МІНІСТЕРСТВО ОХОРОНИ ЗДОРОВ'Я УКРАЇНИ
ХАРКІВСЬКИЙ НАЦІОНАЛЬНИЙ МЕДИЧНИЙ УНІВЕРСИТЕТ

CLASSIFICATION OF CHEMICAL REACTIONS. REACTIVITY OF ALKANES, ALKENES, ARENES, ALCOHOLS AND PHENOLS

Methodical instructions for 1st year students' self-work
in Biological and Bioorganic Chemistry

КЛАСИФІКАЦІЯ ХІМІЧНИХ РЕАКЦІЙ. РЕАКЦІЙНА ЗДАТНІСТЬ АЛКАНІВ, АЛКЕНІВ, АРЕНІВ, СПИРТІВ ТА ФЕНОЛІВ

Методичні вказівки для самостійної роботи студентів 1-го курсу
з біологічної та біоорганічної хімії

Затверджено
Вченою радою ХНМУ.
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Classification of chemical reactions. Reactivity of alkanes, alkenes, arenes, alcohols and phenols: Methodical instructions for the 1st-year students' self-work in biological and bioorganic chemistry (module 1) / compiled by A.O. Syrovaya, V.N. Petyunina, V.O. Makarov et al. – 2nd edition, revised, corrected and expanded – Kharkiv: KhNMU, 2018. – 24 p.

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Subject 2. CLASSIFICATION OF CHEMICAL REACTIONS. REACTIVITY OF ALKANES, ALKENES, ARENES, ALCOHOLS AND PHENOLS

1. Number of hours – 4

2. **Material and methodological support.**

Tables:

1. Scheme of structure of the subject.
2. Mechanism of covalent bond breaking.
3. Reaction of lipid peroxidation.
4. Scheme of vitamin E anti-oxidant action

3. Educational literature**:**

1. Biological and Bioorganic chemistry: in two books: Textbook. Textbook 1. Bioorganic chemistry / B.S. Zimenkovsky, V.A.Muzyhenko, I.V. Nizhenkovska, G.O. Syrova; edited by B.S. Zimenkovsky, I.V. Nizhenkovska. – K.: AUP "Medicina", 2017. – 288 p.
2. Fundamentals of bioorganic chemistry : manual / A. O. Syrovaya, E. R. Grabovetskaya, V. N. Petiunina. – Kharkiv : KhNMU, 2016. – 191 p.
3. Main types and mechanisms of the reactions in organic chemistry: methodical instructions for 1st year students' self-work in Biological and Bioorganic Chemistry (module 1) / compiled by A.O. Syrovaya, L.G. Shapoval, V.N. Petyunina et al. – Kharkiv: KhNMU, 2014. – p. 30.
4. Classification of chemical reactions. Reactivity of alkanes, alkenes, arenes, alcohols and phenols: Methodical instructions for the 1st-year students' self-work in biological and bioorganic chemistry (module 1) / compiled by A.O. Syrovaya, V.N. Petyunina, V.O. Makarov et al. – 2nd edition, revised, corrected and expanded – Kharkiv: KhNMU, 2018. – 24 p.
5. Text of Lectures.

4. Motivational characteristic of the subject

This subject is the basis for understanding some biochemical reactions taking place in living organisms during metabolism (lipid peroxide oxidation, formation of hydroxyacids from unsaturated acids in Krebs cycle and others). This subject is important for understanding the mechanism of similar reactions at the synthesis of drugs and analogues of natural compounds.

While studying the chemical processes occurring in the organism, You meet with numerous and a variety of organic compounds. To orientate in this variety of compounds you need to know their scientific classification and nomenclature.

Chemical behavior of these compounds, including biochemical transformations, is determined by their composition, the electronic and spatial structure, the mutual influence of atoms in these compounds. That's why knowledge of this subject is important for successful studying of biochemistry, physiology, pharmacology and hygiene.

5. The purpose of the subject:

- general:

to be able to predict ability of main classes of organic compounds to undergo hemolytic and heterolytic reactions accordance with their electronic structure and electronic effects of substituents.

- specific:

To be able to characterize chemical behavior of organic compounds in the following reactions: radical substitution, electrophilic addition, electrophilic substitution, nucleophilic substitution.

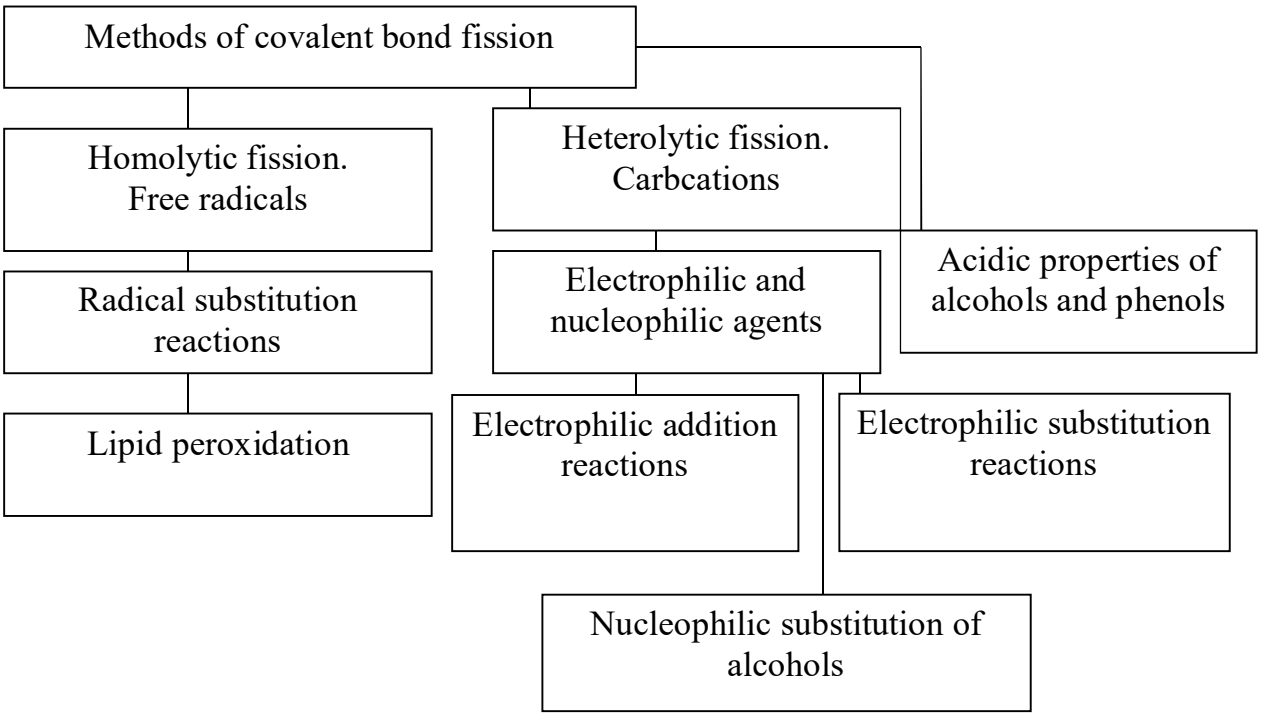
a) **to know:** the mechanisms of the radical substitution, electrophilic addition, electrophilic substitution, nucleophilic substitution, chemical properties of different classes of organic compounds;

b) **to be able:** to explain effects of substituents on reactivity at the electrophilic interactions using knowledge about their electronic effects.

c) **practical skills:**

- to be able to classify organic and bioorganic compounds, to name bioorganic compounds according to IUPAC nomenclature and radico-functional nomenclature.
- to be able to give formulas of bioorganic compounds according their name.
- to be able to make scheme and describe the mechanisms of the following reactions: radical substitution (S_R), electrophilic addition (A_E), electrophilic substitution (S_E), nucleophilic substitution (S_N), elimination (E).
- to be able to perform qualitative reactions for hydrocarbons, alcohols and phenols.

6. Scheme of structure of the subject.



7. Plan of students' work.

№	Stages	Time (min.)	Training and visual aids	Location
1.	Motivation description and plan of subject. Answers on students' questions.	25	Methodical instructions	Class room
2.	Incoming control	20	Test	
3.	Independent work of students with methodical literature, the solution of educational problems, filling of work-book	50	Methodical instructions for students, text of lecture, manual for students' self-work, work-book, reference data, tables	
4.	Laboratory work	45	Methodical instructions for students, text of lecture, manual for students' self-work, work-book, reference data	
5.	Final control	25	Test	
6.	Analysis and conclusions Home work	15		

8. Tasks for self-work:

- List of questions to be studied:

1. Ways of covalent bond fission. Radicals, electrophilic and nucleophilic reagents.
2. Chemica properties of alkanes: radical substitution reactions. Lipid peroxidation. Mechanism of radical substitution reaction.
3. Chemica properties of unsaturated compounds: electrophilic addition reactions, its mechanism. Markovnikov's rule ant its modern interpretation.
4. Reactivity of arenes. Electrophilic substitution reactions. Orienting effect of substituents in benzene ring and heteroatoms in the cycle.
5. Chemical properties of alcohols and phenols: acidity of monoatomic, polyatomic alcohols and phenols; elimination, oxidation. The concept of mechanism of nucleophilic substitution reaction and elimination reaction.

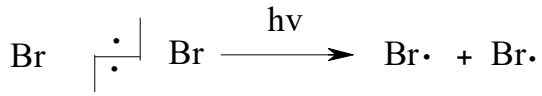
Teaching tasks and solution algorithms

Task №1. Decribe the mechanism of isobutene and cyclopentane bromination reaction at exposure to UV light.

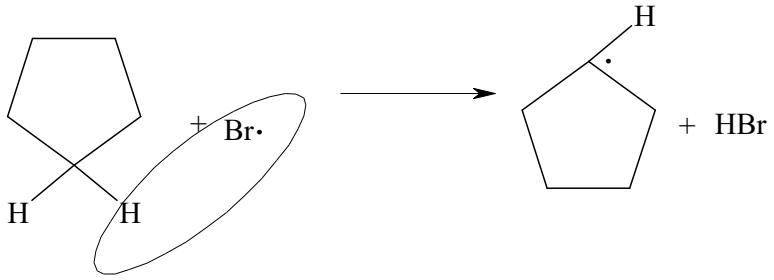
Solution. Molecules of isobutene and cyclopentane consist of sp^3- hybridized carbon atoms. C – C-bonds in their molecules are nonpolar, but C – H-bonds are low-polar. These bonds are undergone hemolytic fision readily that leads to the formation of free radicals – particles having unpaired electrons. Thus, radical substitution reactions - R_s – reaction or chain - should take place in the molecules of these substances.

The stages of any R_S –reaction are: chain initiation, chain propagation and chain termination.

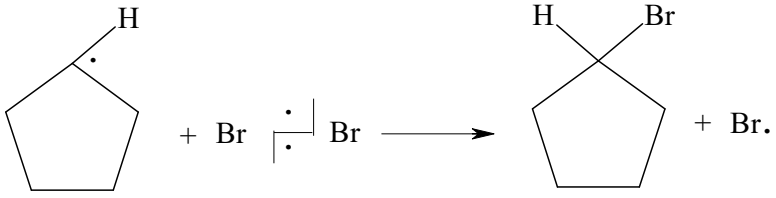
Chain initiation is a process of formation of free radicals at the high temperature and at exposure to UV light:



Chain propagation occurs at the expense of interaction of high-reactive free radical ·Br with low polar C – H-bond in the cyclopentane molecule that leads to the formation of new cyclopentyl-radical:

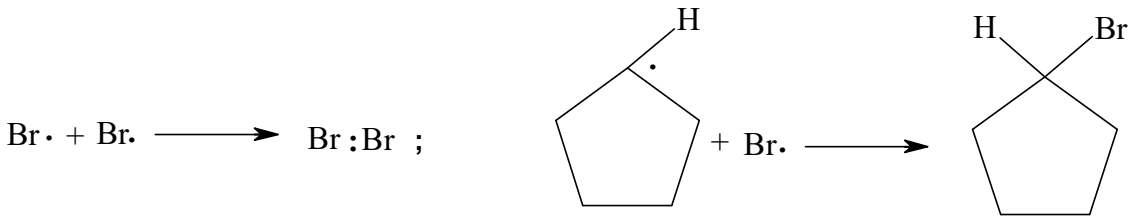


Cyclopentyl-radical reacts with new bromine molecule, resulting in it hemolytic fision of bond and forming bromocyclopentane and new bromine radical:



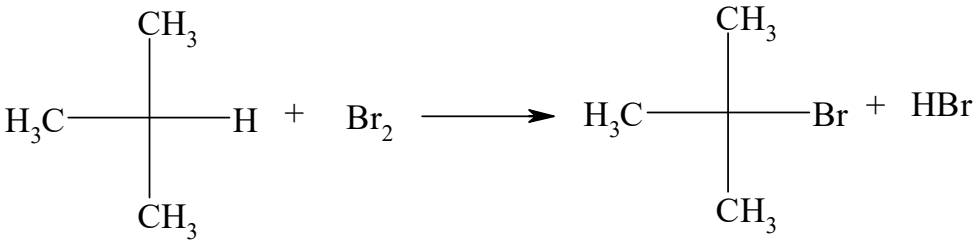
Free bromine radical attacks new cyclopentane molecule. Thus, chain propagation repeats many times, i.e., chain reaction takes place.

Chain termination completes chain reaction at the expense of combination of different radicals:



Whereas all carbon atoms in the cyclopentane molecule are equivalent, only monocyclobromopentane forms.

C – H-bonds are not equivalent in isobutane. They differ in the energy of hemolytic dissociation and stability of formed fre radicals. It is known that dissociation energy of C – H-bond increases from tertiary to primary carbon atom, stability of free radicals descreases in the same order. That is why in the molecule of isobutane bromination reaction proceeds regioselectively – using tertiary carbon atom:

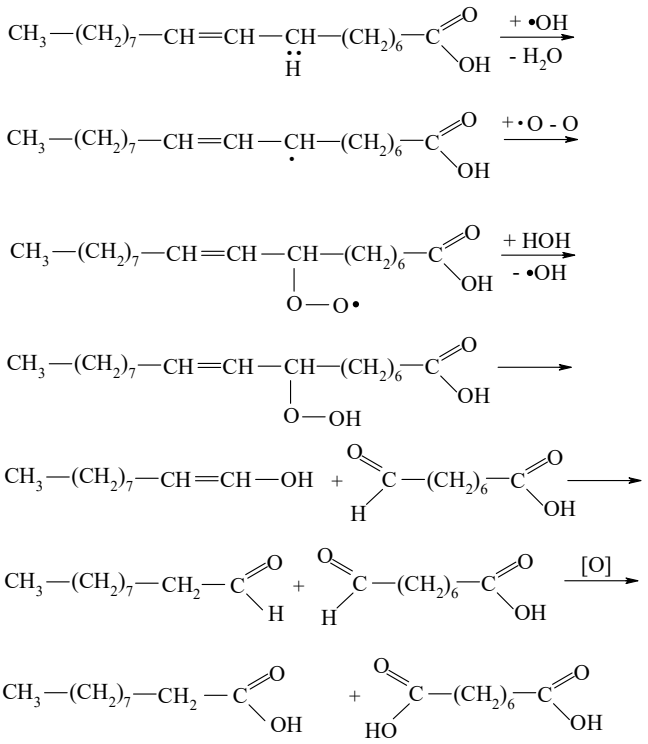


It should be pointed out that for more active chlorine radical regioselectivity is not kept to the full extent. Hydrogen atoms can be substituted at any carbon atoms under the chlorination, but quantity of substitution product at the tertiary carbon will be the greatest.

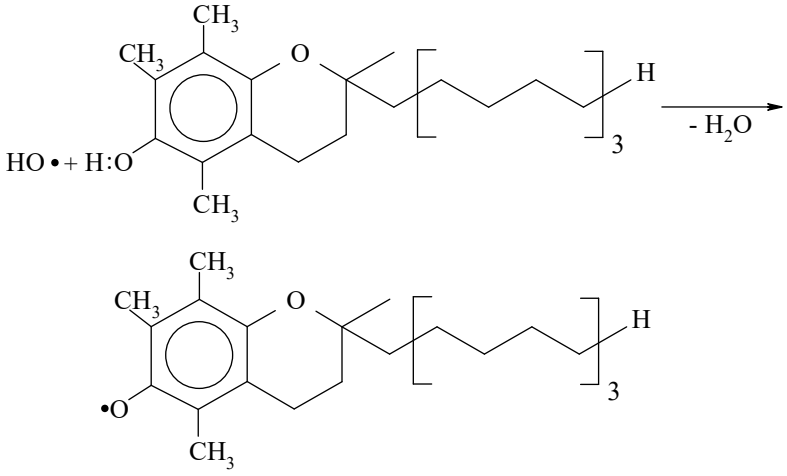
Task №2. Describe the mechanism of oleic acid peroxidation which takes place at radiation sickness as a result of damage of cellular membranes. What compounds do serve as antioxidants in our organism?

Solution. Example of radical reaction is peroxidation when unsaturated faty acids are undergone free radical effect. Unsaturated fatty acids are a part of cellular membranes. Breakage on radicals of water molecules is possible at radiation

exposure. Hydroxyl radicals attack molecule of unsaturated acid in methylene group, neighboring with double bond, because free radical, stabilized at the expense of participation of unpaired electron in conjugation with electrons of π-cbonds, forms in such a case. Further organic radical reacts with biradical oxygen molecule forming unstable hydroperoxides. These hydroperoxides dissociate forming aldehydes which are oxidized to acids – terminal products of the reaction. Damage of cellular membrame is a consequence of peroxidation:



Inhibiting effect of vitamin E (tocopherol) in the organism is conditioned with its ability to combine free radicals, forming in the cells:

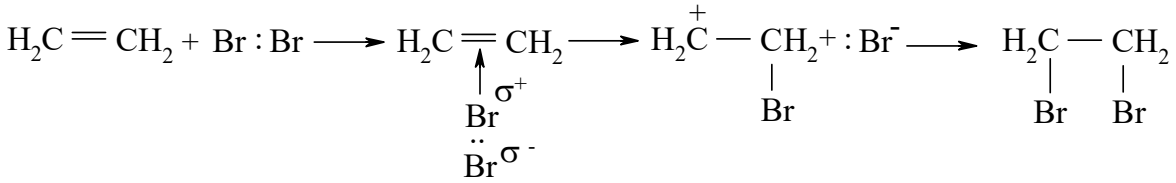


In the formed phenoxide radical unpaired electron is in the conjugation with π-electronic cloud of aromatic ring that reslts in its relative stability.

Task №3. Give the mechanism of ethylene bromination reaction.

Solution. Reactions which undergo π-bonds fision, i.e., addition reactions, are typical for compounds which consist of carbon atoms in the state of sp^2- or sp-hybridization. These reactions can pass on radical or onic mechanism depending on reagent nature, solvet polaity, temperature and others. Ionic reactions proceed under action of electrophilic reagents having electron affinity, or nucleophilic reagents, which donate their electrons. As electrophilic reagents can be catuins and compounds which have atoms with incomplete electron shells. Elementary electrophilic reagent is roton. Nucleophilic reagents are anions, or compounds with atoms having unshared electron pairs.

Reactions of electrophilic addition - A_E-reactions- are typical for alkenes – compounds having sp^2 - or sp-hybridized carbon atom. Halogenation reaction proceeds by ionic mechanism with the formation of carbocations in the polar solvents:

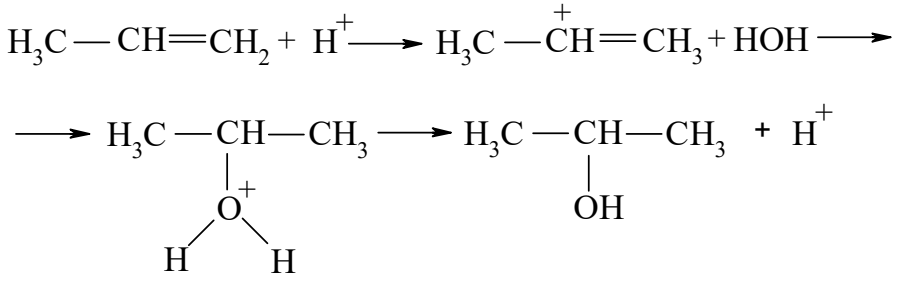


Bromine molecule is polarized under the action of π-bond of ethylene molecule causing the formation of unstable π-complex, which transforms into a carbocation. In this carbocation bromine is bound with carbon using π-bond. Process is terminated with interaction of bromine anion with this carbocation that results in the formation of final product of reaction - dibromoethane.

Task №4. Substantiate Markovnikov's rule by the example of propene hydration reaction.

Solution. As water molecule is nucleophilic reagent then its addition across the double bond without catalyst is impossible. Acids serve as catalyst in such reactions.

Formation of carbocations occurs at the addition of proton of acid at the fission of π-bond:

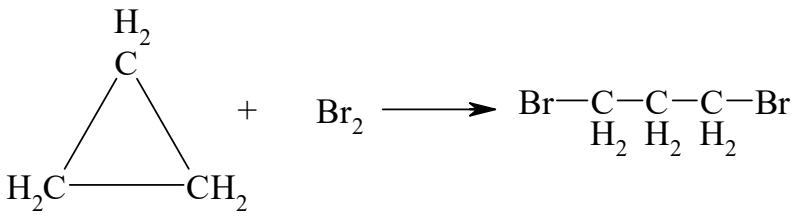


Water molecule attaches to the formed carbocation at the expense of paired electrons of oxygen atom. Stable alkyl derivative of oxonium stabilized with proton elimination is formed. Product of reaction is secondary propanol (propan-2-ol).

In hydration reaction proton attaches in accordance with Markovnikov's rule – to the carbon atom with more hydrogen atoms, as electron dencity shifts to this atom because of positive inductive effect of CH_3-group. Besides, formed after addition tertiary carbocation is more stable than primary (influence of two alkyl-groups).

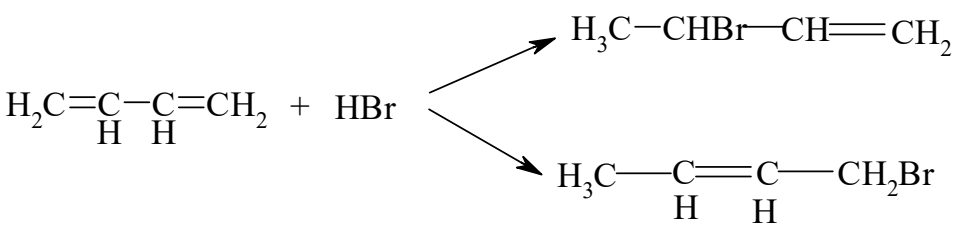
Task № 5. Substantiate ability to form 1,3-dibromopropane at the cyclopropane bromination.

Solution. Molecules which are three- or four-membered cycles (cyclopropane and cyclobutane) exhibit properties of unsaturated compounds, because electronic state of their "banana" bonds resemble π-bond. That's why they undergo addition reactions with cycle breakage like unsaturated compounds:

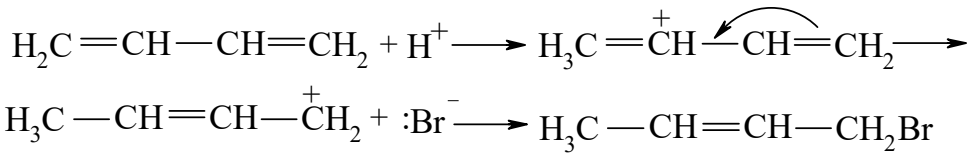


Task № 6. Describe reaction between hydrobromide and butadiene -1,3. What is the feature of this reaction?

Solution. 1,2 Adition products (1) and 1,4 addition products (2) form after interaction between hydrobromide and butadiene -1,3:



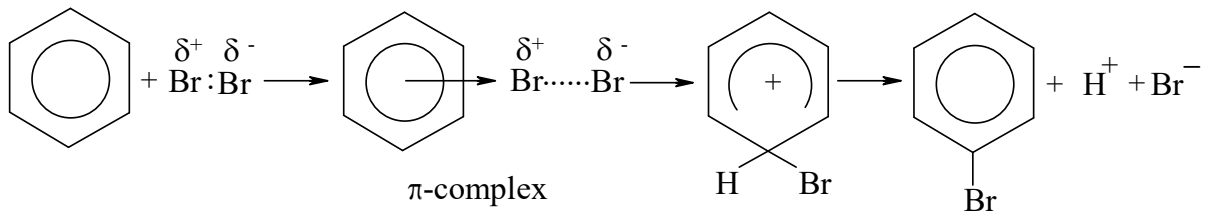
Formation of product (2) is stipulated with presence of common to whole molecule π-electron cloud in the conjugated system, hereupon it undergoes electrophilic addition reaction (A_E- reaction) as whole block:



Task № 7. Describe mechanism of benzene bromination.

Solution. Electrophilic substitution reactions are typical for aromatic compounds having closed conjugate-electronic system and which because of it have significant stability. Presence of increased electron density on both sides of ring protects its from attack with nucleophilic reagents and vice versa it simplifies capability of attack with nucleophilic reagents and vice versa - it simplifies capability of attack with cations and other electrophilic reagents.

Interaction between benzene and halogens proceeds in the presence of catalysts - $AlCl_3$, $FeCl_3$ (so called Lewis acid). They provoke polarization of halogen molecule, after which it attacks π-electrons of benzene ring:



At first π-complex forms, which slowly transfers into σ - complex, where bromine forms covalent bond with one of the carbon atoms at the expense of two of six electrons of aromatic ring. Four retained π-electrons are dispensed between five atoms of carbon ring; σ-complex is less convenient structure because of disturbance of aromaticity, which restores by poton separation.

Sulphonation and nitration refer to electrophilic substitution reactions in aromatic compounds. Nitroyl-cation - NO^{2+}, formed under interaction between concentrated sujphuric acid and nitric acid (nitrated mixture), serves as nitrating agent; cation SO_3H^+, or sulfur oxide (IV) serves as sulphonating agent, if sulphonation is performed with oleum.

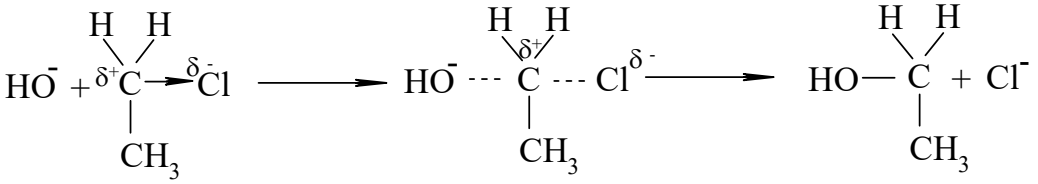
Task № 8. Obtain ethanol and ethylene from chloroethane.

Solution. There is a presence of the polar covalent bond in the molecule of chloroethane because of the difference in electronegativity between carbon $C^{\delta+}\rightarrow Cl^{\delta-}$ and chlorine. The reaction of chloroethane with nucleophile i.e. $OH^-; H_2\ddot{O}; H_2\ddot{S}; \ddot{N}H_3$ goes with the heterolytic cleavage and substitution of Cl^- for another nucleophile (OH^-). The haloalkane splits heterolytically to form a carbocation and a free halide ion.

Hence, it is the nucleophilic substitution reaction – S_N. Water solution of KOH is used as a source of OH^- ions.

This is an ionic reaction. In S_N reactions there is a loss of the leaving group, formation of an intermediate product (or activated complex) - carbocation, which is then, undergone a rapid reaction with an electron rich nucleophile.

In the reaction of haloalkane with alkali solutions, hydroxyl ion attacks positively charged carbon from the opposite side to the negatively charged halogen:

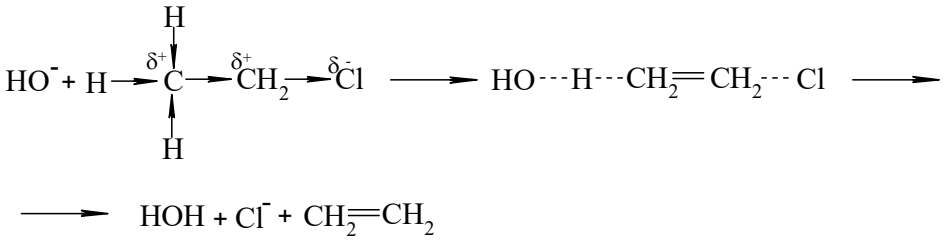


Intermidiate state

In the presence of a sufficient amount of energy OH^- ion moves in such distance that it forms bond with carbon but bond between carbon atom and halogen weakens.

In the formed activated complex carbon atom is in sp^2-hybridization and this complex has planar structure. Then sequentially the bond with chlorine is broken and alcohol forms. Reaction proceeds in mild conditions taking into consideration that Cl^- is more stable then OH^--ion, which reacts, i.e., belongs to good leaving groups. Based on S_N reactions, with the aid of halogen derivatives, very important vital substances are synthesized such as hormone adrenaline, vasoconstrictive drug ephedrine, spasmodic agent tetranium, natural α-hydroxyacids ect.

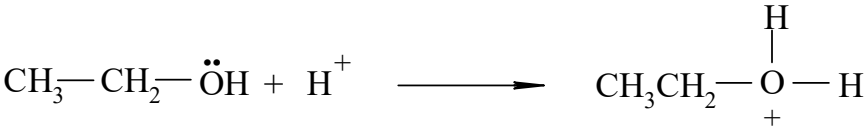
Elimination reactions (E) compete with nucleophilic substitution (S_N) reactions. In the reaction of alkyl halides with an aqueous alcoholic solution of the alkali hydroxide unsaturated hydrocarbons forms. In this case, nucleophile, a strong base, attacks the hydrogen atom on a β-carbon having a partial positive charge because of -I-effect of the halogen (C-H acidity). The activated complex forms an intermediate product in this reaction.



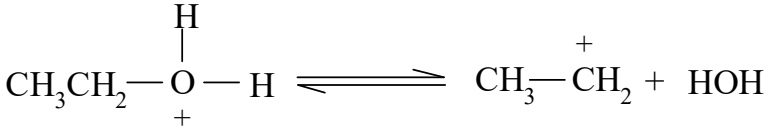
Task № 9. Describe the mechanism of chloroethane (ethyl chloride) formation (a mild topical anaesthetic) and competitive to it the elimination reaction.

Solution. Hydroxyl group of alcohol in S_N reaction can be substituted by nucleophile such as halogen. The nucleophilic substitution reaction occurs when the leaving group is more stable than the incoming group. Whereas the OH^- ion is less stable than Cl^-, the reaction goes under acidic condition. When hydroxyl group is

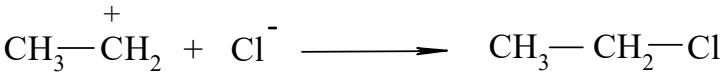
protonated, it is transformed into the better leaving group – H_2O. Hydrogen is attached to the alcoholic oxygen due to the lone pair on it:



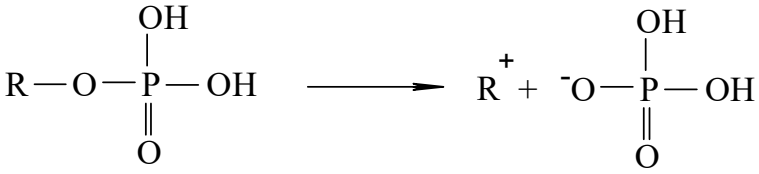
Oxonium (Lewis) base stays in equilibrium with a carbocation:



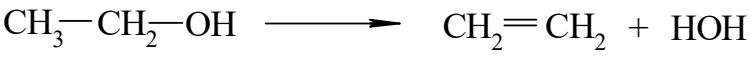
Carbocation is stabilized by the nucleophilic attack of Cl- ion:



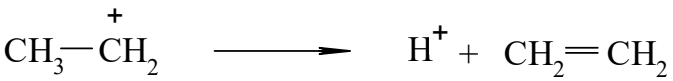
In the organism, the substitution of the alcoholic hydroxyl group proceeds by the transformation step into phosphoric, diphosphoric or triphosphoric acids because ethers formed from these acids are good leaving groups:



S_N reactions for alkyl halides and alcohols compete with elimination reactions. When alcohol is heated with concentrated H_2SO_4, dehydration of alcohol takes place and hydrocarbon of ethylene series form:



In this case carbocation is stabilized by the deprotonation:



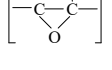
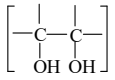
Task № 10. Describe oxidation capacity of alkane, alkene, and arenes.

Solution. Oxidation of organic compounds is the process that involves increasing its oxygen in an organic substrate or decreasing its hydrogen content, accompanied by π-bond formation or a new bond between carbon and more electronegative atoms such as oxygen, nitrogen, sulphur etc. The transfer of electrons from a substrate to an oxidant determines the oxidation of a compound. Therefore, highly electronegative elements that easily accept electrons can be oxidizing agents. Examples of oxidizing agents include oxygen, peroxides, nitric acid, potassium permanganate, potassium dichromate and others.

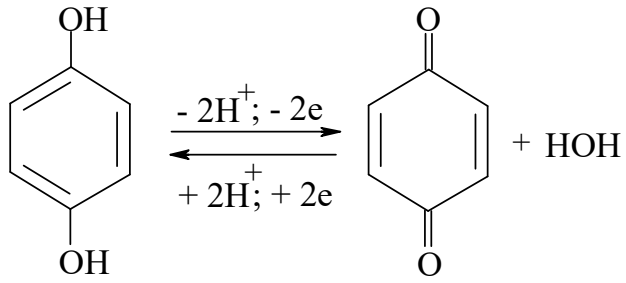
Reduction of an organic compound usually involves increasing its hydrogen content accompanied by electrons transfer from reducing agent to organic substrate. Hydrogen is used as the reducing agent in the presence of heterogenic catalysts (Pt, Pd, Ni), metal hydride in acidic medium (NaH, $NaBH_4$, $ZiBH_4$).

The capacity of organic compounds to oxidation depends on their ability to loose electrons. The easier the substrate looses electrons, the faster it oxidizes. Thereby, saturated hydrocarbons (alkanes) are the most difficult to oxidize. Strong conditions (chromic acid solution typically $K_2Cr_2O_7^{2-}{}_{(aq)}$) are required for their oxidation. Oxidation proceeds in a sequence: alkane oxidizes to alcohols, alcohols to aldehydes or ketones, which can be oxidized to carboxylic acids. The ability for oxidation increases in the following order:

$$-CH_3 \quad < \quad -CH_2- \quad < \quad -CH-$$

Homologous series of benzene and heterocyclic compounds oxidizes similar to alkanes. Compounds with double and triple bonds such as alkenes, alkynes oxidize much easier then alkanes. Alkenes oxidation products can be epoxides  , diols  , ketones  , and carboxylic acids  . Epoxides are formed from condensed aromatic systems in the organism and exhibit cancerogenic effects.

Benzene is extremely stable towards oxidation. It can react only in the presence of catalyst and require high activation energy. The presence of the electronegative substituents in benzene ring such as –OH increases its reactivity. The specificity of redox reaction with 1,4-dihydroxybenzene (hydroquinone) is its reversibility that has a significant biological role. This process represents the fundamental interaction in multiple chemical and biological processes:

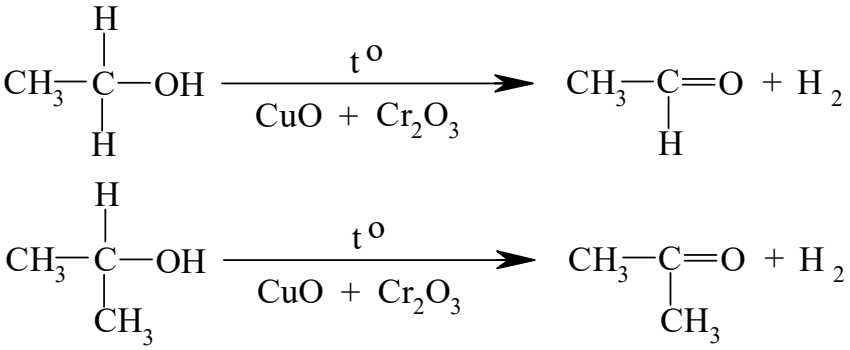


Hydroquinone Quinone

The electron transfer in mitochondrial respiration chain by coenzymes Q (ubiquinones) is a similar process.

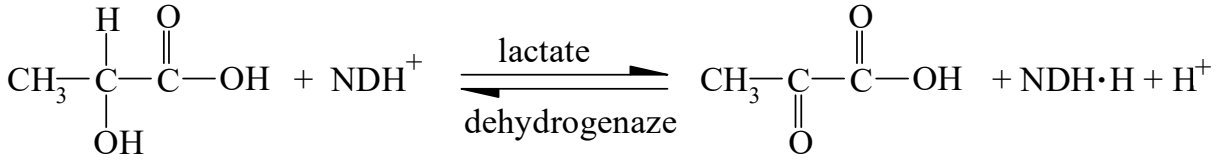
Task № 11. Give the scheme of the lactic acid oxidation *in vivo*.

Solution. Primary and secondary alcohols are oxidized much easier to the corresponding alkanes. Oxidation of alcohols can be done under the high temperature and in the presence of catalyst:



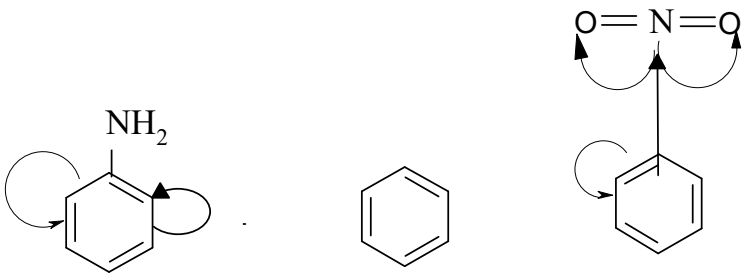
This is the dehydration reaction, which takes place in the organism upon the biological oxidation. This process is catalyzed by enzymes dehydrogenase, whose

cofactor is NAD^+ (nicotinamide adenine dinucleotide). In the dehydration reaction the substrate looses 2 electrons and 2 protons or 1 proton and 1 hydride ion which is accepted by NAD^+:



Evaluate reactivity of benzene, aniline, nitrobenzene, pyrrol and pyridine electrophilic substitution reactions (S_E-reactions).

Solution. Activity of compounds in S_E-reactions depends on value of electron demcity in aromatic ring (direct dependence). Depending on this reactivity of compounds should be considered with reference with electronic effects of substituents and heteroatoms.



Amino group in aninline exhibits + M-effect, that results in increasing of dencity in benzene ring and its greatest concentration is in orto- and para-positions. Reaction behavior is facilitated.

Nitro group has -I and –M-effects in nitrobenzen, that's why it desctivates benzene ring notably in orto- and para-positions. Since interaction of electrophile occurs in the place of highest electron dencity then meta-isomers form. Thus, electron-donating substituents – these orto- and para-orientants (orientants of I type and activators of S_E-reactions; electron withdrawing substituents – metha-orientants (orientants of II type) deactivators of S_E-reactions.

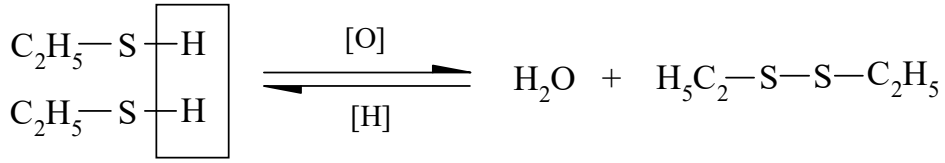
In five-membered heterocycles (pyrrole, furan, thiophen), which are π-excessive systems, S_E-reactions proceed easier then in benzene; in this case α-position is more reactive.

Heterocyclic systems with pyridine nitrogen are π –deficient, that's why they undergo electrophilic substitution reactions more difficult; in such a case electrophile occupies β-position in relation to nitrogen atom.

Task № 12. Give the scheme of ethyl mercaptan (ethylthiol) oxidation.

S o l u t i o n . Unlike alcohols in thiols oxidation undergoes the sulphur atom instead of carbon, because the S-H bond is less stabile then the O-H bond. In the reaction with strong oxidant the сульсеновые, sulfinic acids and sulfonic acids are formed.

D i s u l p h i d e s a r e f o r m e d u n d e r m i l d c o n d i t i o n o f o x i d a t i o n (p e r o x i d e s) :



Disulphide formation and reduction reactions tale an important place in vital processes, e.g. interconversion of lipoic and dihydrolipoic acids take place in lipid and carbohydrate metabolisms, cystein-cystine reaction in the formation of the protein space structure.

4. Laboratory work

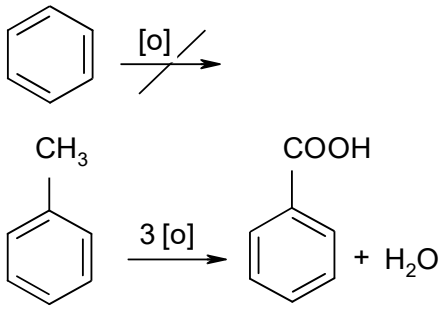
Experiment 1. Reactivity of alkanes.

Apply one drop of potassium permanganate and concentrated sulfuric acid on the slide at the
short distance from one another. Mix every drop with paraffin oil.

Experiment 2. Oxidation reaction of arenes.

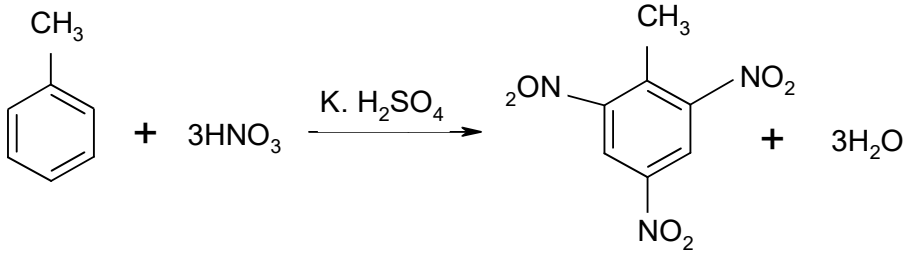
Add 1 drop of $KMnO_4$ and 1 drop of H_2SO_4 solution to the test tube containing two drops of water. Add 1 drop of benzene to the obtained solution. Add 1 drop of

toluene to the another test tube containing 5 drops of water, 1 drop of $KMnO_4$ solution and 1 drop of H_2SO_4 solution. Heat at the burner flame shaking vigorously.



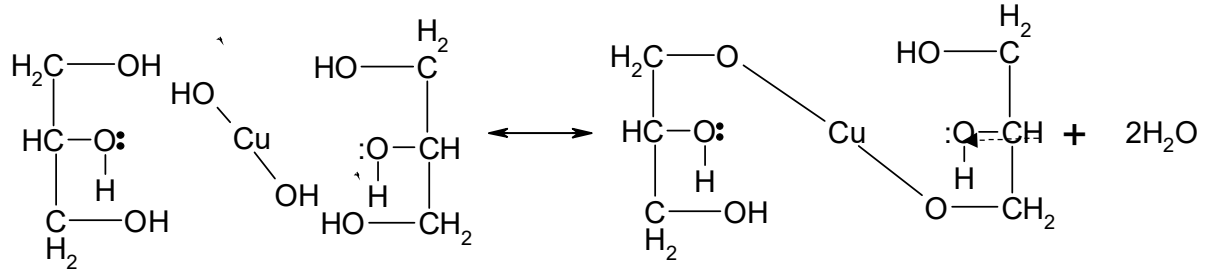
Experiment 3. Nitration of toluene.

Add 3 drops of the concentrated H_2SO_4 and 2 drops of the concentrated HNO_3 to the test tube. Then add 2 drops of toluene and slowly bring down to boiling. Allow the contents of the test tube to cool and pour it to another test tube containing 8 – 10 drops of water. Gently shake the contents of the test tube and identify the nitrotoluene according to the smell which is similar to the bitter almond smell, this is characteristic feature of aromatic mononitrocompounds.



Experiment 4. Reaction of glycerol with $Cu(OH)_2$ in alkaline medium.

Add 2 drops of 2 % $CuSO_4$ solution and 2 drops of 10% NaOH solution to the test tube. Blue precipitate of $Cu(OH)_2$ forms. Add 1 drop of glycerol to this precipitate and gently shake the contents of the test tube. Blue chelate compound forms after the reaction of cupper (II) hydroxide with glycerol.



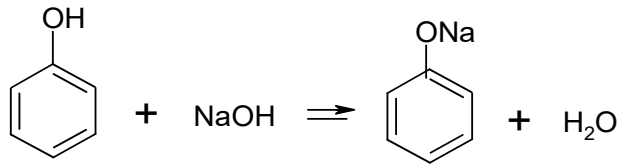
Experiment 5. Colour reaction of phenol with iron (III) chloride.

Add 1 drop of liquid phenol and 1 drop of water to the test tube. While shaking emulsion of phenol forms and then it becomes broken. Add water dropwise till clear solution of phenol in water (phenolic water) forms. Add 3 drops of prepared phenolic water and 1 drop of 1% iron chloride solution to another test tube. Purple colour forms that is caused by the formation of mixture of the following complex compounds: $C_6H_5OFeCl_2$, $(C_6H_5O)_2FeCl$, $(C_6H_5O)_3Fe$. Intensity of colour increases during the dilution with water and reduces or completely disappears after the addition of ethanol.

$$3C_6H_5OH + FeCl_3 \rightleftharpoons (C_6H_5O)_3Fe + 3HCl$$

Experiment 6. Proof the acidic properties of phenol.

Add 1 drop of phenol to the residue of phenolic water and shake. Add of 1 drop of 100% NaOH solution to the obtained emulsion of phenol in water. Clear solution of sodium phenolate forms and it is freely soluble in water.



Experiment 7. Precipitation of protein bodies with phenol.

Add 1 – 2 drops of liquid phenol and 1 drop of protein solution on the slide. Mixture grows turbid as a result of protein denaturation by phenol. This is the base of phenol usage for disinfection.

Revision exercises

№1

1. What is the name of the product obtained after 2-methylbutane bromination reaction at exposure to UV light? Describe mechanism of the reaction.
2. Describe mechanism of the reaction between butene-1 with hydrobromide. What is the type of this reaction?
3. Write the reaction equation for aniline (aminobenzene) bromination. Point out orienting effect of amino group. What is easier to brominate – benzene or aniline? Why?

№2

1. Describe mechanism of 2-methylpropane chlorination reaction at exposure to UV light.
2. Write the mechanisms of interaction reaction between butadiene-1,3 and hydrobromide.
3. Write the reaction equation of nitration of benzoic taking into account orienting influence of carboxyl group. What is easier to nitrate: benzene or benzoic acid? Why?

№3

1. Write mechanism of the cyclohexane chlorination reaction. Write predominant conformation of chlorocyclohexane.
2. Write the mechanism for HCl addition reaction to acrylic (propenoic) acid. Explain why this addition takes place against Markovnikov's rule.
3. Write the reaction equation for pyridine bromination taking into account orienting influence of heteroatom. What is easier to brominate: benzene or pyridine? Why?

№4

1. What is the name of the substance obtained at the toluene (methylbenzene) chlorination at exposure to UV light? Describe the mechanism of the reaction.
2. Write the mechanism of the butendioic acid chlorination reaction.
3. Write the reaction equation for phenol nitration taking into account orienting influence of hydroxyl. What is easier to nitrate: benzene or phenol? Why?

№5

1. Write the mechanism for propane bromination reaction. Explain where C-H-bond is and why in this case attacking place of free radical is bond.
2. Describe the mechanism of the interaction reaction between propen and water. What is the role of sulfuric acid in this process.
3. Write the reaction equation for benzaldehyde bromination. Compare this reaction with benzene bromination reaction.

№6

1. Write the mechanism of the cyclopentane bromination reaction.
2. Describe the mechanism of interaction reaction between isoprene (methylbutadiene) with 1 mol of bromine.
3. Write the reaction equation for toluene (methylbenzene) nitration taking into account orienting influence of methyl group. Does CH_3-group facilitate or trouble nitration reaction?

№7

1. Write the reaction equation for cyclopropane bromination. Explain direction of the reaction.
2. Justify Markovnikov's rule at the example of 2-methylpropen hydrochlorination reaction. Describe the mechanism of the reaction.
3. Write the reaction equation for pyrrol bromination. Point out orienting influence of heteroatom.

№8

1. What is the name of the substance obtained at the ethylbenzene chlorination at exposure to UV light? Describe the mechanism of this reaction.
2. Give the mechanism of transformation of fumaric acid (trans-butenedioic acid) into malic acid (2-hydroxybutanedioic acid) at metabolism in living organisms on one of the stage of Krebs cycle.
3. What products are formed at the chlorination of bromobenzene and benzoic acid? What compound will be active in the chlorination reaction?

№9

1. Give the mechanism of isobutene bromination at exposure to UV light.
2. Compare reactivity of vinyl chloride (chloroethene), ethylene and propene in the electrophilic addition reactions. Write hydrobromination reaction for one of the more active compound from them.
3. Describe the mechanism of the aniline bromination reaction with account of electronic effect of the amino group. Does presence amino-group in the benzene ring facilitate or trouble reaction?

№10

1. Give the mechanism of cyclohexane chlorination at exposure to UV light.
2. Give the mechanism of HBr addition reaction to the acrolein (propenal). Does reaction proceed in accordance with Markovnikov's rule? Substantiate answer.
3. Write the mechanism of the phenacetin (antipyretic) formation reaction using phenetole nitration reaction (ethoxy benzene).

№11

1. Write the reaction equation of cyclobutane with chlorine. Explain the direction of the reaction.
2. Give the mechanism of acrylic (propenoic) acid hydration reaction. What is the role of sulfuric acid in this reaction?
3. Write the reaction equation of toluene bromination. What is easier to nitrate – benzene or toluene and why?

№12

1. Give the mechanism of the 2-methylpentane chlorination reaction at exposure to UV light. Is regioselectivity observed in this case?
2. Give the mechanism of the pentene-1chlorination reaction.
3. Give the mechanism of the pyrrole bromination reaction. What is easier to brominate: pyrrole or pyridine and why?

№13

1. What is the product in 3-methylpentene bromination reaction at exposure to UV light? Give the mechanism of the reaction.
2. Give the mechanism of the reaction between butadiene-1,3 with 1 mol of HBr.
3. Write the mechanism of the methyl-phenyl ketone nitration reaction at the synthesis of mesatonum (adrenoceptor agonist).

№14

1. What is the product in the toluene bromination reaction at exposure to UV light? Write the mechanism of this reaction.
2. Give the mechanism of vinyl chloride (chloroethene) bromination reaction.
3. Write the reaction equation of nicotinic acid (β-pyridine carboxylic acid) nitration with account of electronic effect of heteroatom. Which compound is easier to brominate: pyridine or benzene? Why?

№15

1. Give the mechanism of cyclohexane bromination reaction.
2. Give the mechanism of the 2- butenoic acid in the presence of H_2SO_4.
3. Write the reaction equation of furfural (furan-2-aldehyde) nitration, on the base of which bactericides: furacilin, nitrofurantoin, furasolidone and others are synthesized.

SUGGESTED READINGS

1. Biological and Bioorganic Chemistry : in two books : Textbook. Textbook 1. Bioorganic Chemistry / B.S.Zimenkovsky, V.A.Muzychenko, I.V.Nizhenkovska, G.O.Syrova; edited by B.S.Zimenkovsky, I.V.Nizhenkovska. —K. :AUP «Medicina», 2017. — 288 p.

2. Biologically important classes of bioorganic connections. Biopolymers and their structural components: Theoretical course of biological and bioorganic chemistry, Module 1 / A. O. Syrovaya, E. R. Grabovetskaya, N. M. Tkachuk, L. G. Shapoval, V. N. Petiunina, S. A. Nakonechnaya. – X.: «Цифровая типография № 1». – 2013. – 183 p.

3. Zurabyn S. E. Fundamentals of Bioorganic Chemistry. – M.: GEOTAR-MED, 2003. – 320 p.

Навчальне видання
Класифікація хімічних реакцій. Реакційна здатність алканів, алкенів, аренів, спиртів та фенолів
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