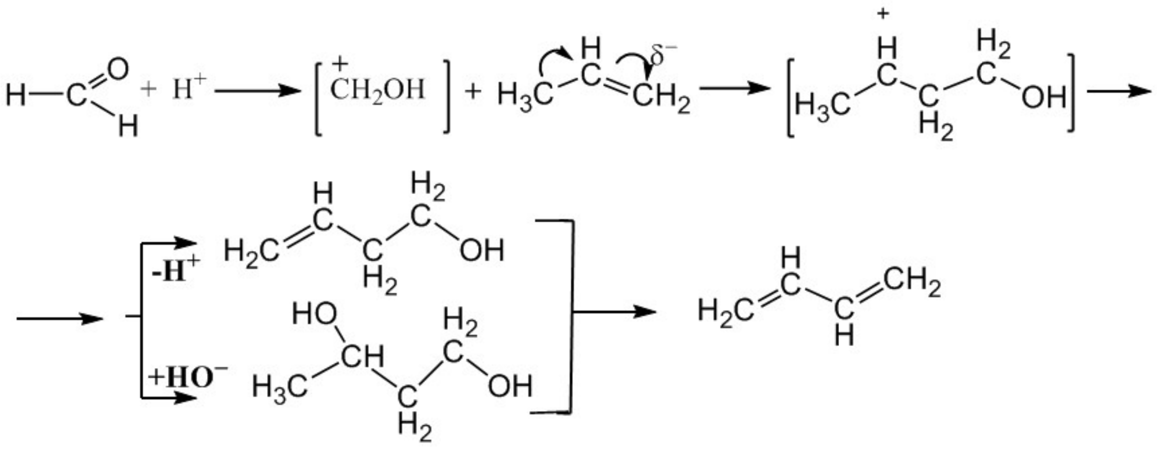
acetic aldehyde



$$2H_3C-C(=O)H \longrightarrow H_3C-\underset{OH}{CH}-CH_2-C(=O)H \xrightarrow{+H_2}$$

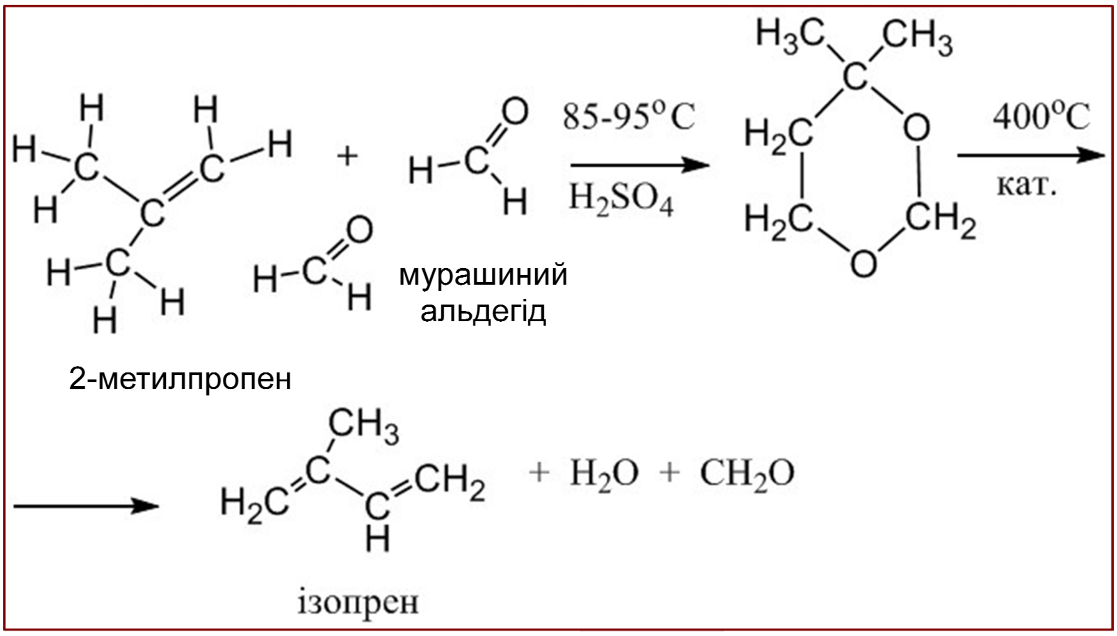
$$\longrightarrow H_3C-\underset{OH}{CH}-CH_2-CH_2OH \longrightarrow H_2C=CH-CH=CH_2 + 2H_2O$$

5. Prince's Method:

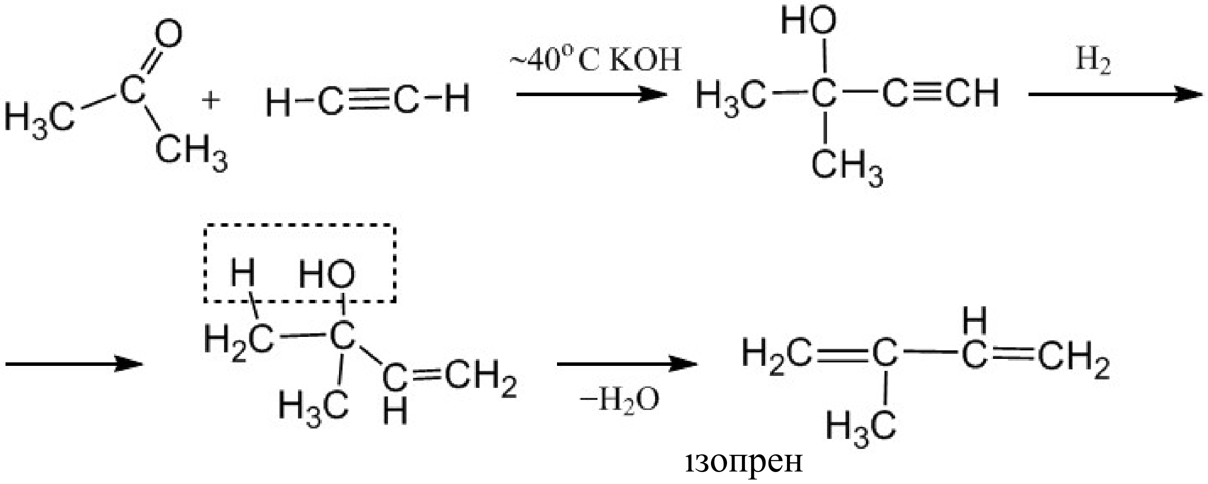


Isoprene is obtained by the same reaction in industry (Farber-Nemtsov method).

6. Method of M.I. Farber, M.S. Nemtsov:



7. Favorsky's method:

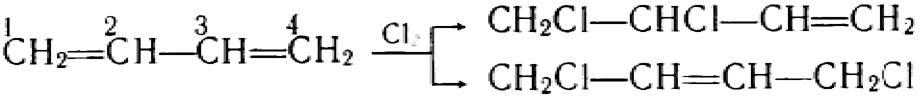


CHEMICAL PROPERTIES OF ALKADIENES

1.Реакції приєднання:

$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 + 2Br_2 \rightarrow CH_2Br{-}CHBr{-}CH_2{-}CH_2{-}CHBr{-}CH_2Br$$

гексадієн-1,5 1,2,5,6-тетрабромгексан



$$\overset{1}{C}H_2{=}\overset{2}{C}H{-}\overset{3}{C}H{=}\overset{4}{C}H_2 \xrightarrow{Cl_2} \begin{cases} CH_2Cl{-}CHCl{-}CH{=}CH_2 & \text{1,2- accession} \\ CH_2Cl{-}CH{=}CH{-}CH_2Cl & \text{1,4- accession} \end{cases}$$

$$CH_2{=}CH{-}CH{=}CH_2 + 2H \rightarrow CH_3{-}CH{=}CH{-}CH_3$$

butene-2

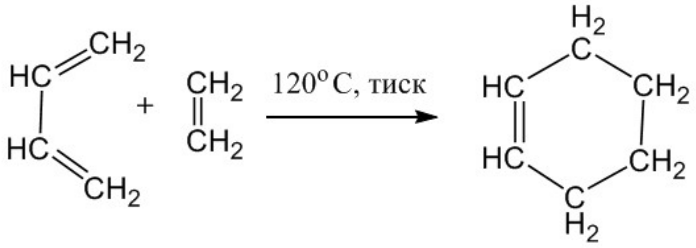
$$CH_2{=}CH{-}CH{=}CH_2 + 2H_2 \xrightarrow{Ni} CH_3{-}CH_2{-}CH_2{-}CH_3$$

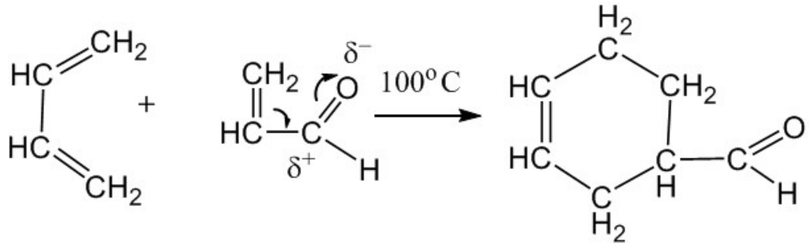
n-butane

$$CH_2{=}CH{-}CH{=}CH_2 + H_2 \xrightarrow{Ni} CH_3{-}CH_2{-}CH{=}CH_2$$

butene-1

2. Diene syntheses





acrolein tetrahydrobenzoic aldehyde

1. Polymerization reactions

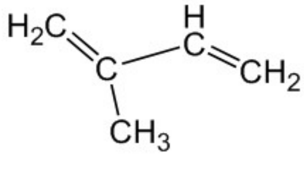
$$\overset{1}{C}H_2{=}\overset{2}{C}H{-}\overset{3}{C}H{=}\overset{4}{C}H_2 + \overset{1}{C}H_2{=}\overset{2}{C}H{-}\overset{3}{C}H{=}\overset{4}{C}H_2 + \ldots + \rightarrow$$

$$\rightarrow \ldots {-}\overset{1}{C}H_2{-}\overset{2}{C}H{=}\overset{3}{C}H{-}\overset{4}{C}H_2{-}\overset{1}{C}H_2{-}\overset{2}{C}H{=}\overset{3}{C}H{-}\overset{4}{C}H_2{-} \ldots$$

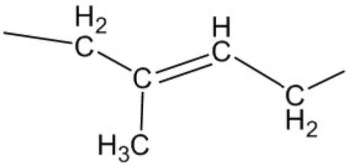
Individual representatives

Butadiene-1,3 (divinyl) CH2=CH-CH=CH2 is a colorless gas with a characteristic unpleasant smell. It is one of the most important monomers for the production of synthetic rubbers and latexes, plastics and other organic compounds.

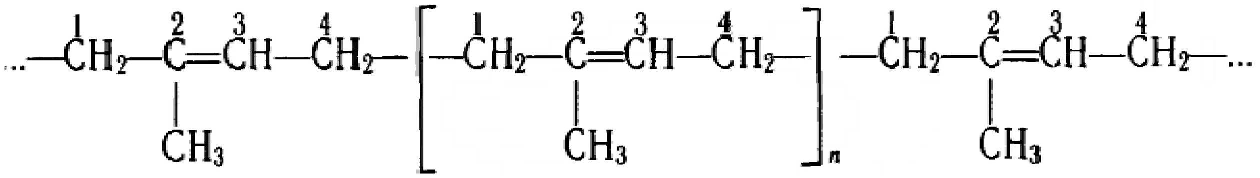
2-Methylbutadiene-1,3 (isoprene) is a colorless liquid with a boiling point = 34.10 oC. It is the main structural unit of natural (natural) rubber and other compounds. It serves as a monomer for obtaining synthetic rubber.



Rubber is a high-molecular compound that serves as the basis for the production of various rubber products. Rubbers are divided into two broad classes: natural rubbers and synthetic rubbers. The structural unit of natural rubber is the isoprene group:



Such groups combine in the 1,4-position and form a cis-structure rubber macromolecule:



$$\ldots-\overset{1}{C}H_2-\underset{\underset{CH_3}{|}}{\overset{2}{C}}=\overset{3}{C}H-\overset{4}{C}H_2-\left[-\overset{1}{C}H_2-\underset{\underset{CH_3}{|}}{\overset{2}{C}}=\overset{3}{C}H-\overset{4}{C}H_2-\right]_n-\overset{1}{C}H_2-\underset{\underset{CH_3}{|}}{\overset{2}{C}}=\overset{3}{C}H-\overset{4}{C}H_2-\ldots$$

Synthetic rubbers

Butadiene rubbers are the most common type of synthetic rubbers. They are obtained by polymerization of butadiene-1,3 (divinyl) using peroxide catalysts:

Use - tire production, rubber shoes.

There are: isoprene rubber, butadiene-styrene rubber, butadiene-nitrile rubber, chloroprene rubber or polychloroprene (nairite).

Lecture 7.

ALICYCLIC CARBOHYDRATES

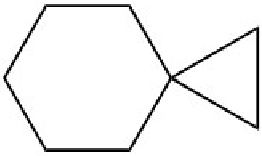
Alicyclic compounds are hydrocarbons, the molecules of which contain one or more cycles (rings) of a non-aromatic nature. In terms of properties, they are similar to the corresponding compounds of the aliphatic series.

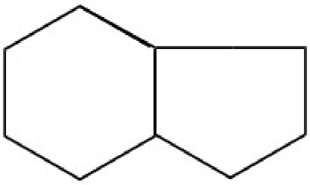
The term "alicyclic" means aliphatic cyclic hydrocarbons. But despite the great similarity between aliphatic and alicyclic compounds, there are some peculiarities in the behavior of the latter, which can be explained by the presence of a cyclic structure in them.

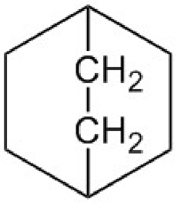
Alicyclic compounds differ among themselves in the size of the cycle, the length and structure of the side chains, and their position.

A simple alicycle is three-membered, but cycles with the number of carbon atoms up to 30 or more are known.

Polyalicyclic compounds are distinguished by the mutual arrangement of cycles in the molecule. They are divided into **spirane compounds, or spirals (I); compounds with condensed cycles (I I) and bridged (III):**





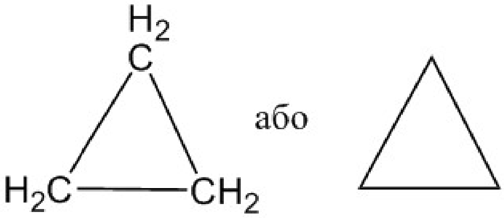


I II III

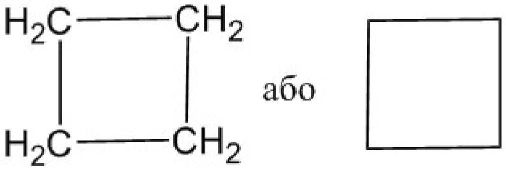
, saturated alicyclic compounds (cycloalkanes) and unsaturated (cycloalkenes) containing one or more multiple bonds are distinguished .

CYCLOALKANES

Cycloalkanes are otherwise called polymethylene hydrocarbons (which consist of methylene groups linked together in a ring), or **naphthenes,** as derivatives of cyclopentane and cyclohexane are contained in some types of oil.



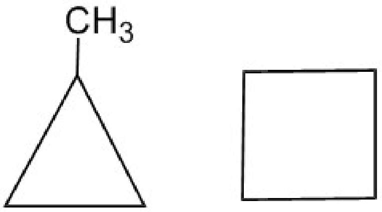
Циклопропан



циклобутан

циклопентан

STRUCTURAL ISOMERS OF CYCLOALKANS



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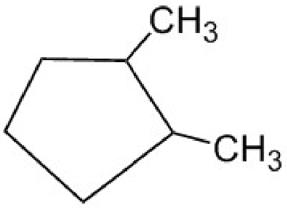
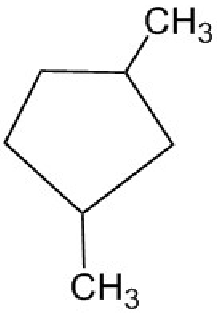
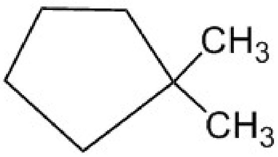


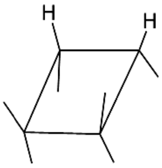
1,2-диметил-
циклопентан

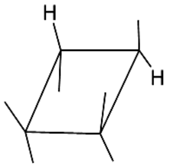


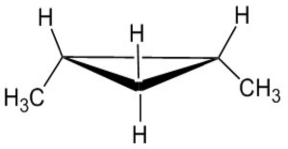
1,3-диметил-
циклопентан

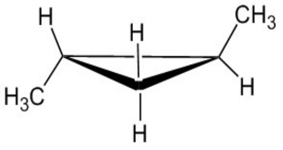


1,1-диметил-
циклопентан









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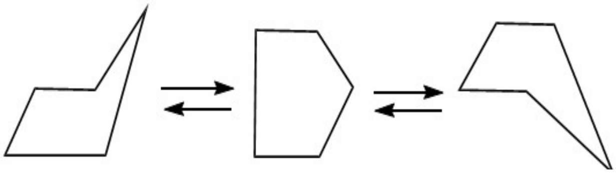

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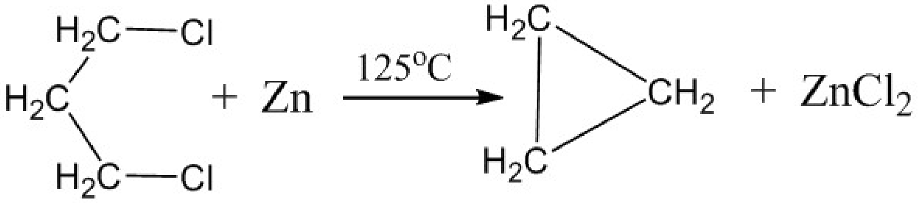
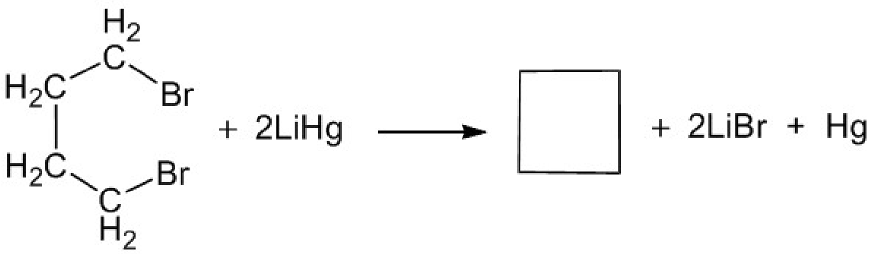
PREPARATION OF CYCLOALKANES

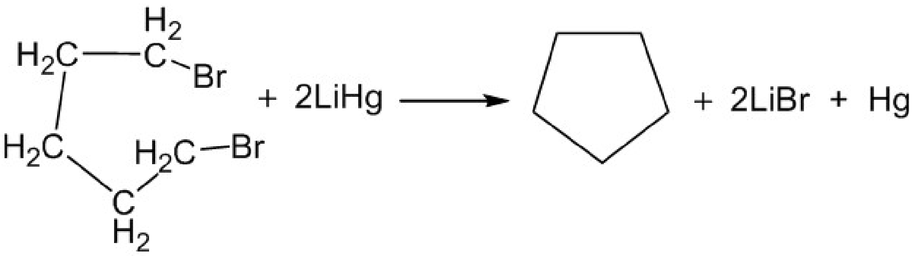
1. Lower cycles are synthesized from dihalogen derivatives. For example, the action of zinc dust in an alcoholic solution on 1,3-dichloropropane keeps cyclopropane:



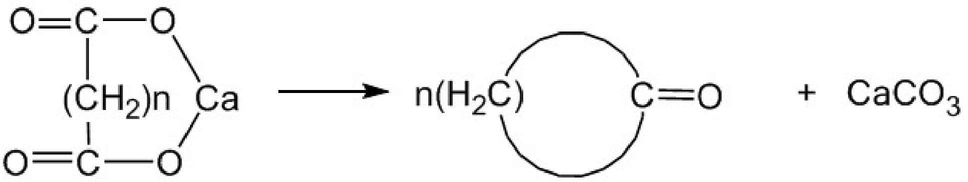
1,3-дихлорпропан циклопропан

2. 1,4-Dibromobutane and 1,5-dibromopentane in dioxane (or tetrahydrofuran) **in the presence of lithium amalgam** form cyclobutane and cyclopentane, respectively (Conner, Wilson, 1967):



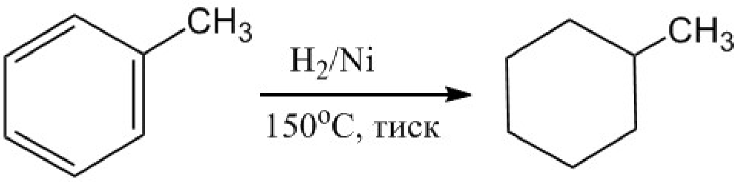


3. **Cycles with five or more carbon atoms** can be obtained by pyrolysis of calcium or thorium salts of dibasic acids:



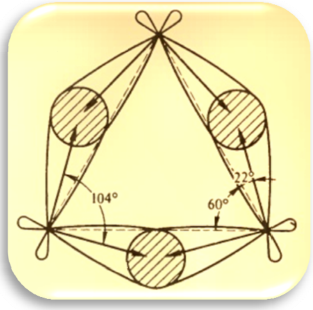
The cyclic ketone formed is reduced to the corresponding hydrocarbon.

4. **Cyclohexane and its homologues** are usually obtained from petroleum or hydrogenation of benzene and its derivatives:

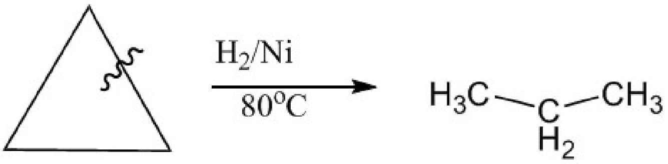


толуен метилциклогексан

CHEMICAL PROPERTIES OF CYCLOALKANS



σ -bonds and the state of carbon atoms in cycloalkanes and in boundary hydrocarbons are different. The overlapping of electron clouds in cycloalkanes does not occur along the C—C axis, but in the area slightly shifted outwards due to the mutual repulsion of these clouds. At the same time, the bond tension decreases (the angle between C–C bonds increases from 60 ° in cyclopropane to 104° in cyclohexane), but the bonds acquire a partially unsaturated character due to the location of the maximum electron density outside the C– bond line C, which resembles π-bonds in alkenes. In cyclobutane, the σ-bonds are also bent relative to the C-C axis, but this deviation is much smaller.



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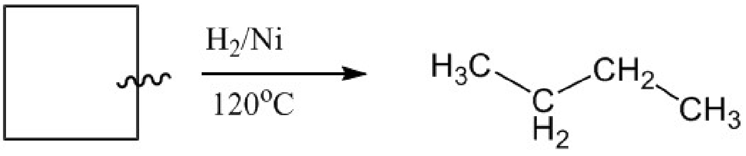
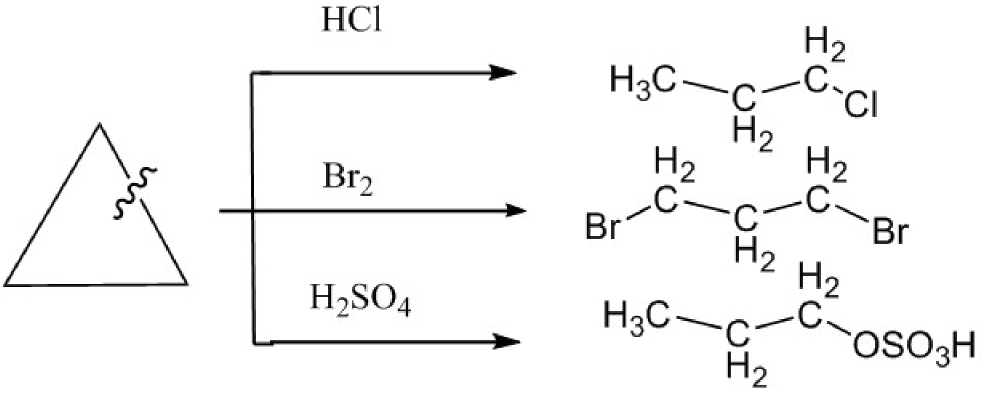
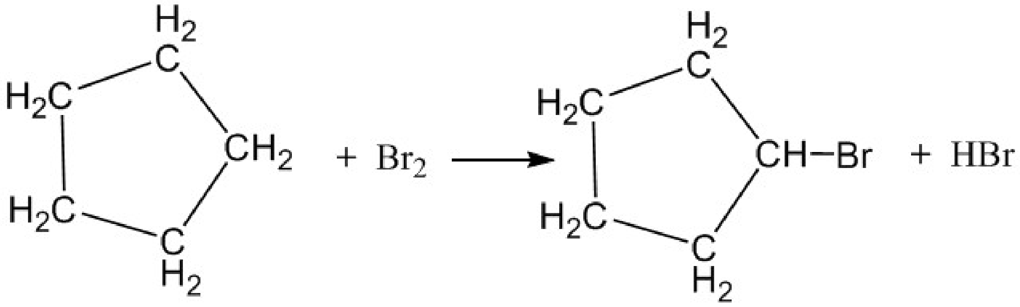


циклобутан бутан

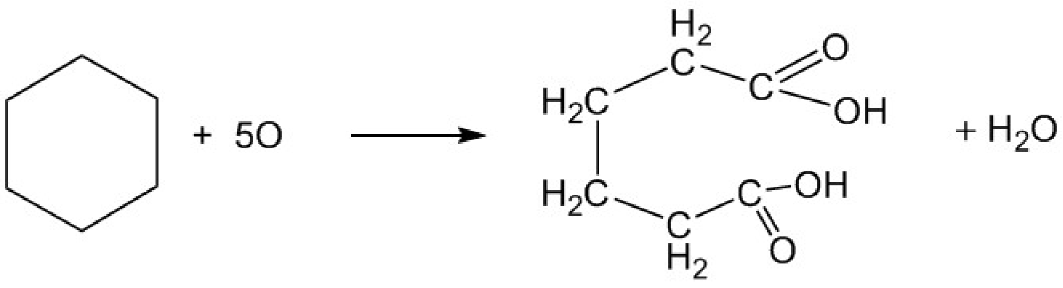
Cyclopropane and cyclobutane can exhibit properties of unsaturated hydrocarbons. This is explained by the instability of the cycles, which are easily opened when interacting with some reagents. For example, cyclopropane at 80°C and cyclobutane at 120°C are hydrogenated in the presence of a Ni-catalyst with C–C bond cleavage.



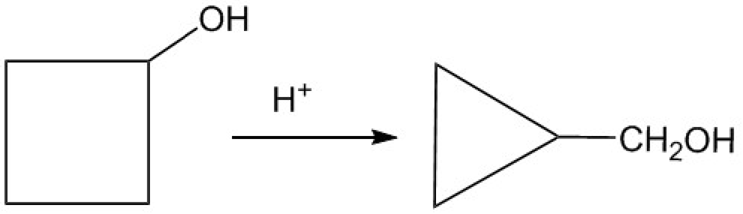
2. **Cycloalkanes with five or more** carbon atoms in the ring are characterized by the usual substitution reactions:



3. Cycloalkanes are relatively easily oxidized, forming dibasic carboxylic acids with the same number of carbon atoms:



4. Cycloalkanes are able to isomerize with ring expansion or contraction, for example:



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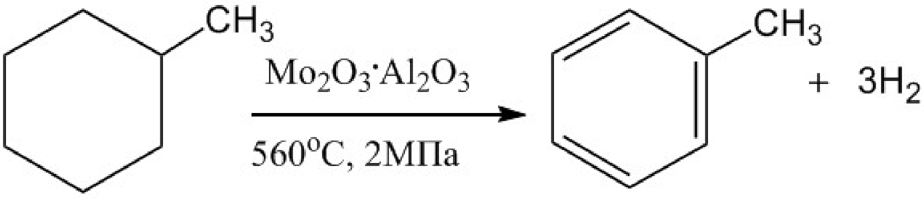
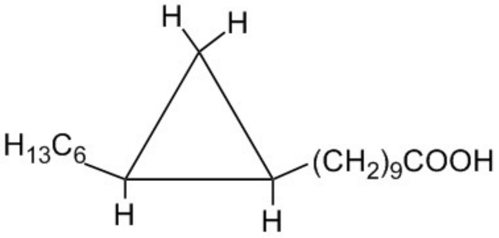
INDIVIDUAL REPRESENTATIVES OF CYCLOALKANS

Cyclopropane C_3H_6 is a gaseous substance with a boiling point of -34 °C. It is used as an anesthetic.

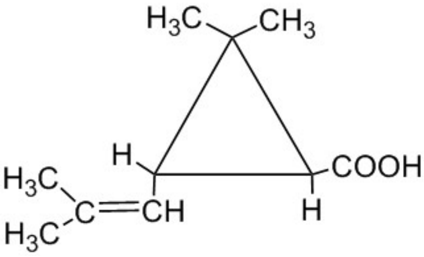
Cyclohexane C_6H_{12} is a liquid with a boiling point of 81 °C. It is used as a solvent. Cyclohexane and its homologues, which are called hydroaromatic hydrocarbons, can be transformed into aromatic compounds at high temperature in the presence of catalysts (N.D. Zelinsky, 1911):



The cyclopropane ring is noted in lactobacillus acid (lipoid fraction of Lactobacillus arabinosus), chrysanthemum acid (pyrethrin - the active principle of the Dalmatian powder insecticide isolated from Dalmatian chamomile Chrysanthemum cinerarifolium):

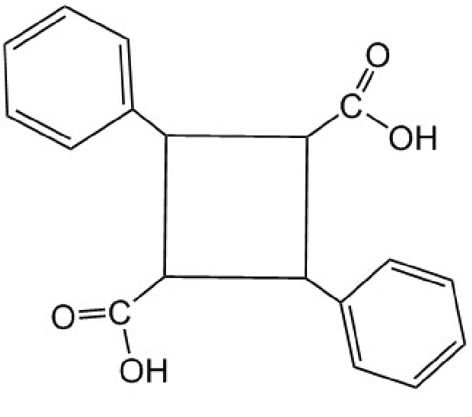


лактобацилова кислота

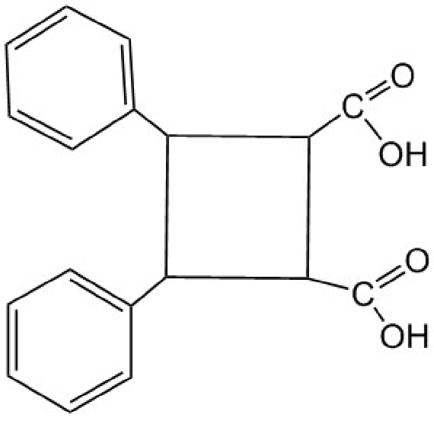


хризантемова кислота

The isomeric truxic and truxylic acids are formed during the hydrolysis of cocaine-associated alkaloids from Coca leaves:



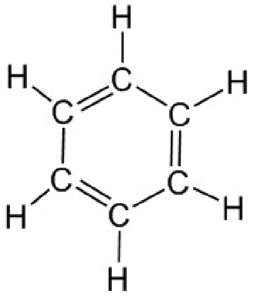
труксілова кислота

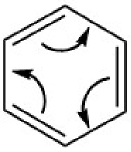


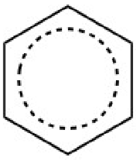
труксінова кислота

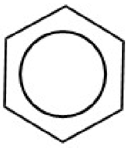
Lecture 8.

AROMATIC COMPOUNDS (ARENES)

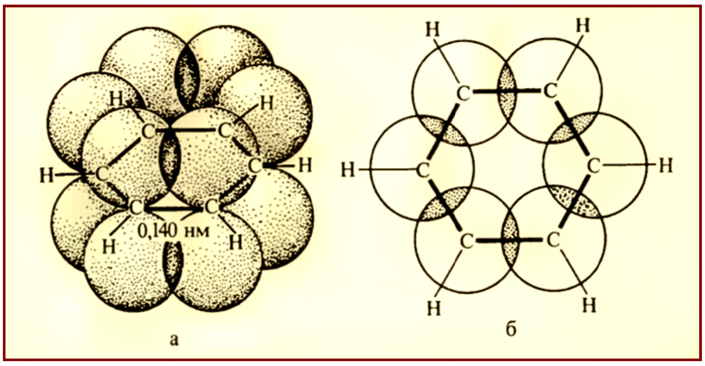






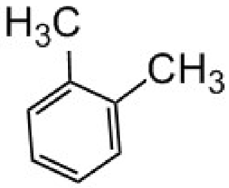


is due to the overlapping of 2p orbitals in the benzene molecule



side view top view

NOMENCLATURE AND ISOMERY



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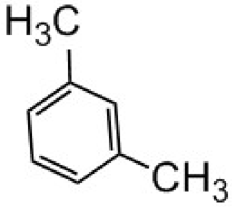
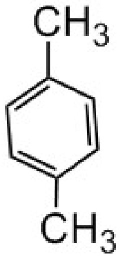
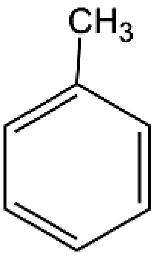
(о-ксилол)



м-диметилбензен
(м-ксилол)



п-диметилбензен
(п-ксилол)



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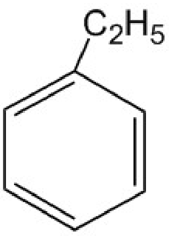
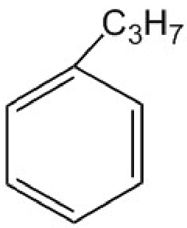
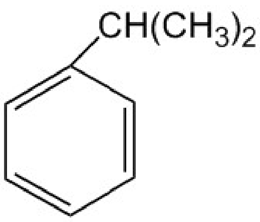


етилбензен



пропілбензен



ізопропілбензен
(кумол)

are used for the names of some homologues of benzene : vinylbenzene is called styrene, methylbenzene, toluene, dimethylbenzene - xylene, isopropylbenzene - cumene, etc.

Aromatic radicals have the general name of aryl (Ar). The C_6H_5 radical is called phenyl, C_6H_5-CH_2 - benzyl, C_6H_5-$CH=$ - benzylidene, $C_6H_4=$ - phenylene.

ACQUISITION OF ARENA

The main natural sources of aromatic hydrocarbons are coal and oil.

Homologs of benzene can be obtained synthetically.

1. Production from hard coal. During the dry distillation of hard coal (at 1000-1200 °C), several products are formed: coke gas, coke, ammonia water and coal tar (tar).

Coke gas is a mixture of gaseous products, when passing through the absorber system, tar, ammonia and light oil vapors can be released. This oil contains about 60% benzene, toluene and other hydrocarbons.

Currently, up to 90% of all benzene obtained is extracted from light oil (the rest from coal tar during its fractionation).

Coke is a solid porous mass. It is used as a reducing agent in the extraction of metals from ores in the metallurgical industry.

Coal tar is formed in small amounts (up to 3%). About 120 different chemical products can be isolated from it, such as phenol, naphthalene, anthracene, pyridine, thiophene and many others. During the distillation of coal tar, the following fractions are separated:

a) light oil (when heated to 170ºC) mainly from aromatic hydrocarbons (benzene, toluene, xylenes, etc.);

b) medium oil (170–230ºC) – contains phenols, naphthalene and pyridine bases;

c) heavy oil (230–270ºC). Cresols, xylenols, naphthalene, quinoline are isolated from this fraction;

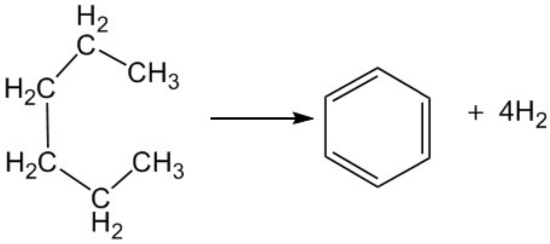
d) anthracene oil (270-340 ºC) consists of anthracene, phenanthrene and other polynuclear hydrocarbons.

After distillation of these fractions, a solid mass remains - peck.

This residue is used for the preparation of varnishes (on wood and metal) and as an impregnation material for sleepers, wooden structures, for underground structures (foundations, piles, etc.) to give them anti-rot properties. It is used as a roofing material.

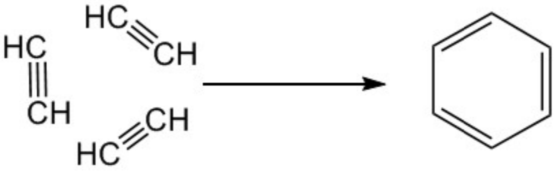
2. Production from oil Another source of production of aromatic hydrocarbons is oil. Some oils contain up to 60% aromatic hydrocarbons, which are isolated by simple distillation or pyrolysis, as well as by catalytic cracking.

3. Aromatization of paraffins

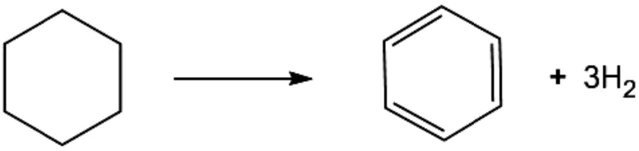


гексан бензен

4. Production from acetylene



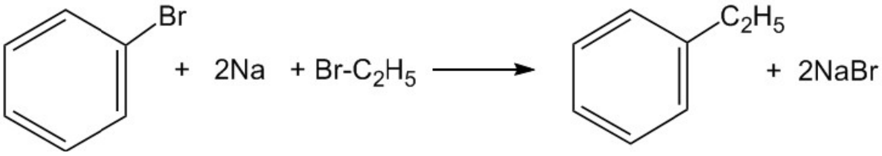
5. Production from alicyclic hydrocarbons



циклогексан бензен

6. Wurtz-Fittig reaction

The reaction is similar to the Wurtz synthesis in the aliphatic series. It also goes through the stage of formation of organometallic compounds, but in this case the reaction products can be relatively easily divided:



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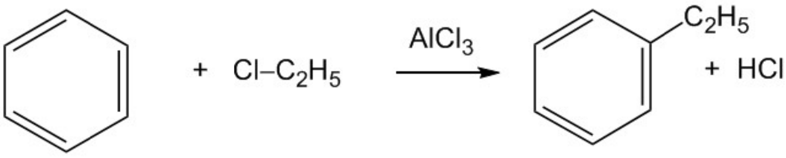
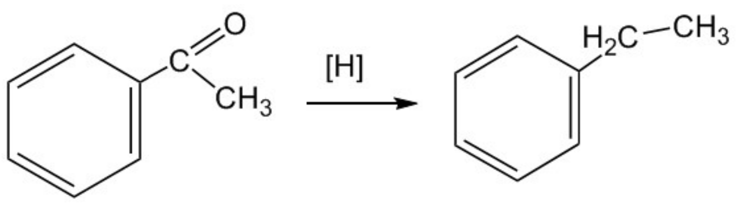
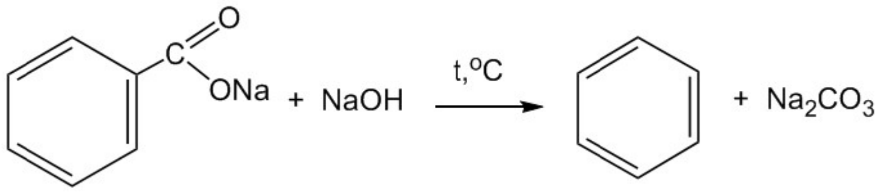
7. Friedel-Crafts reaction:



8. Reduction of ketones (Clemens method)



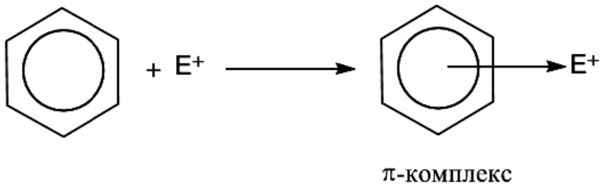
9. Synthesis from salts of aromatic acids



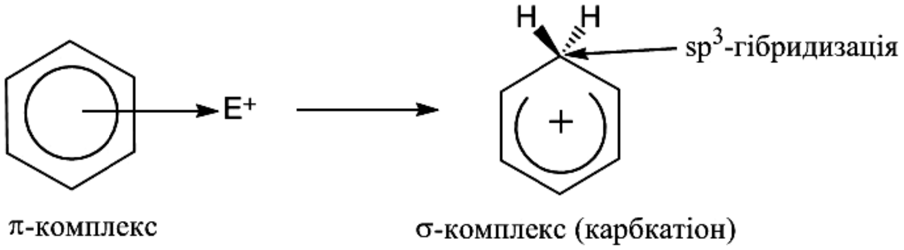
CHEMICAL PROPERTIES

1. Reactions of electrophilic substitution in the aromatic nucleus :

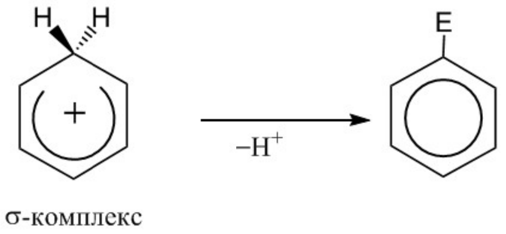
I. _ Formation of π -complex:



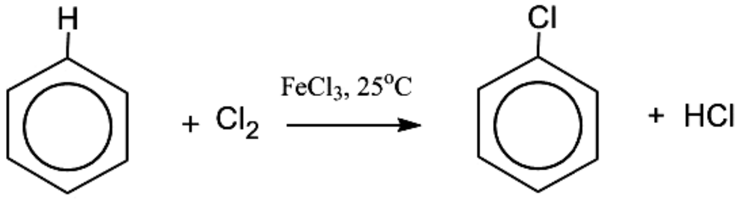
II . Formation of σ -complex:



III . Splitting of a proton:

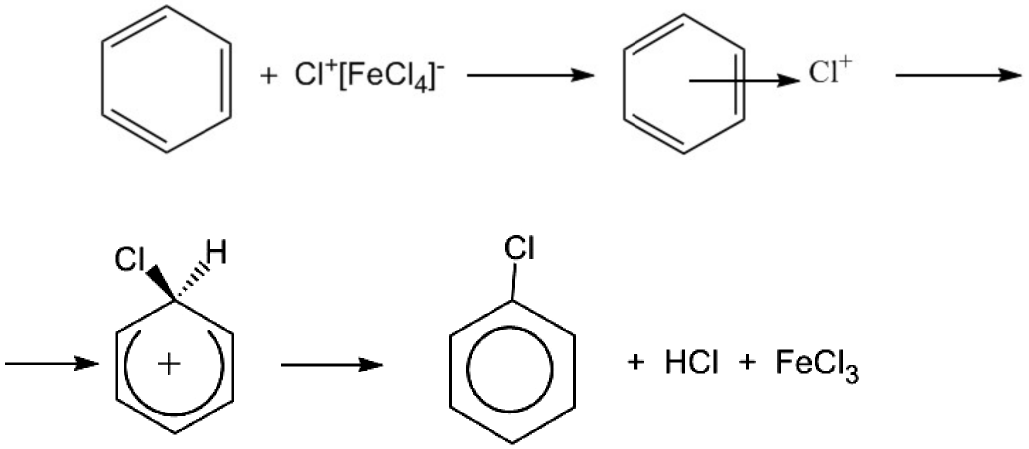


1) <u>Halogenation reaction</u>



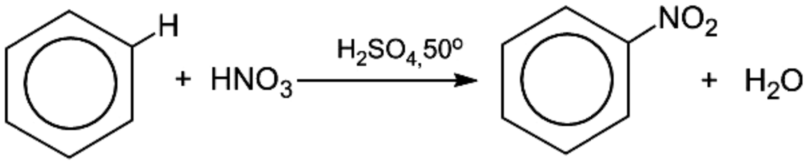
бензен хлорбензен

$$Cl{-}Cl + FeCl_3 \rightleftharpoons Cl^+[FeCl_4]^-$$



σ-комплекс хлорбензен

2) Nitration

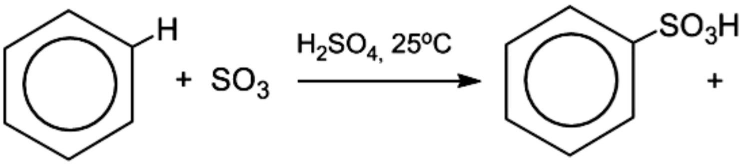


бензен нітробензен

The attacking electrophilic particle is the nitroyl cation NO_2^+, which is formed by the interaction of nitric and sulfuric acids:

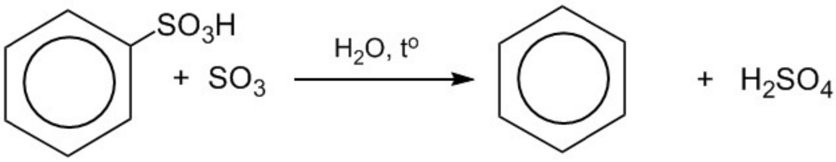
$$HNO_3 + 2H_2SO_4 \rightleftharpoons \underbrace{NO_2^+}_{\text{нітроїл катіон}} + 2HSO_4^- + \underbrace{H_3O^+}_{\text{гідроксоній іон}}$$

3) Sulfation



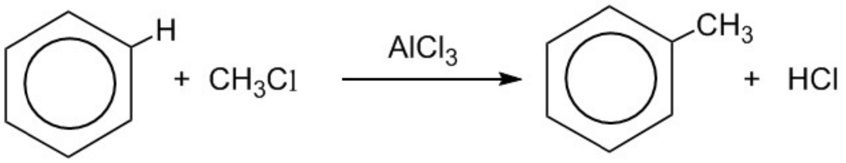
бензен бензенсульфокислота

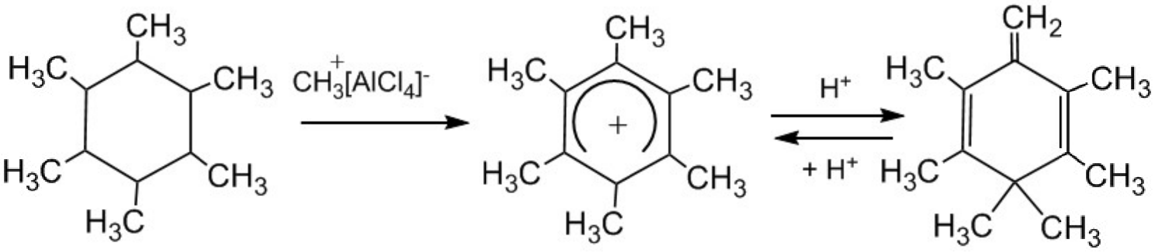
Desulfation



4) **<u>Alkylation</u> (according to the Friedel-Crafts method)**

$$R{-}Cl + ACl_3 \rightleftharpoons R^+[AlCl_4]^-$$



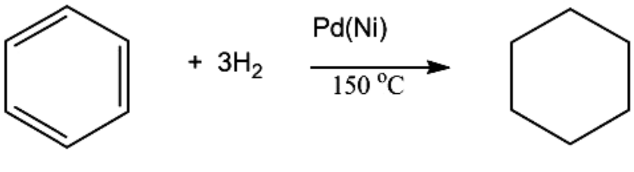


гексаметилбензен катіон (кислота) основа

2. Addition reactions

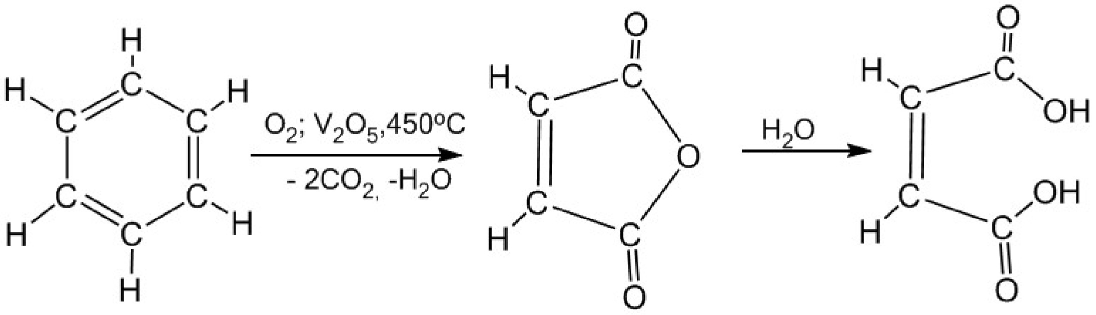
Aromatic compounds hardly undergo addition reactions. Such reactions are few, but they do exist. These include: hydrogenation, addition of halogens, chlorination.

Hydrogenation



циклогексан

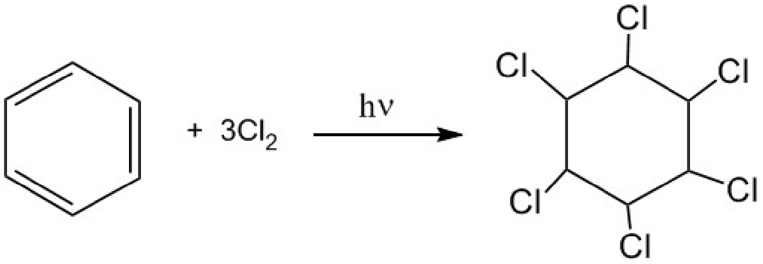
Oxidation



малеїновий ангідрид

малеїнова кислота

Halogenation



hexachlorocyclohexane
(hexachlorane)

CONCEPT OF THE ORIENTATIVE INFLUENCE OF BENZENE RING SUBSTITUENTS

at least one substituent in the benzene ring , then **a violation of the uniform distribution of the π-electron density is inevitable** . As a result, the benzene ring becomes partially polarized, which determines the entry of the attacking reagent into one or another position.

Thus, **the reactivity of the carbon atoms of the benzene ring depends not only on the nature of the attacking reagent, but also on the nature and position of the substituent, which is located in the nucleus and orients the introduction of a new substituent to a certain position of the benzene ring.**

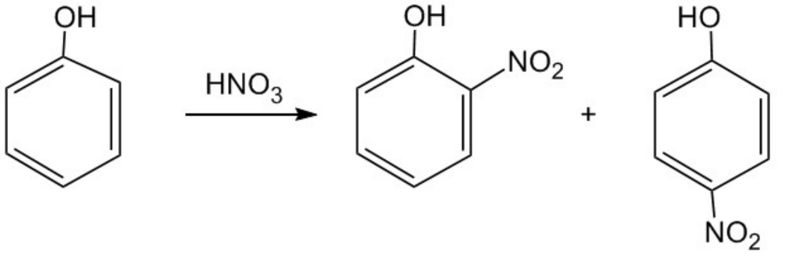
According to the effect on the reactivity of the benzene ring, all substituents are divided into two groups:

1. **Deputies (orientants) of the first kind: OH, OR , OCOR , SH , NH 2, NHR , AIk , HaI .** These substituents shift the electron density toward the ring, i.e., have electron-donating properties. **Facilitating the entry of electrophilic reagents into the benzene ring, they orient the new substituent in the ortho- and para-positions.** Such substituents are called ortho- and para-orientants. Under the action of nucleophilic reagents, the substitution reaction proceeds with difficulty, and the reagent becomes in the meta position.

2. **Substituents (orientants) of the second kind: NO_2 , SO_3H , C ≡ N , COR , COOH , COOR , CCl_3** . These substituents shift the electron density away from the benzene ring, i.e. have electron acceptor properties. They deactivate the benzene ring, making it difficult for electrophilic reagents to enter and orienting the next substituent in **meta-positions (meta-orientants).** At the same time, substituents of the second kind facilitate reactions with nucleophilic reagents, promoting in this case ortho- and para-orientation.

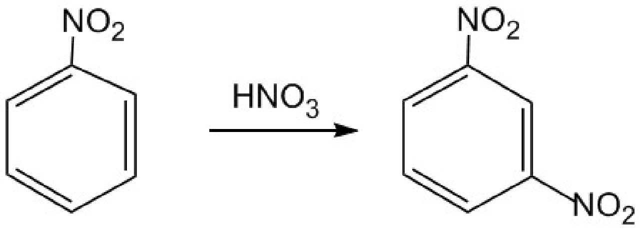
Example:

1. Deputy of the first kind, reagent - electrophilic:



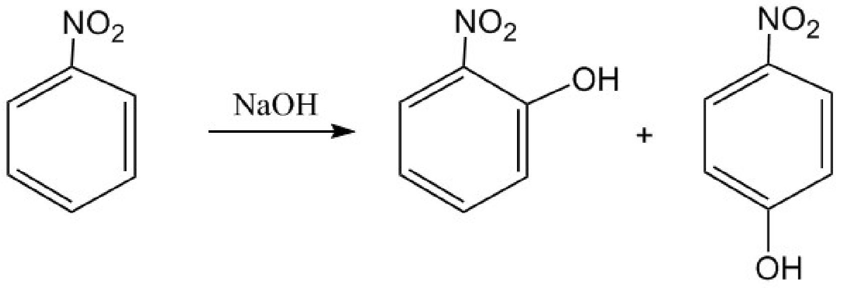
орто-нітрофенол пара-нітрофенол

2. Substitute of the second kind, reagent - electrophilic:



мета-динітробензол

3. Substitute of the second kind, reactant - nucleophilic:



мета-нітрофенол пара-нітрофенол

Individual representatives

Benzene C_6H_6 is a light colorless liquid with a specific smell, sparingly soluble in water (it forms an azeotropic mixture with it). Benzene is a raw material for the production of various chemical products: nitrobenzene, chlorobenzene, aniline, phenol, styrene, etc.

Toluene (methylbenzene) C_6H_5-CHz is a colorless liquid, lighter

water It is used for the production of dyes, drugs and explosives (Tol, TNT). Toluene is used as a starting product in the production of synthetic detergents, caprolactam. It is a good solvent.

Xylenes (dimethylbenzenes) $C_6H_4(CH3)_2$.

Technical xylene is a mixture of three isomers (o-, m- and n-). It is used as a solvent. The division of technical xylene into individual isomers is associated with certain difficulties: their boiling points differ by a small amount. o-Xylene is used to obtain phthalic anhydride; m-xylene - for the synthesis of terephthalic acid, which is the raw material for the production of synthetic fiber - Mylar.

Ethylbenzene C_6H_5-C_2H_5 is a colorless liquid. It is used to obtain styrene.

Isopropylbenzene (cumene) C_bH_5-CH$(CH_3)_2$ – Colorless liquid. Serves as a starting product for the simultaneous production of phenol and acetone.

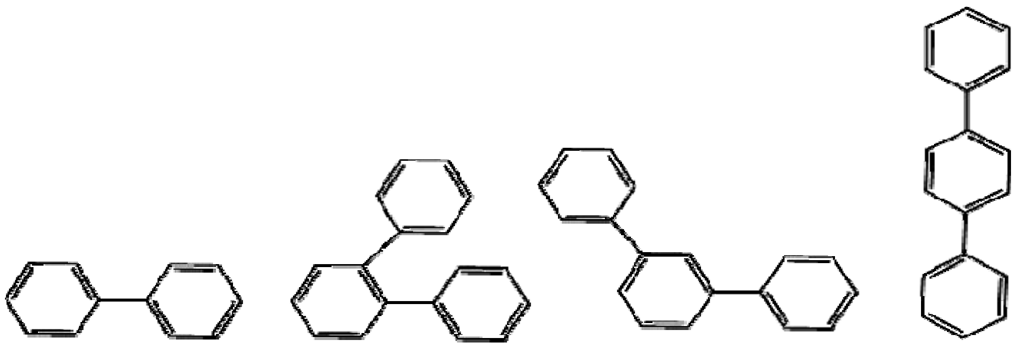
Vinylbenzene (styrene) C_6H_5-CH = CH_2 is a colorless liquid insoluble in water with a pleasant smell. Easily polymerized. It is mainly used to obtain polymer - polystyrene and butadiene styrene rubber.

Lecture 9. POLYNUCLEAR ARENA

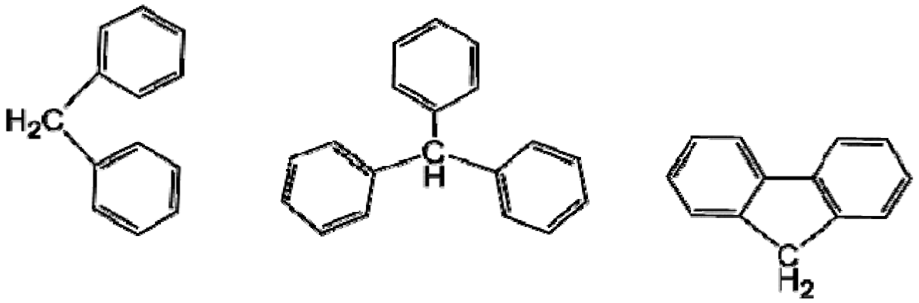
Polynuclear arenes are divided into arenes with isolated cores and condensed cores

ARENA WITH ISOLATED CORE

The simplest examples of compounds of the first type, in addition to benzene and substituted benzenes, can be diphenyl, terphenyl, di- and triphenylmethanes, fluorene:



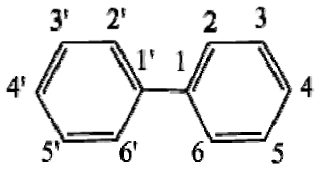
diphenyl terphenyls



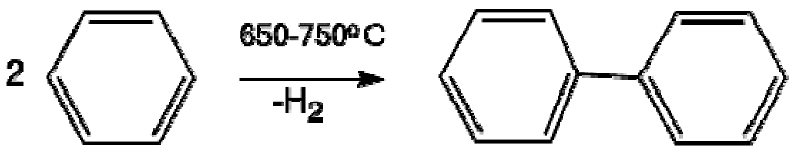
diphenylmethane triphenylmethane fluorene

The properties are similar to those of benzene.

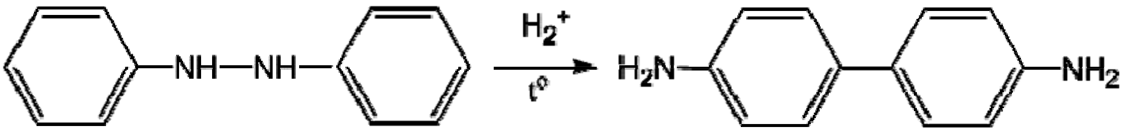
DIPHENYL



Production: 1. Pyrolysis of benzene:



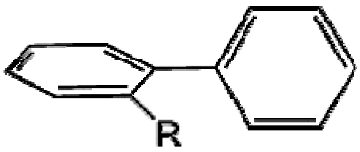
2. Reduction of nitrobenzene to hydrabenzene and its isomerization (benzidine rearrangement):



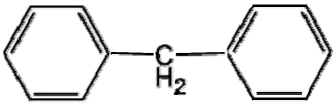
hydrazobenzene 44,4'-diaminodiphenyl

benzidine

Benzidine is used for the synthesis of dyes, for example, Congo red. In the absence of substituents in the positions, two benzene rings of diphenyl can freely rotate relative to each other. If there is at least one substituent in the position, the benzene rings are arranged at an angle:



DIPHENYLMETHANE



Diphenylmethane is obtained **by the Friedel-Crafts reaction from benzene and benzyl chloride:**

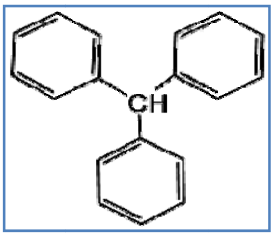
$$C_6H_5-CH_2Cl+C_6H_6\xrightarrow{AlCl_3}C_6H_5-CH_2-C_6H_5+HCl$$

When diphenylmethane is oxidized, benzophenone is formed:

$$C_6H_5-CH_2-C_6H_5\xrightarrow{(O)}C_6H_5-CO-C_6H_5$$

бензофенон

TRIPHENYLMETHANE



Triphenylmethane is a product of replacing three hydrogen atoms in a methane molecule with three phenyl groups.

A distinctive feature of triphenylmethane is the mobility of the hydrogen atom (or the group replacing it) associated with the triphenylmethyl group

$$CHCl_3 + 6C_6H_6 \xrightarrow{AlCl_3} (C_6H_5)_3CH \; + 3HCl$$

$$(C_6H_5)_3C - H \underset{[H]}{\overset{[O]}{\leftrightarrow}} (C_6H_5)_3C - OH \underset{H_2O}{\overset{HCl}{\leftrightarrow}} (C_6H_5)_3C - Cl$$

трифенілмета **трифенілкарбіно** **трифенілхлорметан**

The stability of free radicals (or ions) with phenyl groups is caused by the combination of an unpaired electron (or, accordingly, a charge) of the central carbon atom with the π -electron system of three benzene rings:

$$(C_6H_5)_3C\colon X \leftrightarrow (C_6H_5)_3C\bullet + X\bullet$$

трифенілметильний
радикал

$$(C_6H_5)_3C - X \leftrightarrow (C_6H_5)_3C^+ + X^-$$

трифенілметил-катіон

Triphenylmethane dyes.

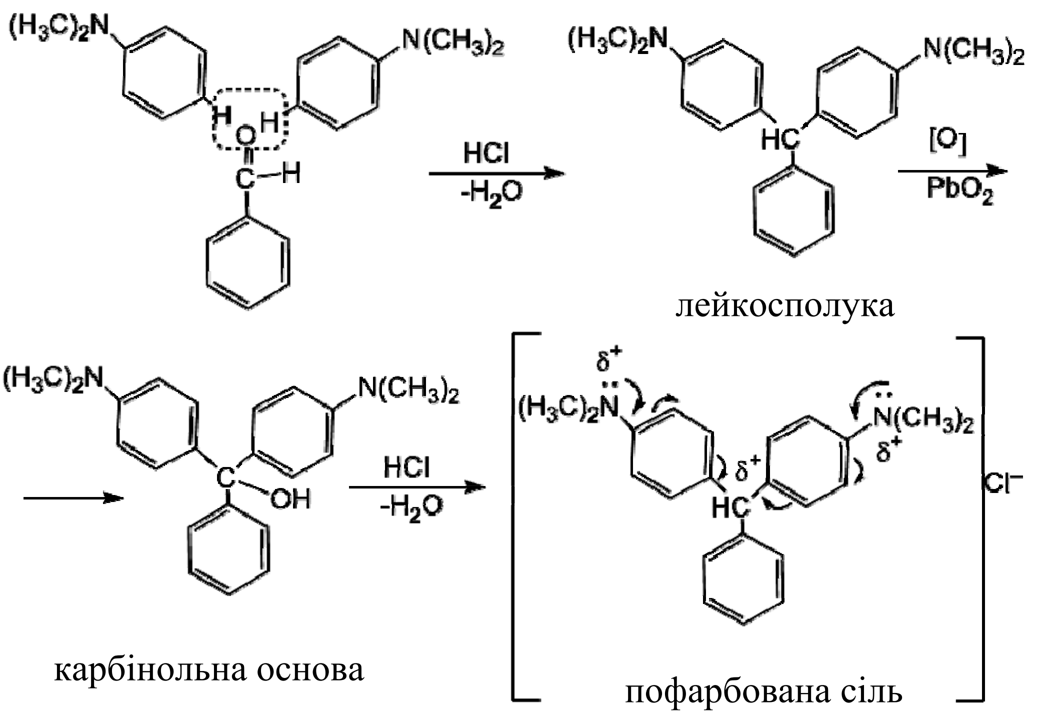
Of the numerous derivatives of triphenylmethane, amino- and oxy-derivatives are the most important, since many of them make up a large class of triphenylmethane dyes.

Amino- and oxyderivatives of triphenylmethane - compounds colorless and therefore called leucospolukami (from the Greek. l eukos - white). When oxidized, they form carbinols (carbinol bases), which with acids give colored salts. These salts are dyes. In the process of obtaining triphenylmethane dye, a transition is observed within the system: triphenylmethane-triphenylcarbinol-triphenylchloromethane.

Consider as an example the formation of the simplest dye of this class - malachite green. He goes out during the condensation of dimethylaniline with benzaldehyde.

By adding alkali to the dye (that is, to salt) you can again isolate the colorless carbinol base.

The dye "malachite green" refers to amino derivatives of triphenylmethane. The color carrier in this dye is a cation. The positive charge of the cation is distributed between carbon and nitrogen atoms, which is the reason for its stability. The uniform distribution of the charge is also associated with a decrease in the total energy of the molecule, which means that it is able to disrupt light waves with lower energy.



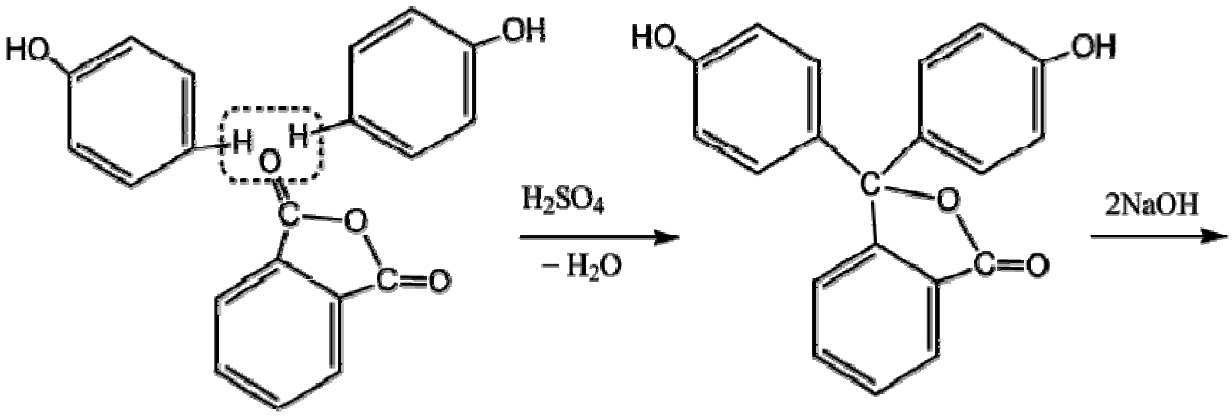
лейкосполука

карбінольна основа

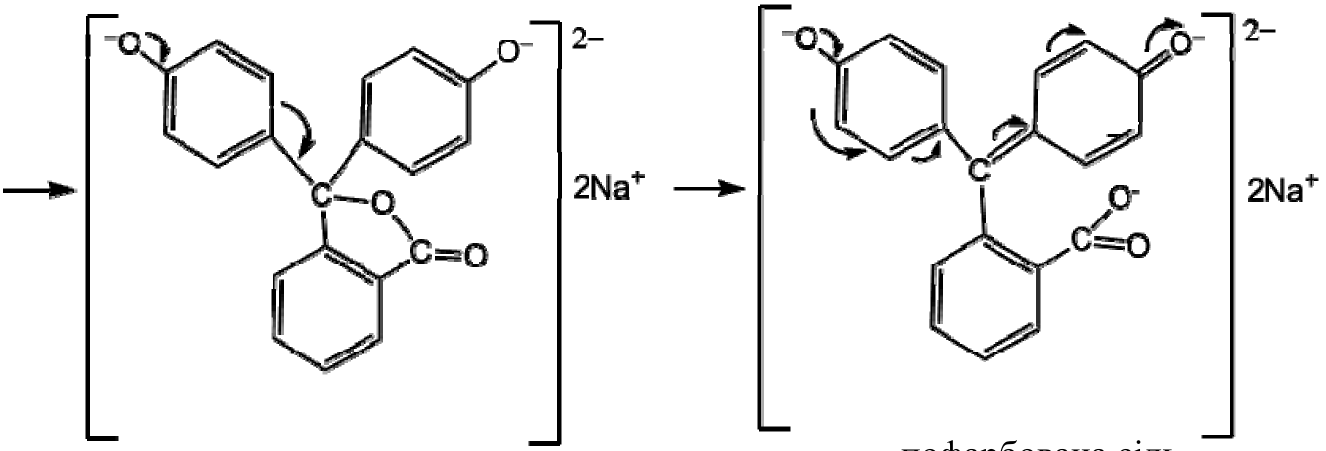
пофарбована сіль
(барвник)

"Malachite green" dye is used for coloring of silk and cotton, and its homolog with four ethyl groups instead of methyl, diamond green is also used in medicine as an antiseptic **.**

Oxyderivatives of triphenylmethane include phthaleins. The simplest representative of phthaleins is **phenolphthalein** . It is obtained by condensation of phenol with phthalic anhydride according to the scheme :



лейкосполука

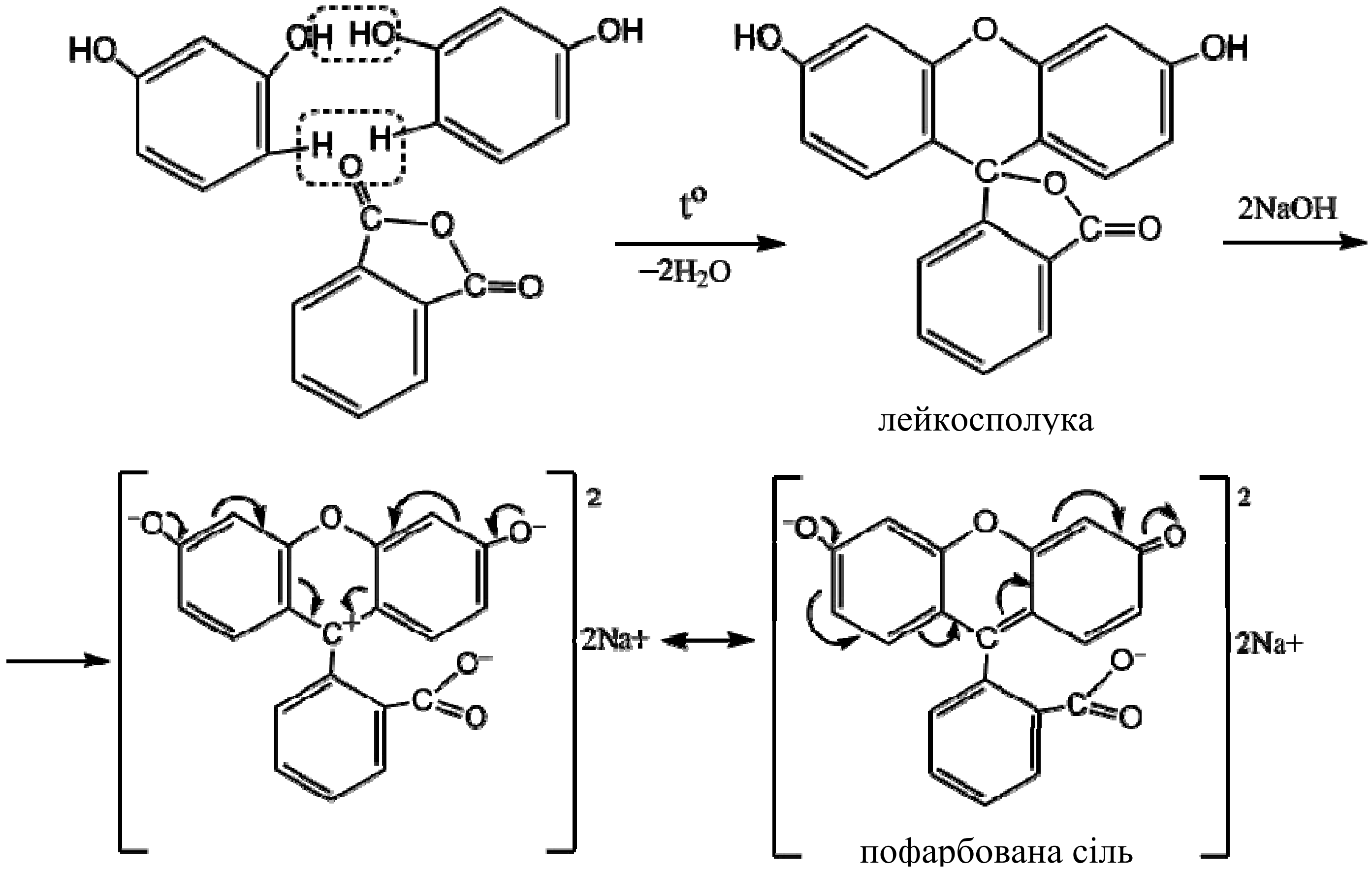


пофарбована сіль

The formation of a colored salt is accompanied intramolecular rearrangement. The color carrier in this case is the salt anion. With an excess of alkali, the red coloring disappears, which is associated with the formation of a three-charged carbinol base .

Upon acidification, a colorless compound is formed again. Phenolphthalein is widely used as an indicator.

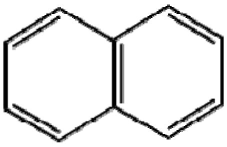
Replacing phenol with resorcinol leads to the formation of a new product - **fluorescein:**



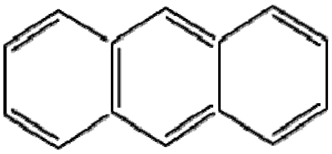
лейкосполука

пофарбована сіль

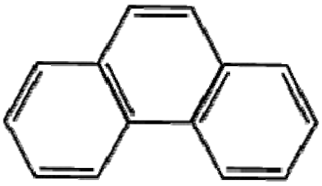
ARENAS WITH CONDENSED NUCLEI



нафталін

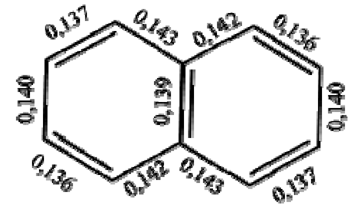


антрацен



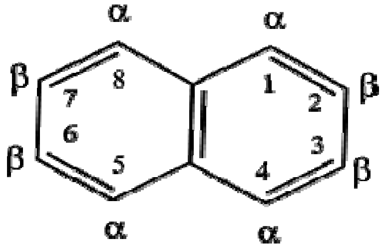
фенантрен

NAPHTHALENE



Structure and isomerism . The naphthalene molecule consists of two benzene rings condensed in the o-positions. according to modern ideas, the naphthalene molecule has a flat structure with a less uniform distribution of π -electron density than in benzene, which is manifested in different lengths of C-C bonds (nm). Provisions 1, 4, 5 and 8 are called α - provisions, and 2, 3, 6 and 7 - β - provisions.

Thus, for naphthalene, the existence of two monosubstituted isomers is possible: α - and β -isomers.



The main industrial **method of obtaining** naphthalene is its separation from coal tar.

Naphthalene is a colorless, rather volatile crystalline substance with a melting $_{\text{point}}$ of 80 °C. It serves as a raw material for the synthesis of phthalic anhydride, phthalic acid and other products. It is used in everyday life to repel moths and other insects.

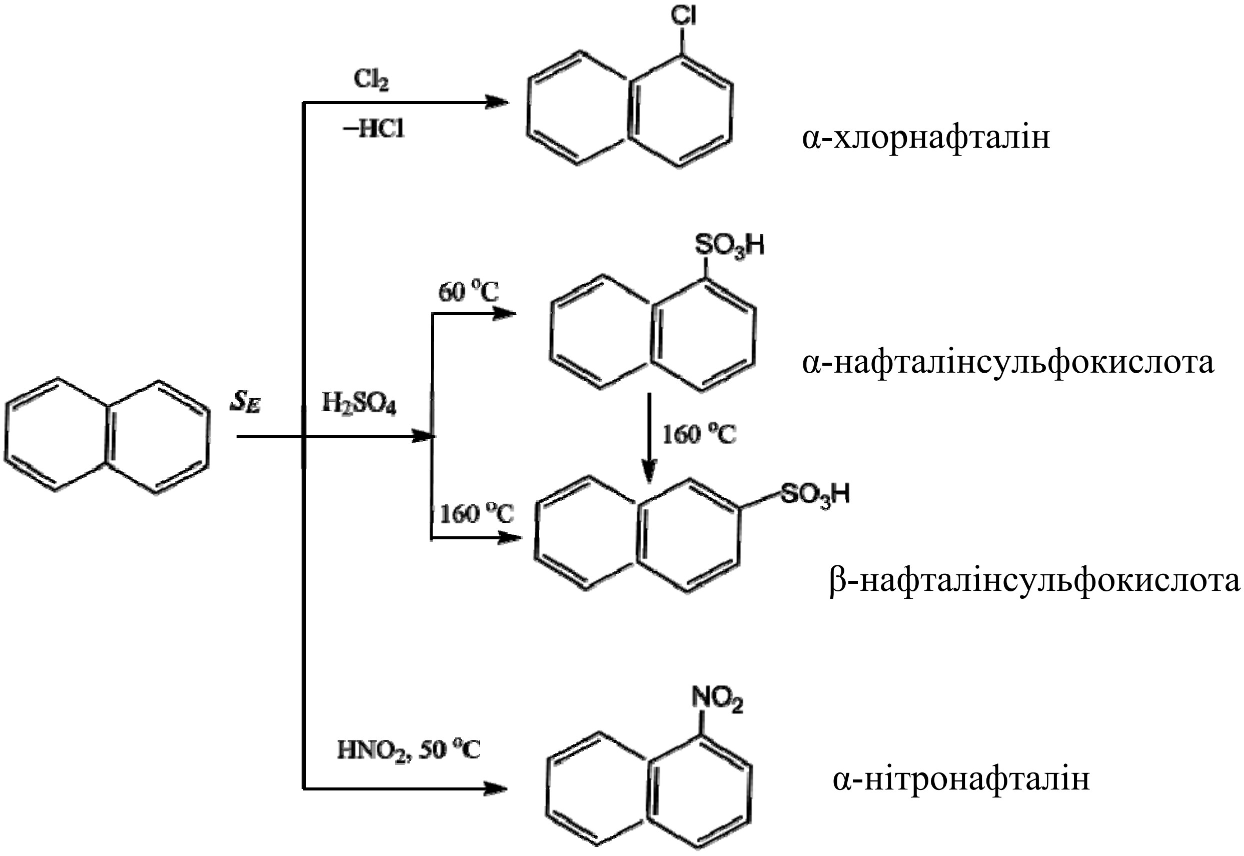
Chemical properties. In chemical behavior, naphthalene has much in common with benzene, but its aromatic properties are much weaker. It enters into substitution, addition and oxidation reactions.

1. **Electrophilic substitution reaction.**

Naphthalene enters these reactions more easily than benzene. At the same time, **mainly α-derivatives are formed.**

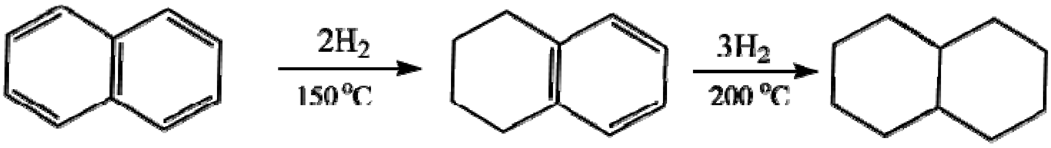
Naphthalene reacts with halogens, sulfuric and nitric acids according to a similar scheme, as a result of which one hydrogen atom is substituted for the functional group of the reagent.

In the case of the action of sulfuric acid, the formation of a mixture of α- and β-naphthalene sulfonic acids is possible:



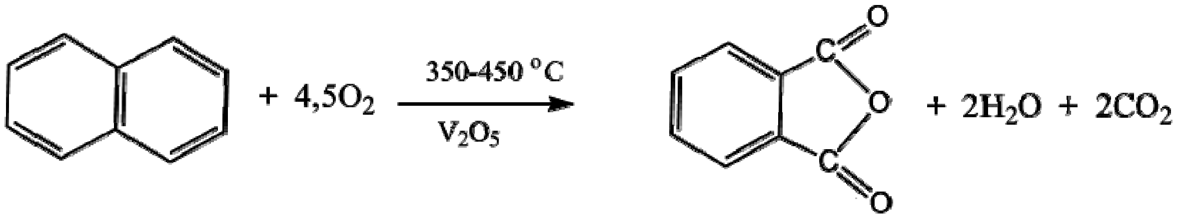
2. Addition reactions

Possessing a less uniform distribution πof the -electron plane in the molecule, naphthalene belongs to more unsaturated compounds than benzene. For example, during **catalytic hydrogenation, tetralin and decalin** are obtained , which are used as solvents:



t etralin decalin

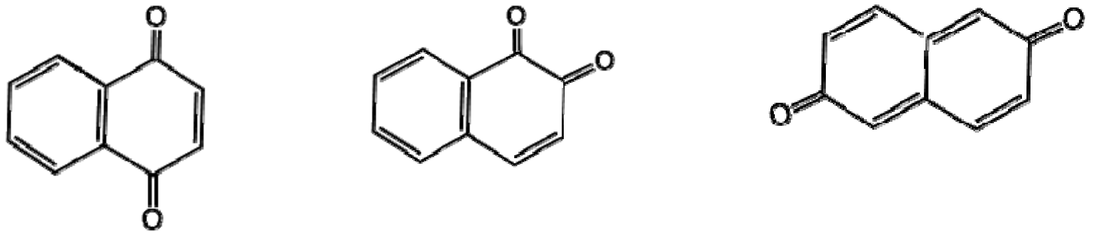
3. Oxidation of naphthalene. During the oxidation of the air-naphthalene mixture over the catalyst, phthalic anhydride is formed:



phthalic anhydride

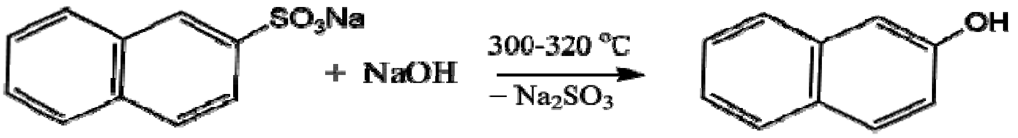
Naphthalene derivatives

Of the numerous naphthalene derivatives, **naphthoquinones should be noted** , which exist in three isomers:



α- naphthoquinone β- naphthoquinone amphi-naphthoquinone

naphthols can be obtained
(α and β -), which are analogues of phenols:

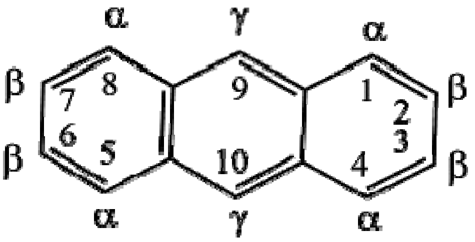


β- naphthol

Naphthols have all the properties common to phenols. However, the hydroxyl group in naphthols is more mobile than in phenols.

ANTHRACENE

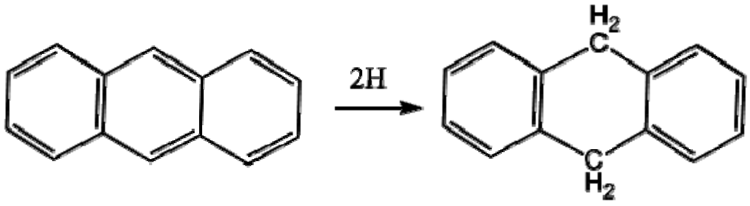
Anthracene is a system consisting of three condensed benzene nuclei lying in the same plane (bond lengths are given in nm):



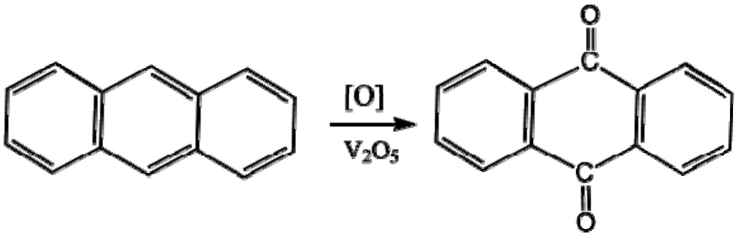
Positions 1, 4, 5 and 8 are called a-position; positions 2, 3, 6 and 7 are p-positions. Provisions 9 and 10 are highlighted in particular and are called y-provisions.

Anthracene is a crystalline substance with a melting point of 213°C. It is obtained from the anthracene fraction of coal tar. Being an aromatic system, anthracene at the same time in a chemical relationship has greater unsaturation than naphthalene, and even more so than benzene. Positions 9 and 10 (meso-positions) are especially active in its molecules, as they are under the influence of two benzene nuclei.

Anthracene enters into addition and oxidation reactions, touching positions 9 and 10:

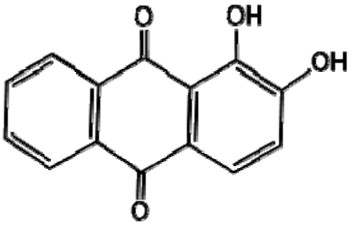


dihydroanthracene



anthraquinone

Anthraquinone and its numerous derivatives are important organic compounds. For example, 1,2-dioxyanthraquinone is known as **alizarin dye:**



1,2-dioxyanthraquinone
alizarin

Alizarin is the most common of the dioxyanthraquinone dyes. It is used for dyeing wool and cotton, in screen printing, as well as in the production of pigments for painting paints, etc. Alizarin is a pro-poisoning dye. He paints bright red with aluminum mordant, and brown with chrome mordant yes, on iron - in purple.

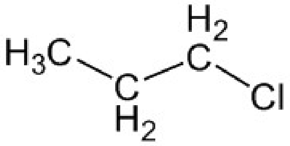
Lecture 10.

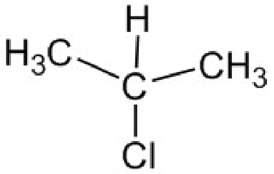
HALOGEN DERIVATIVES OF HYDROCARBONS

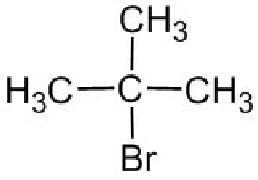
By by reactivity, halogens can be divided into the following series:

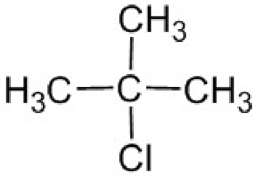
$F_2 > Cl_2 > Br_2 > I_2$

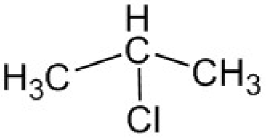
Substitute nomenclature

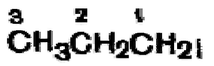




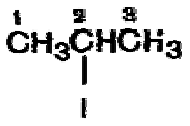




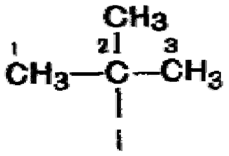




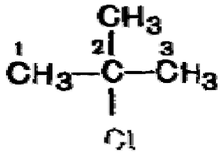
1-Иодпропан



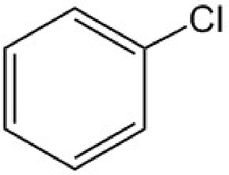
2-Иодпропан

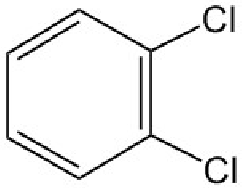


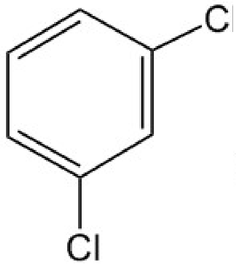
2-Иод-2-метилпропан

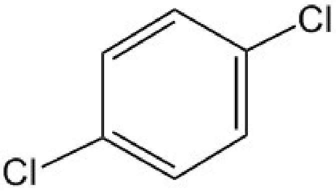


2-Метил-2-хлор-пропан



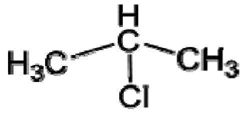






chlorobenzene 1,2-dichlorobenzene 1,3-dichlorobenzene 1,4-dichlorobenzene

Radically - functional nomenclature

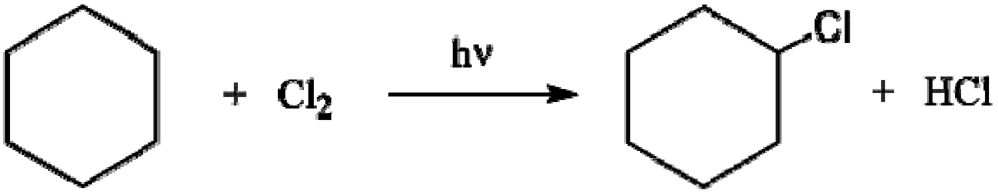
CH_3I CH_3CH_2Cl $CH_3CH_2CH_2$  F

methyl iodide ethyl chloride propyl fluoride isopropyl chloride

RECEIVING OF HALOGEN POHYDROCARBONS

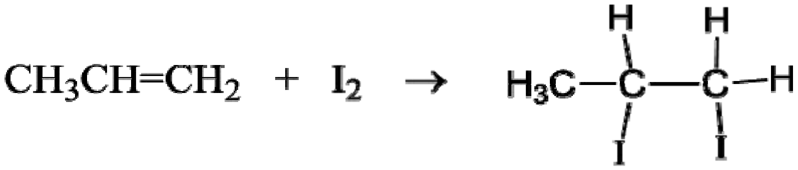
1. The metallepsy reaction is the sequential replacement of hydrogen atoms in saturated hydrocarbons by halogens under the action of light and a catalyst (by **a free radical mechanism**):

$$C_nH_{2n+2} + Cl^{\bullet} \rightarrow C_nH_{2n+1}Cl + HCl$$



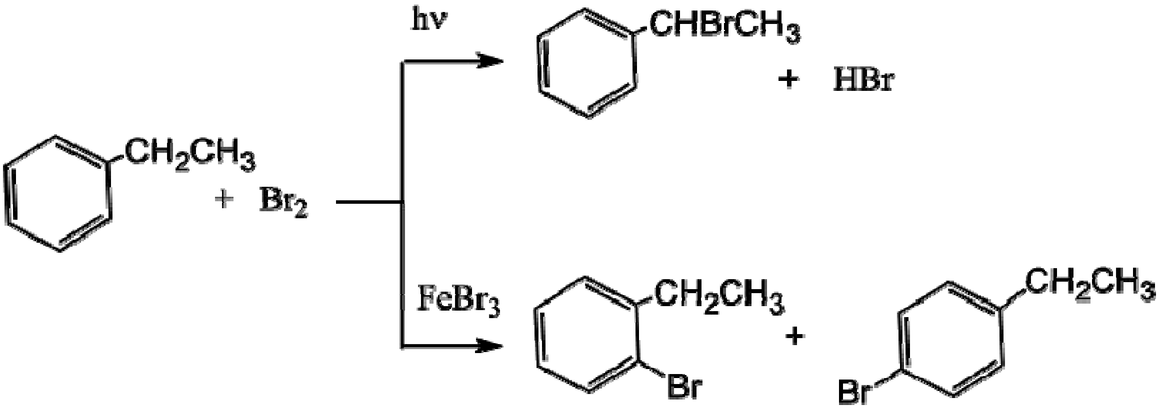
cyclohexane chlorocyclohexane

Electrophilic joining A $_E$:



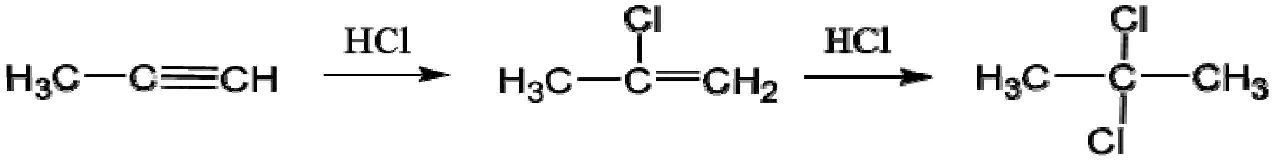
propene 1,2-diiodopropane

Electrophilic substitution S $_e$:



Ethylbenzene 1-bromo,2-ethylbenzene 1-bromo,4-ethylbenzene

2 . Hydrohalogenation:



$$H_3C-C\equiv CH \xrightarrow{HCl} H_3C-\overset{\overset{Cl}{|}}{C}=CH_2 \xrightarrow{HCl} H_3C-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_3$$

propyne 2-chloropropene 2,2-dichloropropane

$$KBr + H_2SO_4 \rightleftharpoons KHSO_4 + HBr$$

$$CH_3CH_2CH_2OH + HBr \rightleftharpoons CH_3CH_2CH_2Br + H_2O$$

propanol-1 1-bromopropane

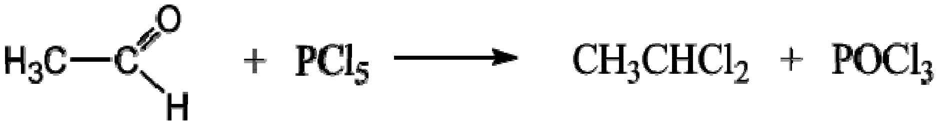
3. Replacement of hydroxyl in alcohols by halogen:

$$R\text{–}OH + PCl_5 \longrightarrow R\text{–}Cl + HCl + POCl_3$$

$$R\text{–}OH + SOCl_2 \longrightarrow R\text{–}Cl + HCl + SO_2$$

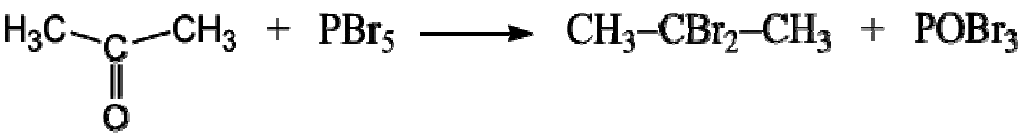
thionyl chloride

4. Reaction of phosphorus halides with aldehydes and ketones:



$$H_3C-CHO + PCl_5 \longrightarrow CH_3CHCl_2 + POCl_3$$

acetaldehyde 1,1-dichloroethane



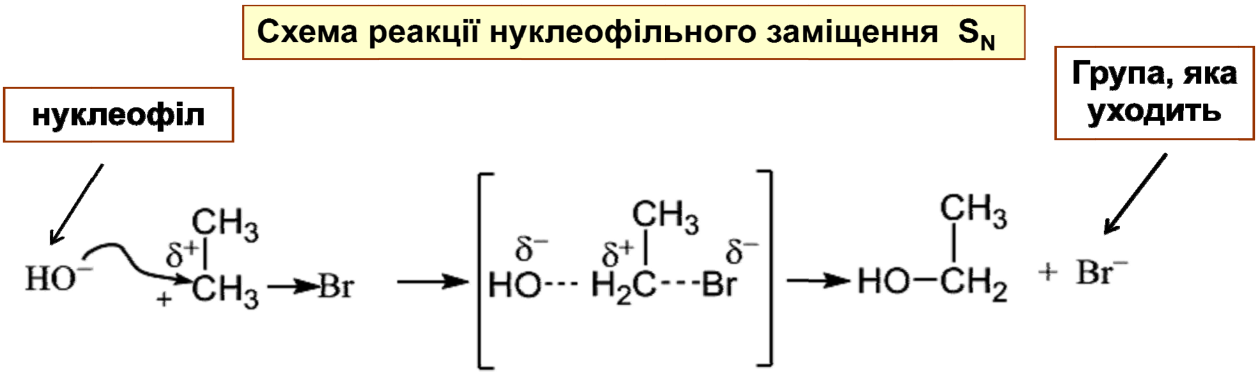
$$H_3C-\underset{\underset{O}{\|}}{C}-CH_3 + PBr_5 \longrightarrow CH_3\text{–}CBr_2\text{–}CH_3 + POBr_3$$

acetone 2,2-dibromopropane

CHEMICAL PROPERTIES

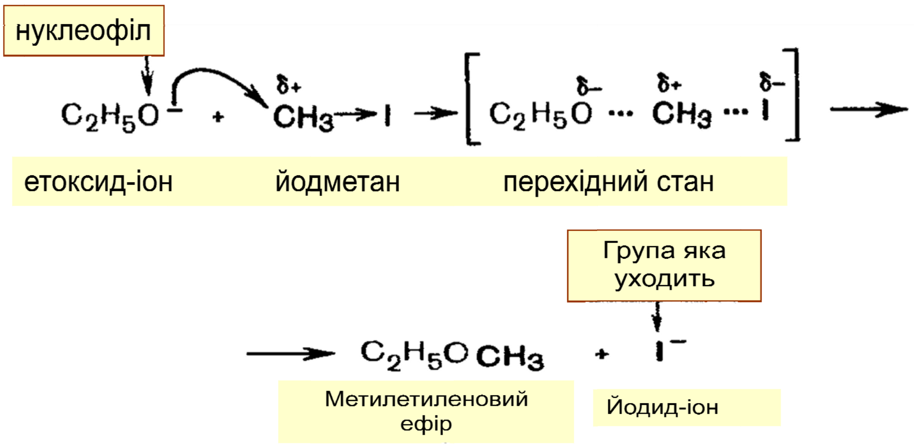
Nucleophilic substitution reactions in haloalkanes

1. **Reaction with alkalis (hydrolysis of haloalkanes):**
   $CH_3CH_2Br + KOH \rightarrow CH_3CH_2OH + KBr$
   bromethane ethanol

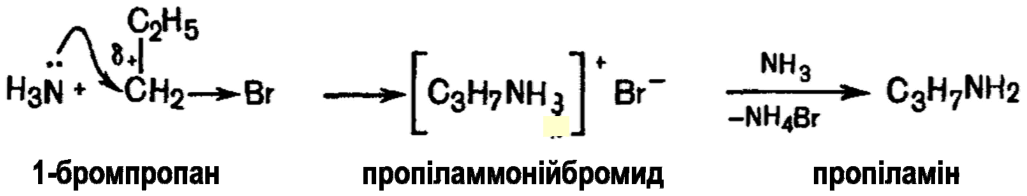


bromoethane transition state ethanol

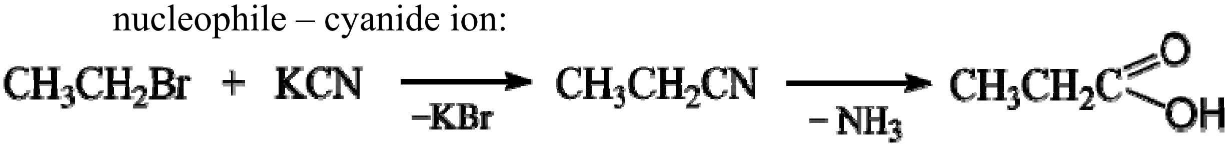
2. **Reaction of alcoholism (with alcohols):**



3. **Ammonolysis reaction (with ammonia):**



4. **Reaction with hydrocyanic acid salts:**
   nucleophile – cyanide ion:

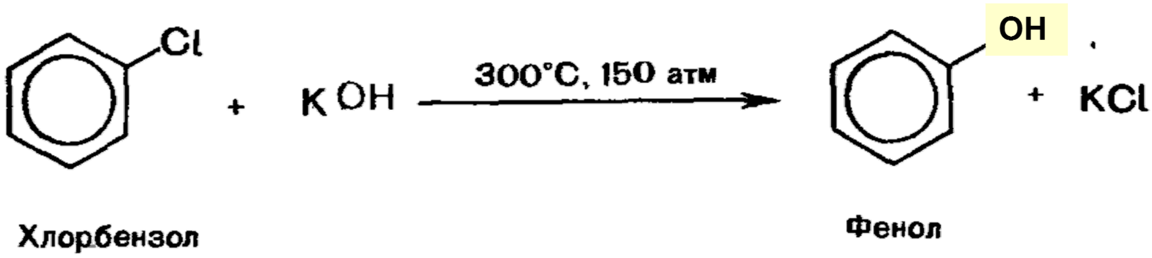


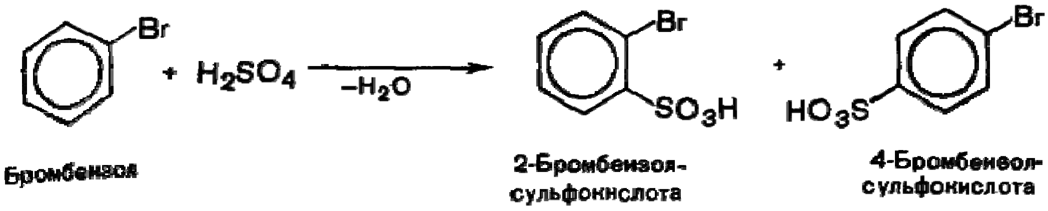
bromethane cyanide propanonitrile propanoic acid
potassium

$$CH_3CH_2CN + 2H_2O \rightarrow CH_3CH_2COOH + NH_3$$

5. Elimination reactions

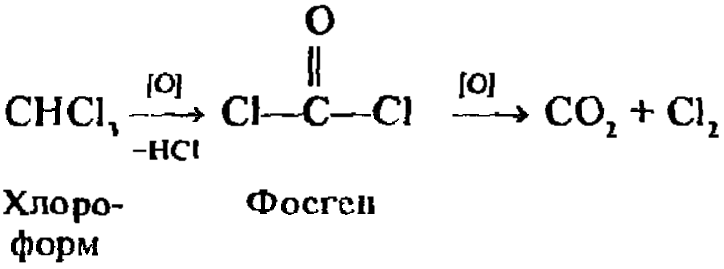
$R\text{-}CH_2\text{-}CHCl\text{-}R' + KOH \rightarrow R\text{-}CH{=}CH\text{-}R' + KCl + HOH$
haloalkane alkene





Main representatives

Chlorethane C_2H_5Cl is an anesthetic
2-bromo-1,1,1-trifluoro-2-chloroethane (fluoroethane) $CF_3CHClBr$ – used for inhalation anesthesia
Tetrachloromethane SS l$_4$ - used in fire extinguishers, a solvent for fats and oils
Difluorodichloromethane CF_2Cl_2 is a refrigerant used in aerosol packaging
Chlorethylene (vinyl chloride) - $CH_2 = CHCl$ - forms a polymer for the manufacture of electrical insulating materials, artificial leather, film
Trichloromethane $CHCl_3$ (chloroform) - a narcotic substance, its use as a narcosis has been shortened. Able to oxidize to phosgene:



$$CHCl_3 \xrightarrow[-HCl]{[O]} Cl-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{[O]} CO_2 + Cl_2$$

PHOSGEN - carbonic acid dichlorohydride (carbonyl chloride)
Obtaining:

$$Cl_2 + CO \leftrightarrow COCl_2 + 26 \text{ kcal}$$

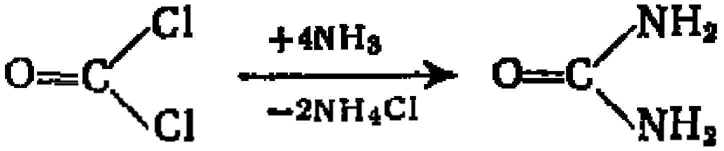
Chemical properties of phosgene:

The phosgene solution is quickly hydrolyzed:

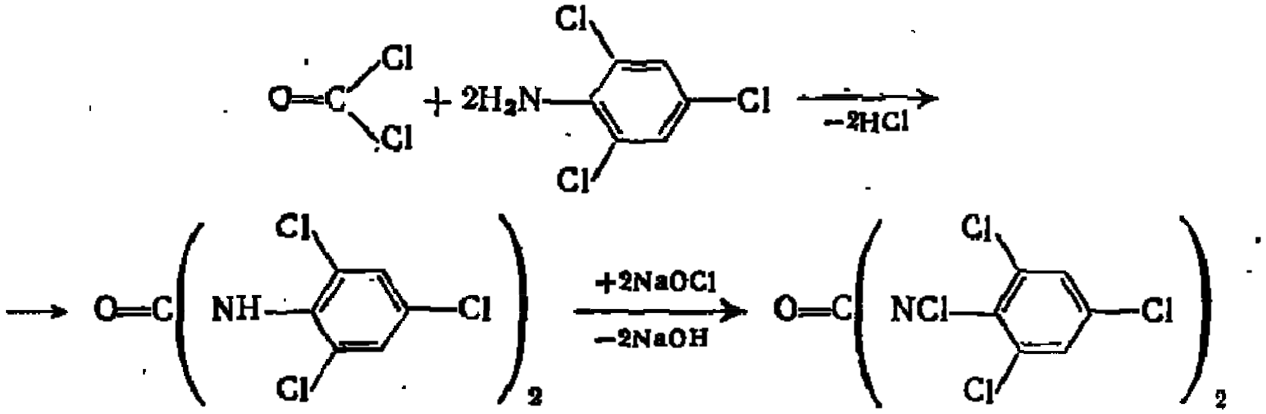
$$COCl_2 + H_2O \rightarrow 2\,HCl + CO_2$$

Phosgene is practically not hydrolyzed by water vapor, so it can be in the air for a long time without obvious changes

The method of degassing phosgene with a mixture of gaseous ammonia and water vapor:



In the American army, this process was used to impregnate uniforms to protect against poisonous substances that cause skin irritation:



Phosgene reacts with tertiary amines, for example:

$$\mathbf{COCl_2 + N_4(CH_2)_6 \rightarrow N_4(CH_2)_6 \cdot COCl_2}$$

Tetramine was used in liquid respirators to protect against phosgene .