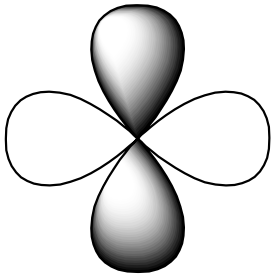
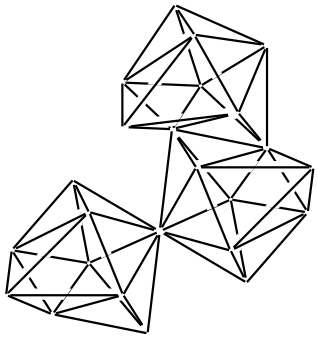
Vinnytsia National Pirogov Memorial Medical University
Biological and General Chemistry Department
Bioorganic chemistry course





SYSTEMATIC COURSE

Module 1. Practical seminars of bioorganic chemistry for foreing students Biological active compounds.

Vinnytsia 2017

A work sheet and methodical developments (Methodical of recommendation for practical classes from Bioorganic chemistry for 1-st year foreign students) are made by the employees of department of biological and general chemistry of VNMMU Pirogov in accordance with a curriculum, worked out on principles of the European credit-transfer system (ECTS) for higher medical establishments of Ukraine III - IV levels of accreditation for specialities of "Medical Affairs" direction of the preparation "Medicine" is in accordance with education qualification descriptions (EQD) and scientific profesional programs (SPP) of the preparation of specialists, approved by an order MES Ukraine from 16.04.03 № 239.

It is considered and accepted on a meeting of the methodical soviet of medical-theoretical disciplines, protocol № 1 from 30.08.2017y.

It is discussed and approved on a meeting of the department of biological and general chemistry, protocol № 1 from 28.08.2017y.

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Contents

SAFETY IN THE CHEMICAL LABORATORY AND FIRST AID RULES.

1. The chemical laboratory must be always clean and kept in the order and silence. No unnecessary staff should be present and everybody must keep to the rules of safety.
2. The students have to wear the laboratory coat and special medical hat in the laboratory.
3. Every student has to know where the fire-preventing means and the first-aid kit are placed in the laboratory.
4. It is forbidden to smoke, eat and drink in the laboratory.
5. It is not allowed to start the laboratory work without knowing the technique of the experiments.
6. Experiments must be carried out only in the clean laboratory dishes. After laboratory work finishing the dishes have to be washed.
7. The students must carefully perform the experiments and avoid getting the chemicals into the eyes, on face and hands skin.
8. Do not taste the chemicals. To smell the substances is necessary to move the hand in the direction of face carefully.
9. Do not use the chemicals without the identified label on the flask or vessel.
10. Do not direct the test-tube towards the front of your face or near standing person during heating of solid or liquid substance. Do not have a look in the test-tube during such procedure.
11. Switch off gas, water, and electricity before leaving the laboratory.
12. It is forbidden to pour out the concentrated acid or base. The students have to use the special glasses, the gas mask working with the poisoning compounds, concentrated acid and base, phenol and others.
13. The experiments with the inflammable compounds (ether, acetone, benzene, alcohol) must be carried out far from fire and switched off instruments.
14. If fire starts, gas must be closed immediately. All inflammable compounds must be shifted far a way from fire and used the antifire stuffs (a fire-extinguisher, sand, antifire coating). Wrap person in fire blanket. DO NOT USE WATER TO PUT OUT FIRE.
15. The below given table is helpful in an accidental situation. Read and remember them.

Situation	Safe Response
Burns	Flush with ethanol solution or diluted solution of $KMnO_4$.
Cuts and Bruises	Treat as directed by instructions included with first aid kit
Fainting or collapse	Provide person with fresh air, have him recline in a position so that his head is lower than his body.
Foreign Matter in Eyes	Flush about 15 min with plenty of water, then go to the doctor
Severe bleeding	Apply pressure or a compress directly to the wound and get medical attention immediately
1. Spills, general 2. Acid burns 3. Base burns	1. Wash the damaged area with plenty of water, use the shower if is necessary 2.Use sodium hydrogen carbonate (baking soda) 3. Use 3 % of boric acid or acetic acid

Short methodical directions for practical lesson:
Practical lesson is started from the general questions (5 min).
Explanation of unclear questions (25 min)
Writing of control test (15 min)
Carrying out a laboratory work, filling a laboratory notebook, signing the laboratory notebook by a teacher, announcing of student marks (45 min).

Technological map of practical lesson:

N	***Steps***	***Time (min)***	***Educational handout***	***Residence***
1	General questions	5		Faculty
2	Correction of theoretical student knowledge	20	Tables, task	
3	Control test	15	Test, questions	
4	Performing of laboratory work	40	Chemicals, chemical dishes, equipments.	
5	Analysis and conclusion of a practical lesson	10		

TOPIC 1. THE CLASSIFICATION, NOMENCLATURE, ISOMERIZM OF BIOORGANIC COMPOUNDS. THE NATURE OF CHEMICAL BOND.

1. Actuality of the topic:

The main meanings that are used in organic chemistry such as the classification, nomenclature, nature of chemical bonds, spatial structure and other properties that are necessary for the explanation of the reactivity of biologically active compounds in normal and pathologic processes.

2. General aim: to use the main definitions of bioorganic chemistry for explanation of the connection between electronic and space structure of bioactive compounds and their reactivity.

3. Special aims:

- to use main bases of IUPAC nomenclature to name the organic compounds;
- to explain the dependence of biological activity on the spatial structure of the compounds;
- to explain the dependence of the reactivity of compounds on the nature of chemical bonds and mutual influence of atoms in molecule.

4. Literature:

4.1. Lecture.

4.2. Zurabyan S.E., Fundumentals of bioorganic chemistry, Moscow, 2004, pp. 225-238.

5. The main questions of the seminar:

5.1. The main aspects of the international (systematic) nomenclature (IUPAC).

5.2. Space isomerization of bioactive compounds:

cis – trans – isomers, enantomers, conformation isomerization (definition, examples, meaning for biological processes).

5.3. Distribution of electron density in organic molecules: electron inductive and mesomeric effects .

6. Questions for independent extra-class study:

6.1. The classification of organic compounds according to the structure of carbon skeleton and the nature of functional groups.

6.2. The hybridization of the carbon atom, electronic structure of its chemical bonds.

6.3. Electronegativity of chemical elements.

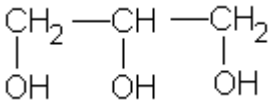
7. Examples of task:

7.1 Name the fumaric acid HOOC – CH = CH – COOH according to IUPAC:

Solution: butendiovic acid.

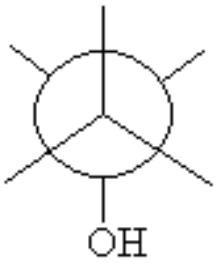
7.2. Write the formula of propantriole:

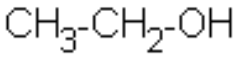
Solution:

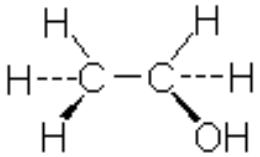


7.3. Write structure and configuration of the compound, that has such braked configuration.

Answer:



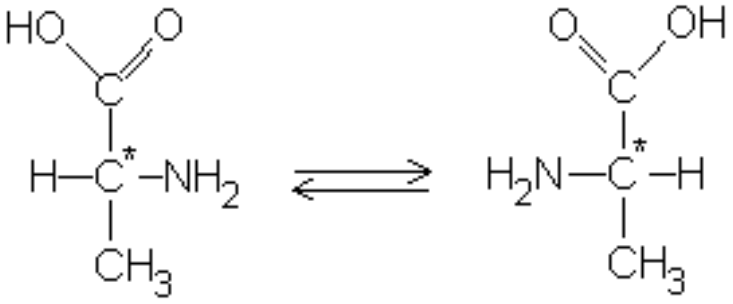




Configuration ***structure***

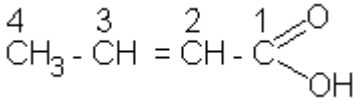
7.4. Write the formulas of enantomers of alanine and show their relative configuration.

Answer:



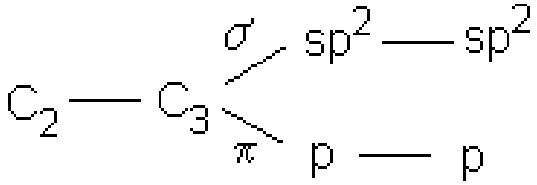
D- *L-*

7.5. Determine the type of hybridization of carbon atoms in the crotonic acid and show the schematic structure of bonds between carbon atoms.



Answer:

$C_{1,2,3}$ - sp^2, C_4 - sp^3; $C_1 \overset{\sigma}{-} C_2$; $sp^2 - sp^2$ $C_3 \overset{\sigma}{-} C_4$; $sp^2 - sp^3$



7.6. Mark graphically and determine the kind of electronic effects of carboxyl-group in acetate (acetic acid) and benzoate (benzoic acid).

Answer:

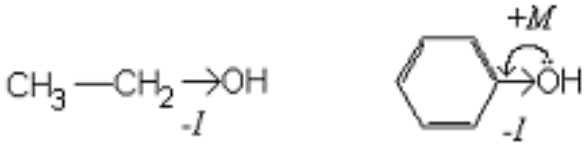
(acetic acid) (benzoic acid)

8. Homework (must be performed in the laboratory notebook):

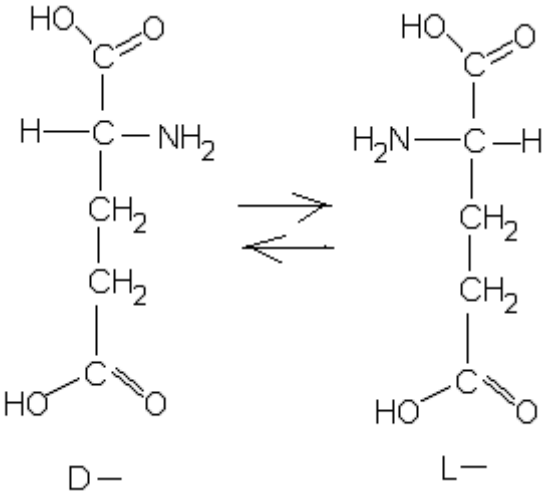
8.1. Write the formulas of such compounds: amino – 3 – mercapthopropanic acid; 2 – oxobudandiolic acid.
8.2. Write the structure, configuration, staggered conformation of colamine.
8.3. Write the enanthomers of valine and show their configuration.
8.4. Determine the kind of hybridization of carbon atom in acetaldehyde and write the scheme of structure of the bonds between carbon atoms.
8.5. Mark graphically the electronic effects in ethanol (C_2H_5OH) and vinyl alcohol (CH_2=CH-OH) molecules.

9. The control test:
For example:
9.1. Mark graphically and determine the kind and the sign of electronic effects of the oxy-group in ethanol and phenol.
9.2 Write formulas of enantomers of glutamic acid and show their relative configuration: HOOC – CH_2 – CH_2 – CH (NH_2) – COOH.
9.3. Write the molecular formula, structure, configuration**,** braked conformation of methylcyclohexane.

Answers:
9.1.

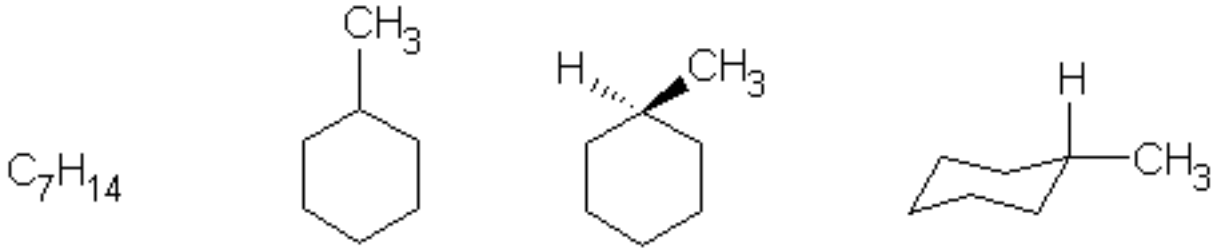


Ethanol Phenol
9.2.



D– L–

9.3.



molecular formula | structure | configuration | conformation

10. The algorithm of lab work:

Construction of molecular models of bioactive compounds.

TOPIC 2: Reactivity of alkanes, alkenes and arenes

1. Actuality of the topic:

The reactions involving **alkanes, alkenes and arenes** take place in human organism. Studying the mechanisms of chemical reactions gives the possibility to explain the processes (in temper) in normal and pathological states. The knowledge of reaction mechanism is used to produce substances (medications, medicaments) with knowing propertits.

2. General aim:

To explain the reactivity of biological active substances using the mechanism.
To compare the reactivity of biological active substances

3. Actual aims and abilities:

- to explain the dependence of the reactivity on nature of chemical bond and type of functional group

To apply the knowledge of mechanisms

- to explain the possibility of application for synthesis

4. Literature:

4.1. Lecture.
4.2. Zurabyan S.E., Fundumentals of bioorganic chemistry, Moscow, 2004, pp. 225-238.

5 . The main questions of the seminar:

5.1. The classsification of chemical reactions by mechanism.
5.2. The types of chemical bond breakage, free radicals, nucleophilic and electrophilic particulares (defenition, examples).
5.3. The mechanism of substitution radical reaction (S_R) beside the carbon atom in alkanes the mechanism of halogenazation reaction, biological meaning of free radicals.

5.4. The mechanism of addition electrophilic reaction in alkenes (A_E); mechanism of halogenation reaction, biological meaning.
5.5. The mechanism of substitution electrophilic reaction in benzene (S_E); mechanism of halogenation reaction, biological meaning. I and II order substituents. The influence of functional group on reactivity of arenas.
5.6. The formulas of ethane, propane, butane, hexane, benzene, methylbenzene, benzoic acid and theire isomers.

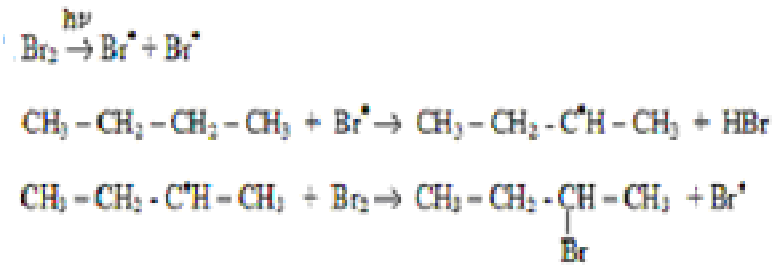
6. Questions for independent extra-class study:

6.1. The substitution, addition and elemination chemical reactions in organic chemistry.
6.2. Classification of chemical reaction by mechanism: the hydrogenation, halogenation, hydration, nitration, sulfonation, alkylation, acylation, hydrohalogenation chemical reactions in organic chemistry.

7. Examples of task:

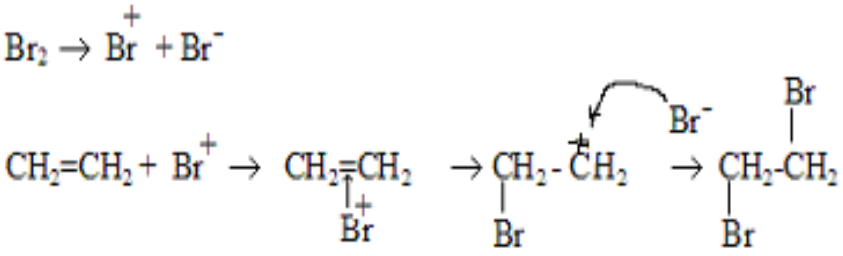
7.1. Describe graphically the reaction mechanism of bromination of butane.

Answer:



7.4. Describe graphically the reaction mechanism of ethene bromination.

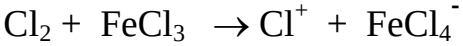
Answer.

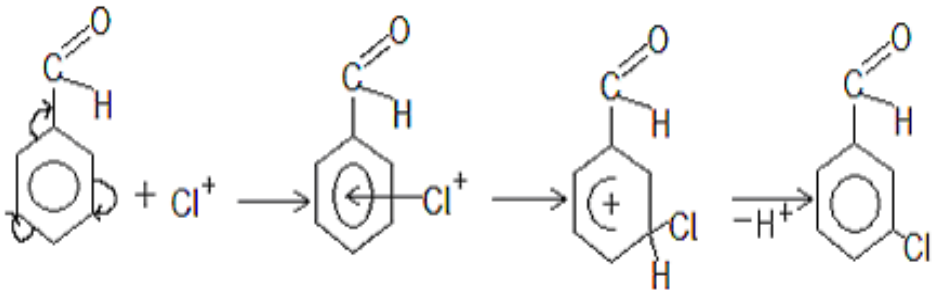


π-copmlex σ - copmlex

7.5. Describe graphically the reaction mechanism of benzaldehyde chlorination.

Answer:





π-complex *σ - complex*

8. Homework (must be performed in the laboratory notebook)

8.1. What are the free radicals and (electron-seeking reagent) the electrophilic particles. Analyse the reactivity**.**

8.2. Write the mechanism of butane bromination.

8.3. Write the mechanism of benzoic acid bromination.

9. Test control:

9.1. Why the substitution in alkanes takes place by radical mechanism?

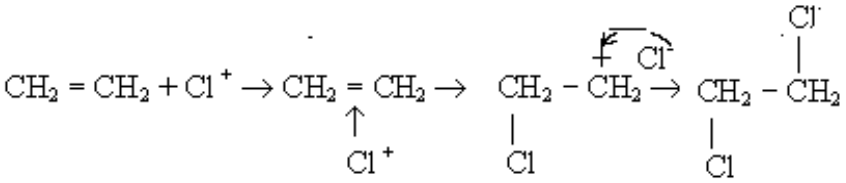
9.2. Write the mechanism of ethene bromination.

9.3. Write the mechanism of benzoic acid chlorination.

Answers:

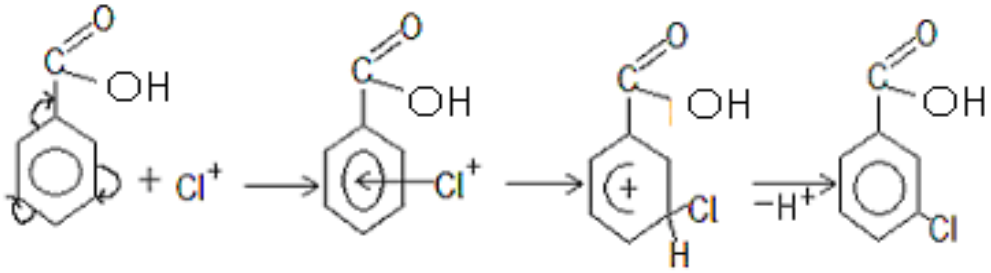
9.1. All carbone atoms in alkanes are in sp^3 state, the type of chemical bond is covalent nonpolar and electrone density does not shift, the formation of active centers (the part of alkane with electron deficiency or with the excess of electrones) is impossible. That is why radical mechanism predominates.

9.2. $Cl_2 \rightarrow Cl^+ + Cl^-$



π - complex *σ - complex*

9.3. $Cl_2 + FeCl_3 \rightarrow Cl^+ + FeCl_4^-$



π-complex ***σ - complex***

10. 10. The algorithm of the experiments:

10.1. Alkane halogenation.
10.2. The synthesis of ethylene.
10.3. The tribromoanilin synthesis.
10.4. Benzene nitration.

11. The detailed description of experiment:

11.1. Alkane halogenation (demonstration).

Into two test-tubes put 1 ml of hexane and 1 ml of bromine water. The first test tube wrap into a black paper. Both tubes shoud be exposed to UV-rays for 2 min. Notify the outer effect. Make the conclusion. Describe graphically the reaction mechanism.

11.2. The synthesis of ethylene (demonstration).

Put 1 ml of ethanol and sulfuric acid mixture (C_2H_5OH и H_2SO_4 concentrated) and aluminium oxide into the dry test-tube with gas-collecting tube and heat carefully. The end of the gas-collecting tube put into the test-tube with 5 ml of of bromine water. Notify the outer effect. Make the conclusion. Describe graphically the reaction mechanism. Explain the practical importance of these reactions.

11.3. The tribromoanilin synthesis.

Put 1 drop of aniline into the dry test-tube, than 1 ml of water. Shake the test-tube with mixture and add 2-3 drops of of bromine water. Notify the outer effect. Make the conclusion. Describe graphically the reaction mechanism. Why the product is 2,4,6-tribromoanilin? Explain the biological importance of bromination reaction.

11.4. Benzene nitration.

Put 10 drop of benzene into the dry test-tube, than 10 ml of nitrating acid (mixture of nitric and sulfuric acid). After mixing put 5 ml of water. Mark the results (smell). Make the conclusion. Describe graphically the nitration reaction mechanism. Explain the practical importance of these reactions.

TOPIC 3: Reactivity of alcohols, phenols, amines and halogenated organic compounds.

1. Actuality of the topic:

The study of reactivity of alcohols, phenols, amines and halogenated organic compounds takes the possibility to forecast the transformation in human organism.

2. General aim: to use the electronic mechanism for explanation reactivity of biological active compounds.

3. Special aims:

- to explain the dependence of the reactivity on nature of chemichal bond and mutual influence of atoms in molecule.

- to explain the acidic properties of alcohols, phenols and basic properties of amines. The medical application of reactivity of alcohols, phenols, amines and halogenated organic compounds as pharmaceuticals.
- to explain the possibility of uses in pharmaceutical synthesis.

4. Literature:

4.1. Lecture.

4.2. Zurabyan S.E., Fundumentals of bioorganic chemistry, Moscow, 2004, pp. 225-238.

5 . The main questions of the topic:

5.1. Acidity and basicity according to Brensted and Loury.

5.2. The dependence of the acidity of alcohols, phenols on carbon chain length and on type of substitute.

5.3. The dependence of the basicity of amines and phenols on carbon chain length and on type of substitute.

5.4. The mechanism of nucleophylic substitution (S_N) beside the nonsaturated carbon atom in halogenated organic compounds. Interaction with a base, ammonia, amines (formation of primary, secondary, tertiary amines and quaternary bases).

5.5. The mechanism of nucleophylic substitution (S_N) in alcohols. Interaction with a halogenated. The mechanism of elemination reaction of alcohols.

5.6. The formulas to know: propanol, isopropanol, butanol, isobutanol, phenol and its derivative; primary, secondary, tertiary and quaternary bases, colamine, aniline.

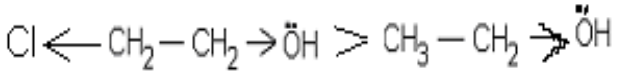
6. The questions for individual learning:

6.1. Write the chemical equation: Novocaine and hydrochloric acid.

7. The examples of the task:

7.1. Describe graphically the electronic effects (M and I) and explain which alcohol is more acidic – ethanol or chloroethanol.

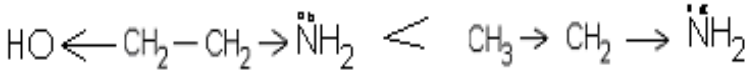
Answer:



Chlorine atom as more electronegative (I-) shifts the electrone density from alkyl grup (I+) therefore on oxygen atom the deficiency of electrons arises. In addition to that Oxygen atom as more electronegative (I-) shifts the electrone density from hydrogen and the atomic mobility increases. Thus the chloroethanol is stronger acid than ethanol.

7.2. Describe graphically the electronic effects (M and I) and explain which amine (colamine or ethylamine) is stronger base. Write the chemical equation of interaction ethylamine with hydrochloric acid.

Answer:



In colamine molecular: Oxygen as more electronegative than carbone atom shifts the electrone density from alkyl group therefore the accessibility of electrons on nitrogen atom decreases. Thus the ethylamine is stronger base than colamine.

$$CH_3 - CH_2 - NH_2 + HCl \rightarrow [CH_3 - CH_2 - \overset{+}{N}H_2] + Cl^-$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad H$$

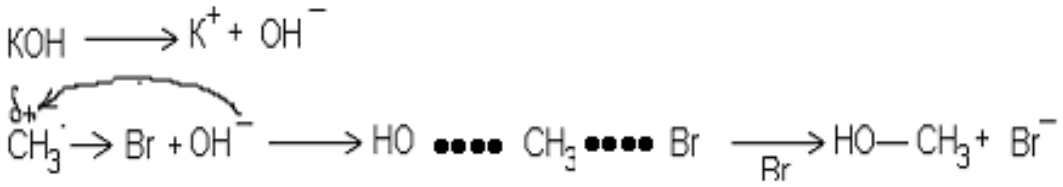
7.3. Why do the nucleophilic particles attack the halogenated organic compound?

Answer: $\overset{\delta+}{}\qquad\overset{\delta-}{}$

In halogenated hydrocarbon (for example in chloroethane $CH_3 - CH_2 \rightarrow Cl$) as a result of negative inductive effect on chloride atom, the partial charge appears: on CI is δ- and on C is δ+. Thus only negatively charged nucleophil attach (attack) to positively charged carbon atom that is bonded with negative centre (chloride atom).

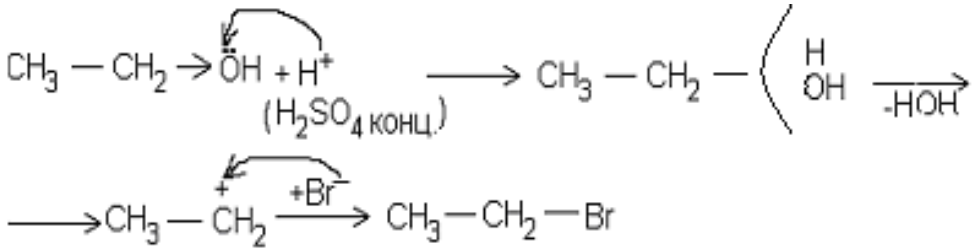
7.4. Describe graphically the reaction mechanism of interaction between bromoethane and potassium hydroxide (alkaline hydrolysis).

Answer:



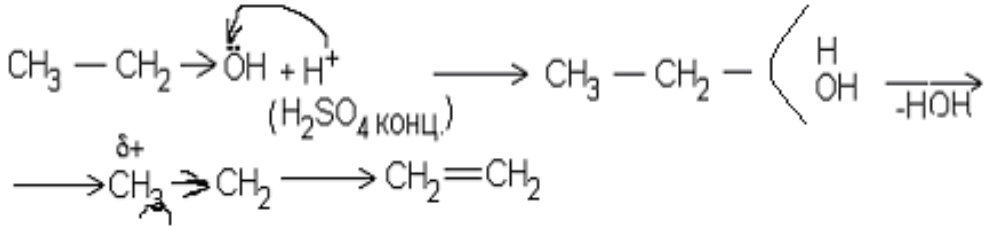
7.5. Describe graphically the reaction mechanism of interaction between ethanol and hydrobromide.

Answer:



7.6. Describe graphically the reaction mechanism of ethanol elimination (ethanol dehydrogenation).

Answer:



8. Homework (must be performed in the laboratory notebook):

8.1 Describe graphically the reaction mechanism of interaction between isobutanol and hydrogen chloride.

8.2. Describe graphically the reaction mechanism of **lactic acid** elimination.

8.3. Write the novocaine and hydrochloric acid interaction.

9. The control test:

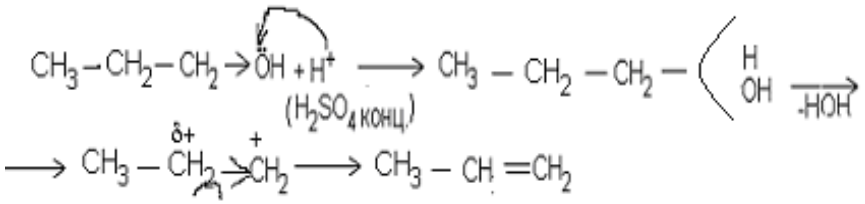
9.1. Describe graphically the reaction mechanism of propanol elimination.

9.2. Describe graphically the reaction mechanism of interaction between chloroethane and methylamine.

9.3. Why does the nucleophilic substitution need an acidic catalyst?

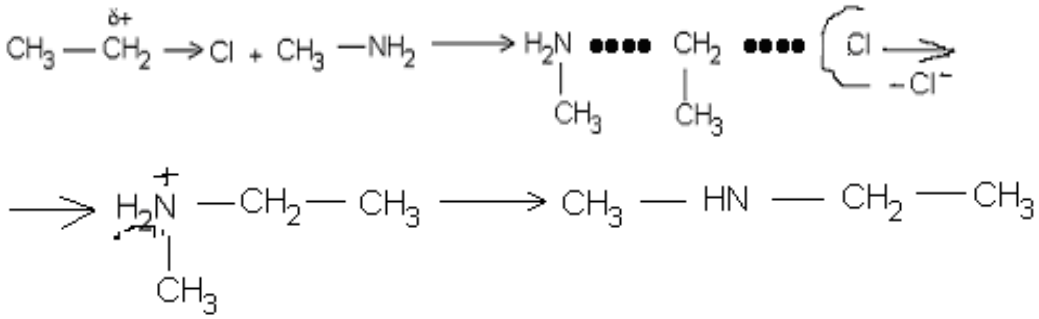
9.4. Compare the acidity of ethanol and bromoethanol.

Answer:



9.1

9.2. Answer:



9.3. The hydroxyl group (OH) is strong nucleophil and covalently bonded with the alkyl radical that is why the elimination segreration of OH group without catalyst is imposible. The proton attachs to the OH group and water molecule forms.

9.4. The bromine atom in 2-bromoethanol molecule Br ← CH_2 – CH_2 –→ OH which is more electronegative than carbon atom shifts the electron density from alkyl radical. Therefore on oxygen atom the excess of electron density decreases, the polarity of O-H bond decreases too. The presence of electron acceptor (electron-seeking group) decreases acidity of oxy-compound.

10. The algorithm of lab work:

10.1. The formation of chloroethane.

10.2. The quanitative test on the glycerin.

10.3. The formation of sodium phenolate.

11.4. The quanitative test on the phenol.

11.5. The quanitative test on the novocaine hydrochloride.

11. The detailed description of experiment:

11.1. The formation of chloroethane from ethanol.

Put the 5 mm layer of sodium chloride into test-tube and add 5 drops of ethanol solution, after that put 4 drops of concentrated sulphuric acid. Mix the test-tube and heat. Mark the effect. Write the chemical reaction. Make the conclusion.

11.2. The quanitative test on the glycerin.

Put 2 drops of $CuS0_4$ into test-tube and add 2 drops of NaOH. Mark the effect. Than add 1 drop of glycerin and mix the solution. Write the chemical reaction. Make the conclusion.

11.3. The formation of sodium phenolate.

Put 3 drops of water into the test-tube and a few crystals of phenol. Estimate the solubility of phenol. Than add drop by drop the sodium hydroxide solution. Mark the effect. After that add drop by drop the hydrochlocic acid. Mark the effect. Write the chemical reactions. Make the conclusion.

11.4. The quanitative test on the phenol.

Put a few crystals of phenol into the test-tube and 1 drop of iron (III) chloride solution. Mark the effect. Write the chemical reactions. Make the conclusion.

11.5. The quanitative test on the novocaine hydrochloride.

Put 5 drops of novocaine hydrochloride into the test-tube and 1-2 drops of silver nitrate solution. Write the chemical reaction. Make the conclusion. Explain the biological meaning of basic properties of amines.

TOPIC 4: Nucleophyllic addition in oxygen-containing compounds.

1. Importance of the topic*:*

Studying of the mechanisms of the nucleophyllic addition in oxo-compounds gives the possibility to forecast the chemical transformations of aldehydes and ketones in human organism.

2. Main questions of the seminar:

2.1.Electronic structure of the oxo-group.The mechanism of nucleophyllic addition reaction (A_N) to the trigonal carbon atom.

2.2. Interaction with alcohols: mechanism of formation of half-acetalles and acetalles. Their biological meaning.

2.3. Interaction with amines: mechanism of addition-detachment. Biological meaning of imines.

2.4. Aldolic condensation: mechanism of alkaline catalysis; biological meaning (synthesis of the citrate in organism (citrate acid) and neuraminic acid).

2.5. Oxidation and reduction of aldehydes and ketones. The examples of these reactions in human organism.

3. Literature:

3.1. Lecture.
3.2. Zurabyan S.E., Fundumentals of bioorganic chemistry, Moscow, 2004, pp.

4. Homework (in protocol note-book).

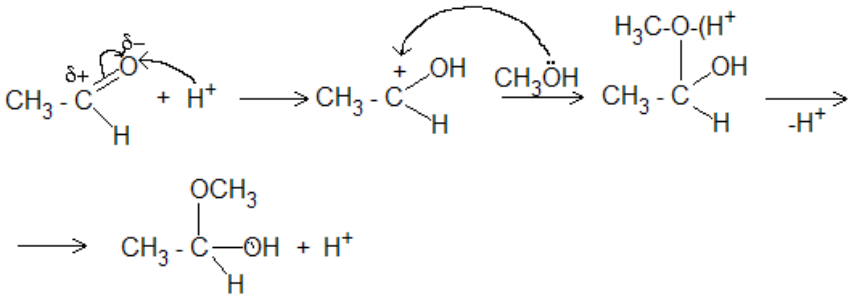
4.1. Describe graphically mechanism of half-acetalle and acetalle formation in interaction of propanalle and ethanol.
4.2. Describe graphically mechanism of interaction of piridoxal-phosphate and methyl-amine.
4.3. Describe graphically mechanism of synthesis of the neuraminic acid.

5. Examples of the test-control:

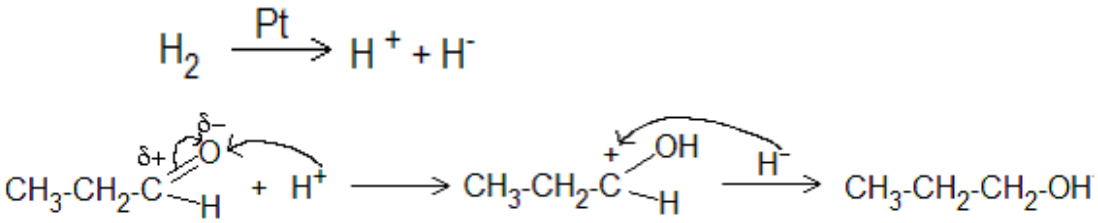
5.1. Describe graphically mechanism of half-acetalle formation in interaction of acetate-aldehyde and methanol.
5.2. Describe mechanism of reduction of propanalle.

Answers:

5.1.



5.2.



6. The detailed description of experiment:

6.1. Oxidation of formaldehyde with copper(II) hydroxide.

Put 5 drops of the sodium hydroxide and water into the test-tube, add 1 drop of the copper (II) sulphate. Note the results. Add 3 drops of formalin solution. Warm the test-tube carefully untill boiling. Write the reaction equations, note the effect, explain the result. Meaning of the reaction for the clinical analysis.

6.2. Determination of the acetone with iodoformic test.

Put 1 drop of the solution of iodine in KI into the test-tube and add the sodium hydroxide dropwisely untill the color disappears. Add 1 drop of acetone. Write the equation of reactions, note the effect and explain the results and biological meaning.

TOPIC 5: Reactivity and biological significance of carboxylic acids and their derivatives.

1. Actuality of the topic: understanding of nucleophylic substitution mechanism in carboxylic acids gives the possibility to predict the chemical conversion of carboxylic acids and their derivatives in human organism.

2. General aim is to interpret the mechanism of nucleophylic substitution in carboxylic acids and their derivatives and predict the consequence of these processes.

3. Actual aims and abilities:

- ✓ to know the mechanisms of conversion and specialities of the carboxylic acids and their functional derivatives;
- ✓ to explain the mechanism of the nucleophylic substitution in carboxylic acids;
- ✓ to predict the processes connected with conversion of carboxylic acids and their biologically active derivatives.
- ✓

4. Literature:

4.1. Lecture.
4.2. Zurabyan S.E., Fundumentals of bioorganic chemistry, Moscow, 2004, pp. 47-61, 149-161.

5. The main questions of the seminar:

5.1. The electronic structure of the carboxyl group and carboxylate anion.
5.2. Acidity of the carboxylic acids. The influence of the different susbtitutes on acidity of carboxylic acids.
5.3. Salts of carboxylic acids, the mechanism of their formation. The formation of salts of carboxylic acids in human organism.

5.4. Mechanism of nucleophylic substitution (S_N) beside the trigonal carbon atom :

a) mechanism of the ester and thioethers formation;

b) mechanism of acidic and alkaline hydrolysis of esters;

5.5. Formation and hydrolysis of esters and thioethers in human organism. Synthesis of biological active substances with acetyl-KoA in human organism.

6. The questions for individual learning:

6.1. Decarboxylation of puruvic and β-ketobuturic acids.

6.2. Mechanism of acyl chloride formation.

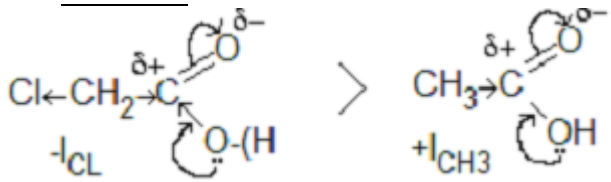
6.3. Mechanism of anhydride formation.

6.4. Mechanism of amideformation. Biological meaning of amides.

7. Examples of the tasks:

7.1. Which acid is stronger and why: acetic acid or monochloroacetic acid.

Answer:

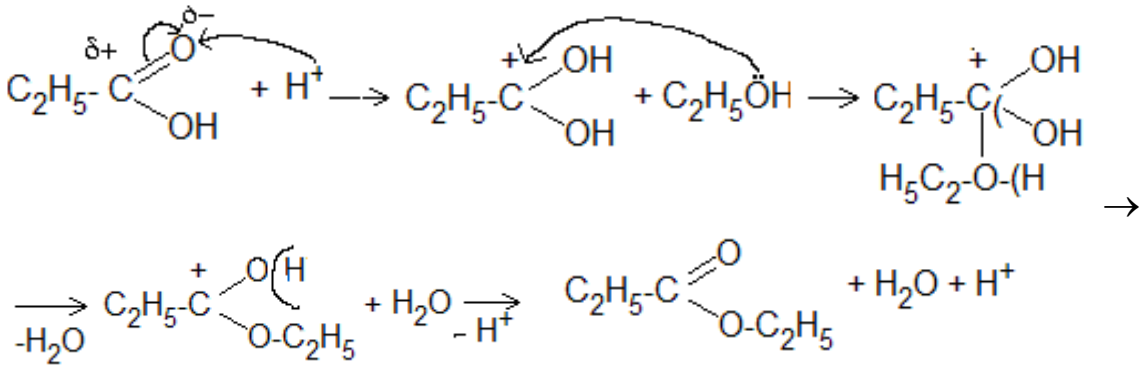


As Cl atom is more electronegative than carbon one in the monochloroacetic acid, the electron density is shifted to Cl atom and the proton in carboxyl group becomes easier to be chipped off.

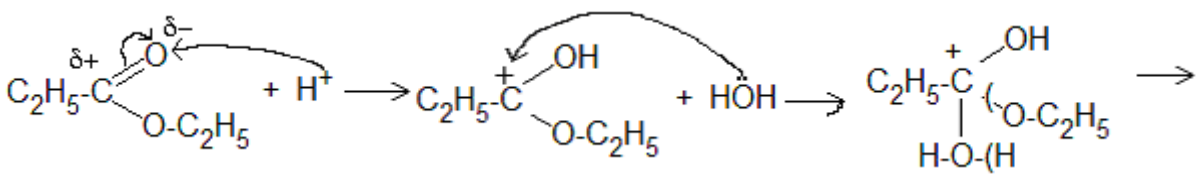
7.2. Describe graphically mechanism of formation and hydrolysis of ethyl propionate using acidic catalysis.

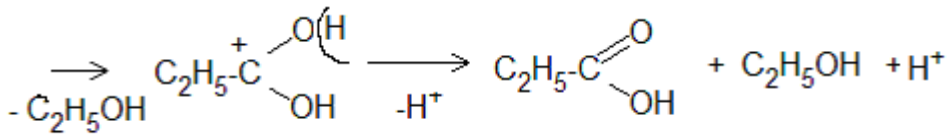
Answer:

Esterification mechanism:

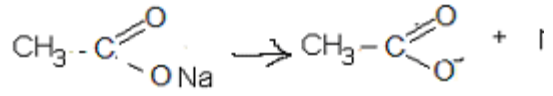


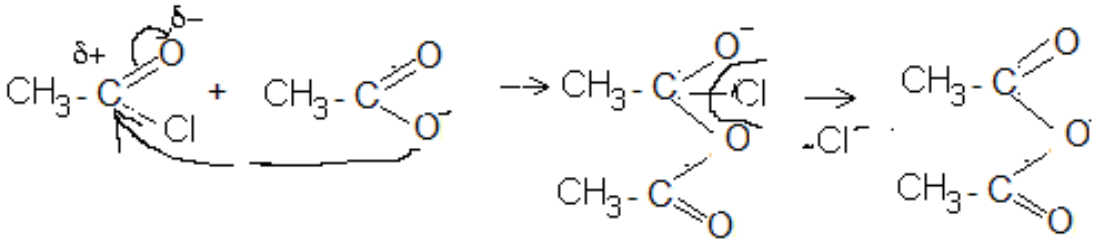
Mechanism of hydrolysis:





7.3. Describe the reaction mechanism of anhydride formation of acetic acid.
Answer:



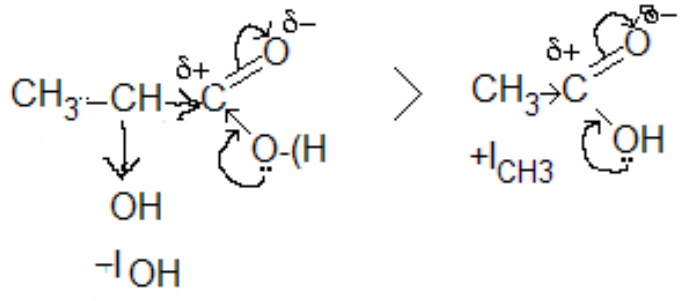


8. Homework (must be performed in the laboratory notebook):

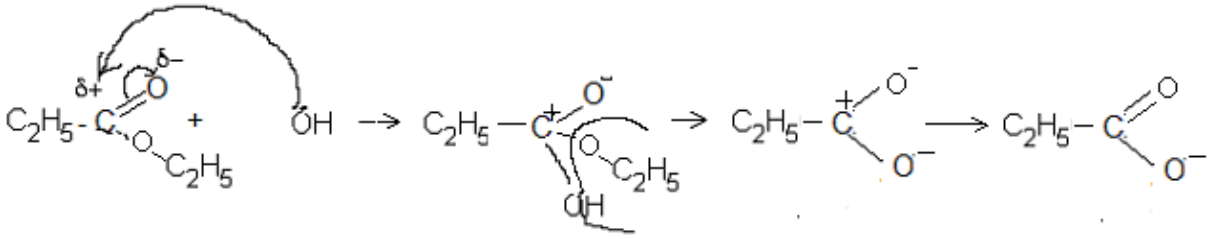
8.1. Write the acids in order of the increasing acidity: oxalate (oxalic acid), acetate (acetic acid), monochloacetate (monochloacetic acid).
8.2. Describe the reaction mechanism of synthesis and hydrolysis (acidic and alkaline) of methyl acetate.
8.3. Write the scheme of synthesis of acetate derivatives: sodium salt, anhydride, chloroanhydride, amide.
8.4. Memorize the structural formulas of formic acid, acetic acid, propionic acid, buturic acid, chloroacetic acid, oxalic acid.

9. Example of control test:

9.1. What acid is stronger, 2-oxopropanoic or lactic acid and why?
Answers:
9.1.



9.2. Describe graphically the reaction mechanism of hydrolysis ethyl propionate with alkaline catalyst.



10. The algorithm of the experiments:

10.1. Correlation of the acid strength.
10.2. Identification of oxalic acid in the form of calcium sault.
10.3. Decomposition of oxalic acid under heating.
10.4. Synthesis of ethyl acetate.

11. Detailed description of experiment:

11.1. Comparism of the acid strength.

Put a drop of every acid (hydrochloric acid, formic acid, acetic acid, oxalic acid) and pure water into a piece of indicator paper. Determine pH and make the conclusions.

11.2. Identification of oxalic acod in the form of calcuim sault.

Put 2 drops of sodium oxalate in the test-tube, add 1 drop of calcuim chloride solution. Divide the precipitation into two test-tubes. Into the first test-tube put 1-2 drops of acetic acid and 1-2 drops of chloroacetic acid in the second one. Explain the results, write the reaction equations.

11.3. Decomposition of oxalic acid with heating.

Put the layer (10-15 mm) of oxalic acid in dry test-tube, close it with cork and gas collecting tube. Heat the mixture passing the formed gas through barium hydroxyde. Write the equations and make the conclusions.

11.4. Synthesis of ethyl acetate.

Put 0.5 ml of ethanol, 0.5ml of acetic acid, 2-3 drops of 96 % sulfuric acid in dry test-tube and heat carefully. Describe the results of the experiment and write the mechanism of the esterification reaction.

TOPIC 6: Higher fatty acids. Lipids. Phosphoglycerides.

1. Actuality of the topic: knowledge of the structure and chemical properties of lipids and their derivatives is necessary to understand the processes of lipids' metabolism in a human organism and the structure of biological membranes.

2. General aim is to interpret the regularity of lipid metabolism in order to predict biochemical reactions, which are accompanied and stimulated by lipids.

3. Actual aims and abilities:

✓ to know the structure and chemical properties of lipids and their structural components;
✓ to be able to use knowledge for understanding of the biological membrane structure and the regularity of the lipid metabolism as the basis of the metabolic changes in human organism.;

4. Literature:

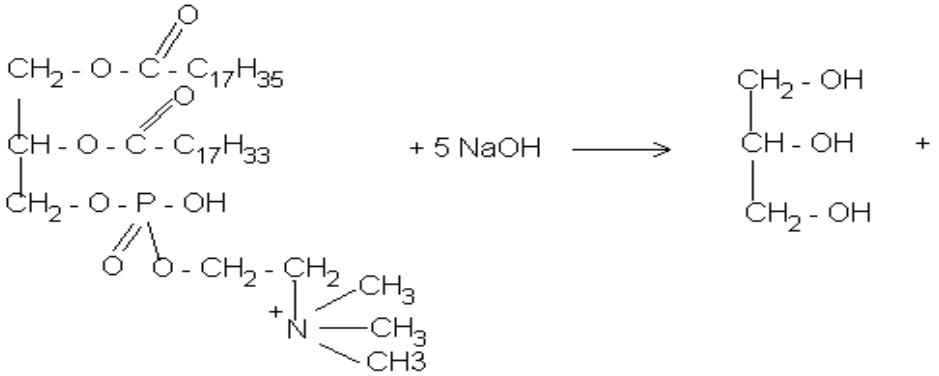
4.1. Lecture.
4.2. Zurabyan S.E., Fundumentals of bioorganic chemistry, Moscow, 2004, pp. 238-249.

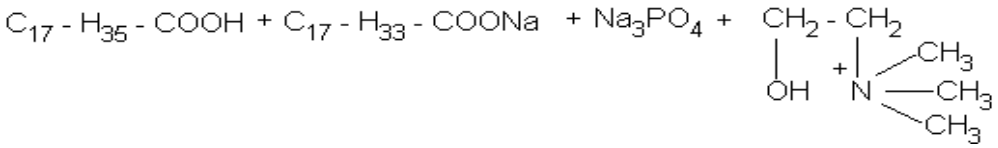
5. The main questions of the seminar:
5.1. Lipids, saponificated lipids (definition).
5.2. Higher faty acids: saturated and unsaturated, spatial structure of unsaturated acids, chemical characteristics.
5.3.Fats as triacylglycerols, their composition, structure, classification, chemical properties (hydrolysis, iodine number, peroxide oxidation).
5.4.Phosphoglycerols: composition, structure of phosphatidylcholine, phosphatidylcolamine, phosphatidylserine and their biological meaning.

6. The questions for individual learning:
6.1. Nonsaponificated lipids (definition).
6.2. Structure of cholesterine, bile acids.

7. Examples of the tasks:
7.1. Write the configuration of oleic acid
7.2. Write the scheme of alkaline hydrolysis of 1 – stearoyl – 2 – oleinoyl – 3 – phosphatidylcholine.
Answers:
7.1.

7.2.





8. Homework (must be performed in the laboratory notebook):

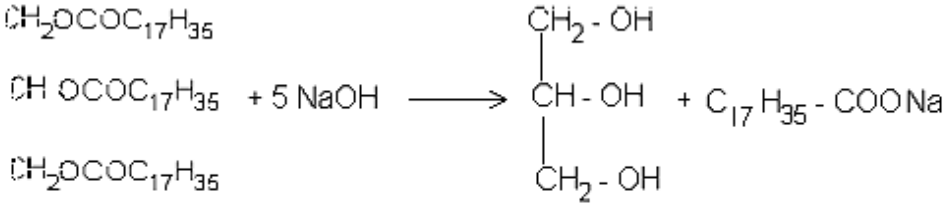
8.1. Write the reaction equation of alkaline hydrolysis of dioleoylstearine.

8.2. Write the structure of phosphatidylcholine.

8.3. Write the spatial structure of unsaturated fatty acids: oleic and linoleic.

9. Examples of control test:

9.1. Write structure and scheme of alkaline hydrolysis of tristearine.



10. The algorithm of the experiments:

10.1**.** Formation of the fatty drop and its extraction.

10.2. Extraction of free fatty acids from soap.

10.3. Formation of unsolutable calcium salts (unsolutable soap).

10.4. Unsaturated fatty acids reaction.

11. Detailed description of experiment:

11.1**.** Formation of the fatty drop and its extraction.

On the filter paper put 3 separated drops of oil with sizes 1 cm. Touch the center of the first drop with the tube that contains diethyl ether, the second with benzine, the third with water. Describe the results of the experiment and make the conclusions.

11.2. Extraction of free fatty acids from soap.

In the test tube put 5 drops of saturated soap solution and 1 drop of sulphuric acid. Point the effect, write reaction equation, make the conclusion.

11.3. Formation of insoluble calcium salts (insoluble soap).
In the test tube put 5 drops of soap solution and 1 drop of calcium chloride solution. Mix the test-tube. Point the effect, write reaction equation, make the conclusion.

11.4. Unsaturated fatty acids reaction.
Put 5 drops of oil and 4 drops of bromine water into a test-tube and mix it**.** Point the effect, write reaction equation, make the conclusion.

TOPIC 7: Reactivity and biological significance of heterofunctional derivatives (hydroxo-acids, oxo-acids, phenol-acids)

1. Actuality of the topic: Heterofunctional derivatives - hydroxo and oxo-acids are the products of metabolism in human organism, phenol-acids are used in medicine as medical products. Reactivity of these compounds is determined by presence of different functional groups in molecule, that determines specialities of their chemical conversion in organism.

2. General aim is to use the knowledge of stereochemistry and reactivity of heterofunctional compounds and interference of the functional groups for the explanation of the specialities of metabolism of carbohydrates, fats and aminoacids and their derivatives in human organism.

3. Actual aims and abilities:

✓ Explain the dependance of reactivity and biological functions of the heterofunctional compounds on their structure and methods of medicines' synthesis on their basis.

4. Literature:
4.1. Lecture.
4.2. Zurabyan S.E., Fundumentals of bioorganic chemistry, Moscow, 2004, pp. 225-238.

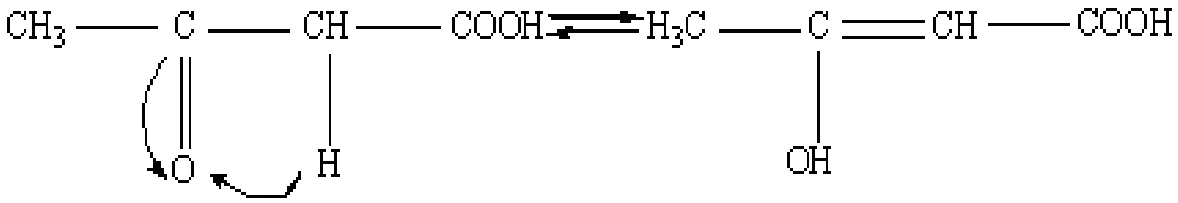
5. The main questions of the seminar:
5.1 Hydroxo-acids (lactic, tartratic, citric, β - oxybutyric, malic acids), properties, specifical reactions: appearance in the organism and biological meaning of these compounds.
5.2. Oxo-aicds (pyruvic, aceto-acetic, oxalo-acetic acids). Keto-enole tautomery. Chemical properties, reaction of decarboxylation.
5.3. Phenol acids and their derivatives. Use of salicylic acid and its derivatives as officinals (Sodium salicylates, methylsalicylate, salol, acetylsalicyllic acid).

6. The questions for individual laearning:
6.1. Classification and isomery of oxoacids. Chirality. Enantomers, diastereomers.
6.2. Keton bodies, their diagnostic significance for identification of pancreatic [insular] diabetes.

7. Examples of tasks:

7.1. What isomerism is more typical for β - ketoacids (for example acetoacetic acid)?

Answer: Due to mutual influence of keton and carboxyllic groups in molecule, the CH-acidic center appears, that cause keto-enol tautomery.



Enol group is more active than keton one.

8. Homework (must be performed in the laboratory notebook):

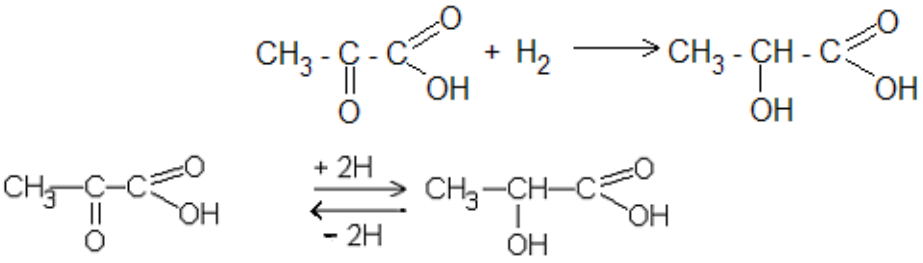
8.1. Write the projectional formulas of lactate enantomers.
8.2. Write piruvate in keton and enol forms, reduction and interaction with ethanol reactions.
8.3. Write the equation of the specific reactions with α –, β – and γ – oxoacids.

9. Example of control test.

9.1. Write the scheme of lactic acid appearance and make the characteristics of its chemical properties.

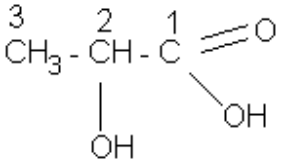
Answers:

9.1. Appearance in human organism:



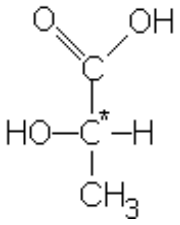
pyruvic acid ***lactic acid***

a)



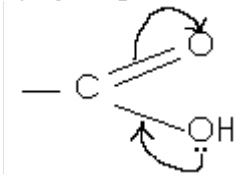
$C_{1,}$– sp^2; $C_{2,3}$ – sp^3 ; $C_1 – C_2$ - σ=> $sp^2 – sp^3$; $C_2 – C_3$ - σ=>$sp^3 – sp^3$;
(C_1 - C_2) (C_2 - C_1)

b) The typical enantomery for lactic acid is:

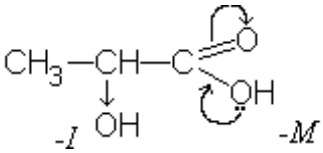


L-configuration

c) p,π -coupling in carboxy-group:



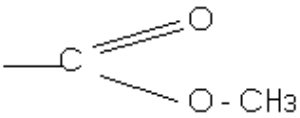
d) electronic effects:



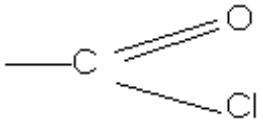
e) oxy-group shows faint acid properties and forms salts (alcoholates R – OMe), carboxy-group is stronger and makes appropiate salts

R –COOMe - lactates.

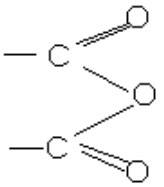
f) due to carboxy-group lactic acid makes derivatives – esters and halogenahydrides:

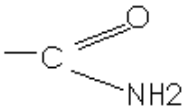


anhydrides



amides





g) oxy-group can move towards halogen.

h) the reversable conversion of lactate into pyruvate takes place in human organism.

10. The algorithm of the experiments:

10.1. Demonstration of the presence of two carboxy-droups in tartratic acid.
10.2. Demonstration of presence of hydroxy-groups in tratratic acid.
10.3. Decomposition of the citric acid.
10.4. Receive and solubility of calcium citrate and calcium tartrate.
10.5. Demonstration of absence of phenol hydroxyle in acetylsalicyllic acid (aspirin) and its hydrolysis (demonstration of acetylsalicyllic acid high quality).

11. Detailed description of experiment:

<u>11.1. Demonstration of the presence of two carboxy-droups in tartratic acid.</u>

Put 5 drops of solution of tartrate (tartratic acid) into a test-tube, add 2 drops of KOH solution and rub the sides of the test-tube until the sediment appearance. Then add 4-5 drops of KOH solution. Write the reaction equation, describe the results and make conclusions. The test-tube with solution must be kept for the next experiment.

11.2. Demonstration of presence of hydroxy-groups in tratratic acid.

Put 2 drops of $CuSO_4$ solution and 2 drops of NaOH solution into a test-tube. The solution from the previous experiment add to the sediment that appeared. Write the reaction equation, describe the results and make the conclusions. Where do we use this solution and what is its name?

11.3. Decomposition of the citric acid.

Put the 1cm layer of citric acid and 1 ml of H_2SO_4 conc. into the dry test-tube with gas-collecting tube and heat. The end of the gas-collecting tube put into the test-tube with 1ml of Barium hydroxyde and then – into the test-tube with Lugol solution that was decolored by NaOH. Write the scheme of the decomposition reaction. Describe the results, make the conclusions.

11.4. Receive and solubility of calcium citrate and calcium tartrate.

Dissolve several crystals of citrate (citric acid) in one test-tube and several crystals of tartrate (tartratic acid) in another one. Neutralize acids with NH_4OH solution (check with indicator), then add 2-3 drops of $CaCl_2$ solution. The sediment will appear right away, and the other test-tube heat for 2-3 minutes. Write the reaction equations, describe the results and make the conclusions.

11.5. Demonstration of absence of phenol hydroxyle in acetylsalicyllic acid (aspirin) and its hydrolysis (demonstration of acetylsalicyllic acid high quality).

Put a piece of aspirin tablett into a test-tube. Add 5-6 drops of water, mix and add 1 drop of $FeCl_3$. Explain the visible effect of reaction. If there are no changes, than boil the test-tube for 0,5min and add 1 drop of $FeCl_3$ solution. What do you see? Write the reaction equation, describe the results and make conclusions about the quality of acetysalicyllic acid.

TOPIC 8: The structure and chemical properties of α -amino acids.

1. Actuality of the topic: amino acids are the sructural element of peptides and proteins. Understanding of structure and chemical properties of amino acids is necessary for realising of their reactivity, conversions and biological significance in human organism.

2. General aim:

to use the knowledge of amino acids properties for explanation of structure and function of proteins in human organism..

3. Actual aims and abilities:

- to interpretate speciatilies of α-amino acids structure as the structural basis of proteins which have their function in human organism;
- to make conclusions about α-amino acids' ways of conversion in human organism;
- to predict appearance of proteins and other physiologically active compounds on the basis of reactivity and structure of amino acids, understanding and predict degradation of aminoacids in human organism.

4. Literature :

4.1. Lecture.

4.2. Zurabyan S.E., Fundumentals of bioorganic chemistry, Moscow, 2004, pp. 225-238.

5. The main questions of the seminar:

5.1. Amino acids: definition, composition, structure.

5.2. Acid-base properties of amino acids.

5.3. Chemical reactions of amino acids by carboxy-group: ester and halogenanhydrydes formation. Biological meaning of these reactions.

5.4. Chemical reactions of amino acids by amino-group: N-acyl derivatives formation, interaction with nitrite acid, formaldehyde, phenylisothyocyanate. Biological significance of these reactions.

5.5. Decarboxylation of amino acids and biological meaning of biogen amines' formation.

6. The questions for individual learning:

6.1. Amino acids classification.

6.2. Amino acids decarboxylation in human organism.

7. Examples of tasks:

7.1. What types of isomery are typical for α-amino acids?

Answer:

a) Isomery of amino-group location: α-amino acids and β-amino acids;

b) carbon skeleton isomery: leucine-isoleucine;

в) enantiomery: D–methionine – L-methionine.

7.2. Explain the amino acids' amphotericity.

Answer:

Amphotericity is explained by the presence of carboxy-group and amonio-group in amino acids. Carboxy-group is the group with acidic properties, it dissociates with appearance of H^+ -ion (or proton); amino-group is the group with basic properties because nitrogen has undivided electron pair. During solution of amino acid in water proton joins to nitrogen, making bipolar ion, that has carboxylate-anion and protonned amine group, and has positive charge. Amphoteric character of amino acids is also confirmed by their interaction with alkalines as well as with acids, making salts.

8. Homework (must be performed in the laboratory notebook):

8.1.Write and learn 20 formules of aminoacids, that form proteins; mark irreplaceable aminoacids.

8.2. Write the reaction of interaction between serine and ethanol equation.

8.3.Write the reaction of interaction between asparagine and phenylisothyocyanate equation.

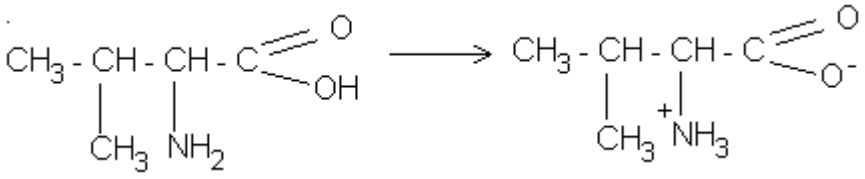
9. Example of control test :

9.1. Write the scheme of appearance of aminoacid – valine - bipolar ion. What pH does its isoelectrical point located in?

9.2. Write the formulas of three possible alanine salts.

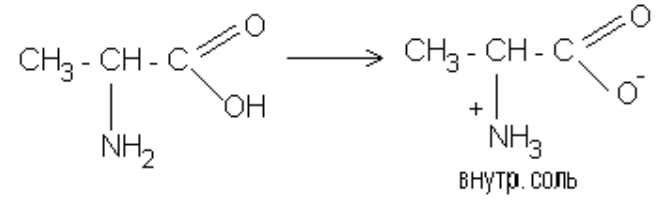
Answers.

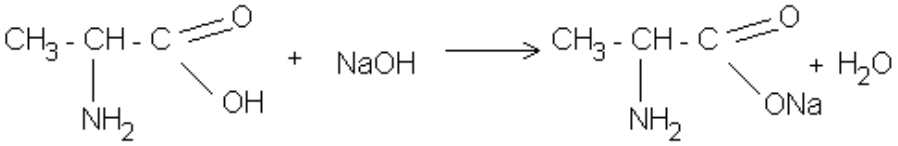
9.2.

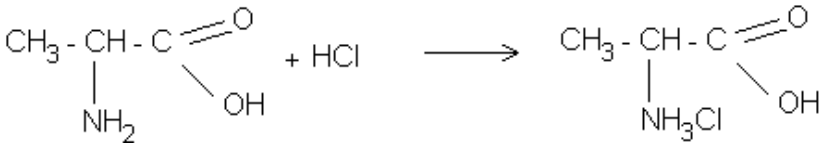


IEP is located in subacid medium.

9.3.







10. The algorithm of the experiments:

10.1. Compairing of the aminoacids and their appropriate carbon acids power.

10.2. Aminoacid and ninhydride interaction.

10.3. Glycin and formaldehyde interaction.

10.4. Glycin and nitrite acid interaction.

11.Detailed description of experiment.

11.1. Compairing of the aminoacids and their appropriate carbon acids power.

Put into three test-tubes: into the first - 1ml of distilate water, the second -1ml of acetic acid, the third – 1ml of glycine. Add 2 drops of indicator methyl-red into each test-tube. Describe results, male conclusions.

11.2. Aminoacid and ninhydride interaction.

Put 4 drops of glycine solution and 2 drops of ninhydrine solution into a test-tube and heat. Describe results and make conclusions.

11.3. Glycin and formaldehyde interaction. Put 5 drops of glycin solution and add 1 drop of methyl-red indicator. Note the color. Then add 6 drops of formaline. Describe results, write the reaction equation and make the conclusion.

11.4. Glycin and nitrite acid interaction. Put 5 drops of glycine solution, 5 drops of $NaNO_2$ solution and 2 drops of CH_3COOH (conc.) into a test-tube. Write the reaction equation, describe the results, make the conclusion.

TOPIC 9: Physical and chemical properties of proteins. Protein structural organisation.

1. Actuality of the topic: Knowledge of composition, structure and chemical properties of peptides is necessary for understanding of their functions in human organism in normal condition and in pathology, as well as for using in clinics for diagnostics and curing, and for the synthesis of proteins and peptides in vitro.

2. General aim : form general idea about proteins as polymeral structural components of all tissues of organism.

3. Actual aims and abilities:

- to explain dependence of physical and chemical properties of proteins on their amino acid composition;
- to use qualitative reactions for amino acids to identificate proteins and determine their amino acidical composition;
- to use the biuret reaction for quantitative determination of proteins.

4. Literature:

4.1. Lecture.

4.2. Zurabyan S.E., Fundumentals of bioorganic chemistry, Moscow, 2004, pp. 225-238.

5. The main questions of the seminar:

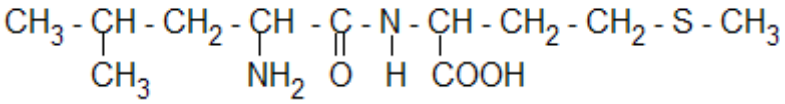
5.1. Proteins, definition, proteins' molar mass.

5.2. Analysis of peptides and proteins: determination of amino acidical composition and amino acidical order. Edman's method.
5.3. Peptide and protein synthesis using protection and activation of functional groups.
5.4. The first decoded and synthesised proteins and peptides: insulin, vasopressin, oxytocin; their composition, structure, biological meaning.

6. The questions for individual learning:
6.1. Appearance and properties of peptide bond.
6.2. Physical and chemical properties of peptides (amphotericity, amphion appearance, salts appearance; isoelectric state (IES), isoelectric point (IEP).
6.3. Levels of protein structural organisation: primary, secondary, tertialy, quaternary. Bond types.
6.4. Methods of extraction, separation and purification of proteins. Determination methods of protein molar mass.

7. Homework (must be performed in the laboratory notebook):
7.1. Write the reaction equations of dipeptide val-cys synthesis using protection and activation of functional droups (6stages).
7.2. Write tripeptide: ala-lys-leu; what medium is its IEP situated in.
7.3. Write the scheme of determination of N-ended amino acid in ser-tri dipeptide using Edman method.

8. Example of control test
8.1. Write dipeptide leu-meth, what medium is its IEP situated in.
8.2. Determine N-ended amino acid in this dipeptide using Edmans method.
Answers.
8.1. IEP is in the neutral medium



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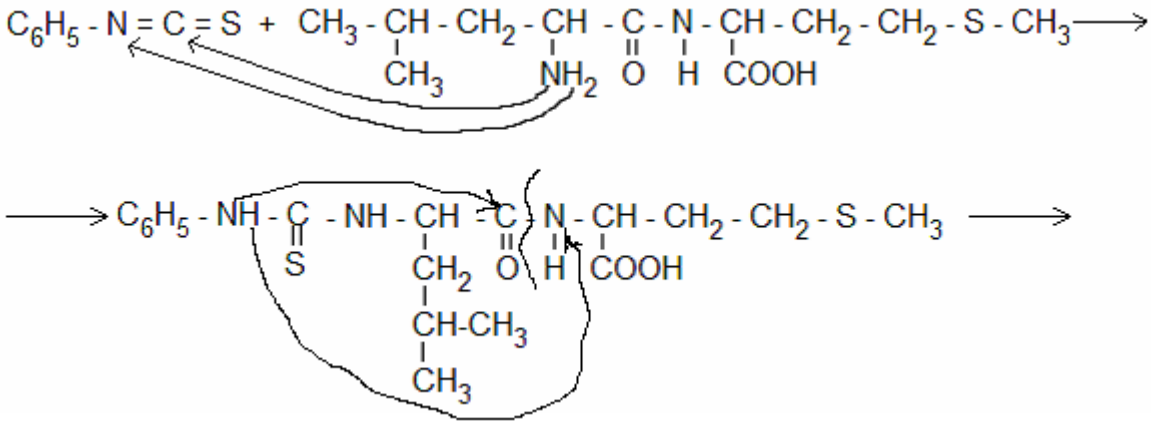
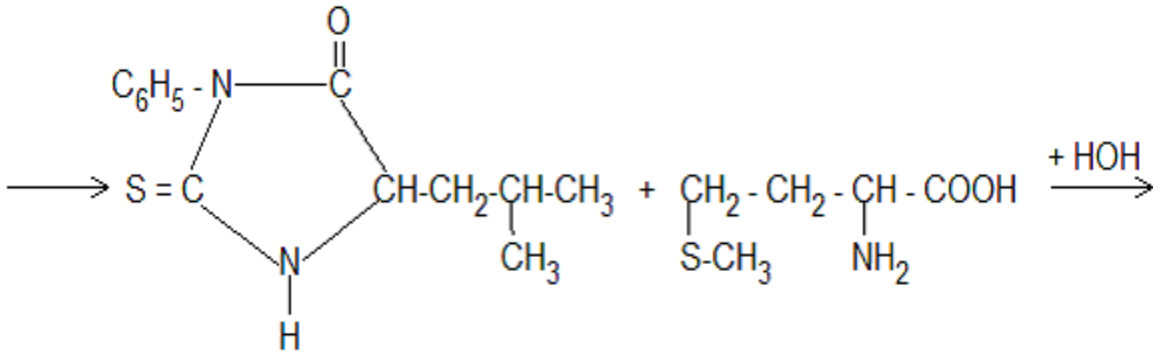
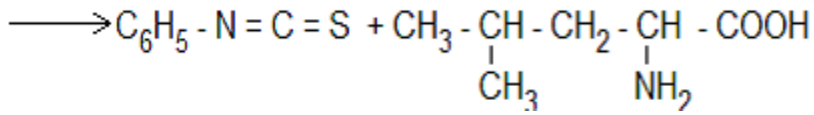






9. The algorithm of the experiments:

9.1. Biuretic reaction.

9.2. Xanthoproteic reaction.

9.3. Foll`s reaction.

10. Detailed description of experiment.

10.1. Biuretic reaction.

Put 5 drops of protein solution, 10 drops of NaOH solution and 1-2 drops $CuSO_4$ solution into the test-tube. Describe the result, make conclusions.

10.2. Xanthoproteic test.

Put 5 drops of protein, 5 drops of HNO_3 (conc.)(carefully!) and heat. Describe the results, write the equation of tyrosine nitrification, make the conclusion.

10.3. Foll reaction.

Put 5 drops of protein solution, 2 drops of NaOH solution into the test-tube, heat until boiling and add 2 drops of $(CH_3COO)_2Pb$ solution. Describe the results, write the reaction equation of sulfur-containing amino acid with Plumbum acetate.

TOPIC 10: Monosaccharides, structure and chemical properties.

1. Actuality of the topic: Carbohydrates are widely spread in living nature they are contained in the cytomembranes. Carbohydrates are the source of energy for human organism. Becides, carbohydrates are the strucutral elements of nucleic acids, coenzymes, vitamins. Some of them are used as drugs.

2. General aim:

To make the conclusions about reactivity of monosaccharides according to their structure and composition.

3. Actual aims and abilities:

to distinguish the tautomeric forms of monosaccharides;
to know the methods of monosaccharide determination in the biological liquids.

4. Literature:

4.1. Lecture.
4.2. Zurabyan S.E., Fundumentals of bioorganic chemistry, Moscow, 2004, pp. 225-238.

5. The main questions of the seminar:

5.1. What is carbohydrate? The classification of carbohydrates.
5.2. Glucose:
- non-cyclic form: Fisher projection, D- and L-configuration;
- cyclic form (pyranose and furanose): Heuorse`s projection, α and β - anomers;
- conformation: α - D and β - D – configuration. Tautorotation (birotation).

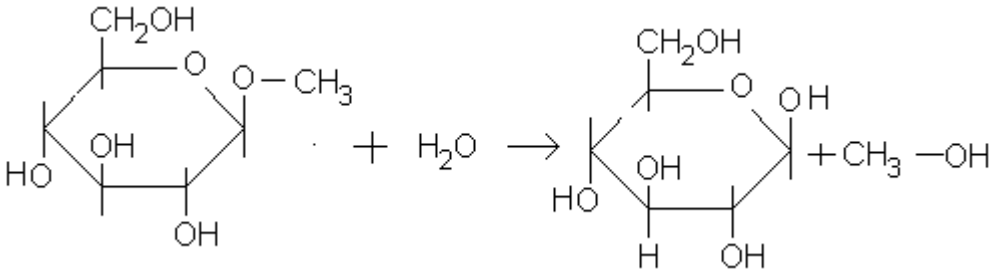
5.3. Chemical properties of glucose: formation of helates, O – and N –glycosides, alkylation, acetylation.
5.4. The formules to know: glucose, fructose, ribose, desoxyribose and their derivatives (glycone, glycarone, glycurone acids, glycosamines, phospho esters).

6. The questions for individual learning:

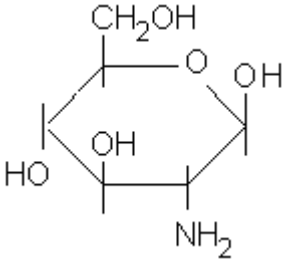
6.1. Ascorbic acid, structure, biological meaning.
6.2. Qualitative reactions on monoatomic alcohols and aldehyde group.
6.3. Qualitative reaction on fructose (Selivanov's reaction).

7. Examples of tasks:

7.1. Write the hydrolysis scheme of O – methyl – β – D – glycopyranoside.



7.2. Write the formule of glycosamine.



8. Homework (must be performed in the laboratory notebook)

8.1. Write the equation of interaction between glucose and ethanol. Show the bond type and determine the product.

8.2. Write the equation of fructose alkylation with chloromethane. Show the bond type and determine the product.

9. Example of control test

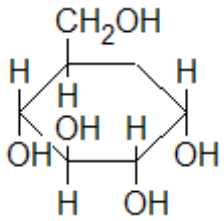
9.1. Write the α - D-glucopyranose formule.

9.2. Write the equation of interaction between α, D-fructofuranose and ethylamine. Determine the product and show the bond type.

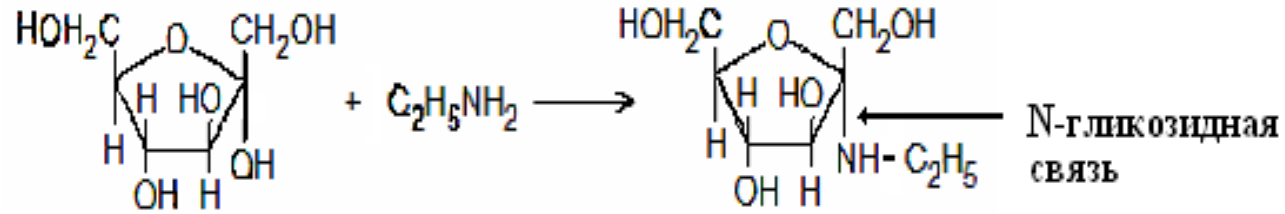
9.3. What is Trommer's reagent and what is it used for?

Answers:

9.1.



9.2.



N-ethyl-β,D-fructofuranoside

9.3. $CuSO_4$ + NaOH, is used for monosaccharide determination in bioliquids.

10. The algorithm of the experiments:

10.1. Demonstration of the presence of hydroxy-groups in D-glucose.

10.2. Reduction of copper (II) hydroxyder with glucos ein alkaline medium (Tromer test).

10.3. Selivanov reaction for determination of fructose.

11. Detailed description of experiment:

11.1. Demonstration of the presence of hydroxy-groups in D-glucose.

Put 1 drop of glucose solution, 6 drops of NaOH solution, 1 drop of $CuSO_4$ solution into a test-tube. Note the results, write the reaction equation, make the conclusions.

11.2. Reduction of copper (II) hydroxyder with glucose in alkaline medium (Tromer test).

Add several drops of water to the solution that appeared in the first experiment. Heat the test-tube until boiling. Mark the results, write the reaction equation and make conclusions.

11.3. Selivanov`s reaction for fructose determination.

Put the resorcinol crystal and 2 drops of HCl (conc.) Add 2 drops of fructose solution and heat until boiling. Mark the result, write the scheme of reaction and male conclusions.

TOPIC 11: Olygo- and polysaccharides, structure and chemical properties.

1. Actuality of the topic: combined hydrocarbones are spread in nature, olygo- and polysacharides are among them. These hydrocarbones are cintained in the cyto-membrane, and they are also the source of energy in the organism (starch and glycogen). Some of them are used as blood substitutes (polyglukine), as loading of powders and tablets.

2. General aim: to make conclusions about reactivity of combined hydrocarbons, according to their structure and contains.

3. Actual aims and abilities:

- to interptretate the specialities of structure and conversion of olygosaccharides in human organism.
- to interpretate the specialitites of structure and conversion of homopolysaccharides in
- human organism as of energy source for living processes.

to explain the mechanism of heteropolysaccharides biological role in human organism.

4. Literature:

4.1. Lecture.

4.2. Zurabyan S.E., Fundumentals of bioorganic chemistry, Moscow, 2004, pp. 225-238.

5. The main questions of the seminar:

5.1. What are disaccharides? Disaccharides classification according to their ability to oxydative-reductive reactions.

5.2. Saccharose structure, lactose structure: reductive abilies and oxy-groups (helates appearance, alkylation, acetylation).

5.3. Homopolysaccharides: starch, glycogen, cellulose, dextranes: composition, structure, primary and secondary structure, chemical properties, biological meaning.

6. The questions for individual learning:

6.1. Starch hydrolysis, qualitative reaction for starch determination.

6.2. Heteropolysaccharides: hyaluronic acid, heparin, chondroitin sulfate, their composition and the structure of disaccharide fragment, biological meaning.

7. Examples of tasks:

7.1. What are homopolysaccharides (examples)?

Answer:

Homoppolysaccharides are the combined hydrocarbons, that consist of units of one polysaccharide. For example: starch, glycogen consist of of α – glucose units; cellulose – β-glucose units.

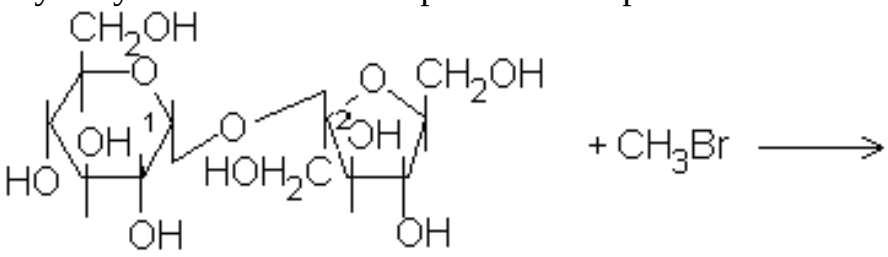
7.2. What products appear as a result of starch hydrolysis.

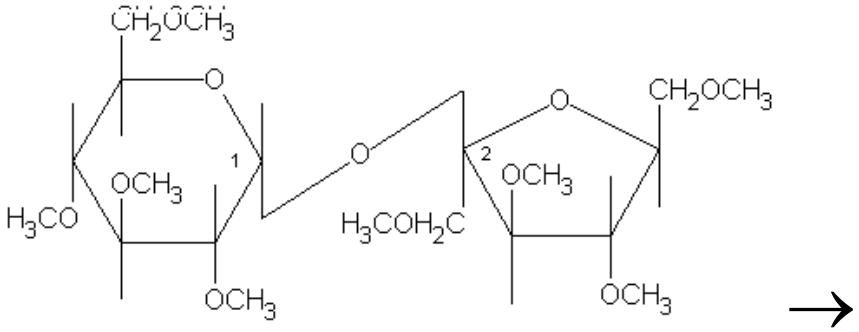
$(C_6H_{10}O_5)n \rightarrow (C_6H_{10}O_5)m \rightarrow (C_{12}H_{22}O_{11}) \rightarrow C_6H_{12}O_6$

Starch dextrines maltose glucose

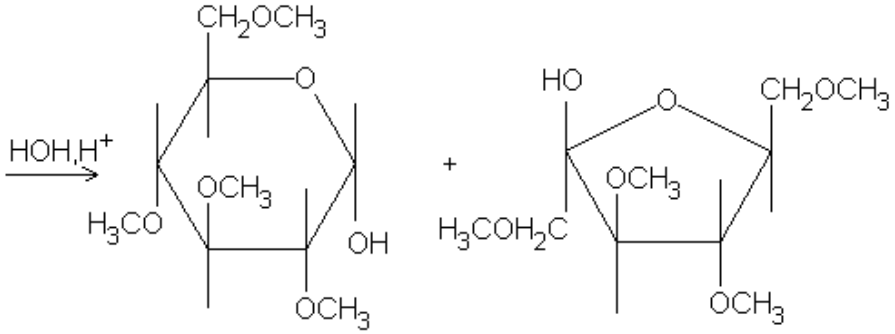
n > m

7.3. Write the scheme of saccharose alkylation, mark the bond types. Write the schema of hydrolysis of received compound and explain witch bond is hydrolyze first.





Bonds – α–1,2-glucoside and simple ether bonds



Only α–1,2–glucoside bond is under hydrolysis

8. Homework (must be performed in the laboratory notebook)

8.1. Write the structural formule of lactose, show the bond type between two monosaccharide units.

8.2 Write the structure of cellulose disaccharide fragment and show the bond type between two monosaccharide units.

Examples of control test:

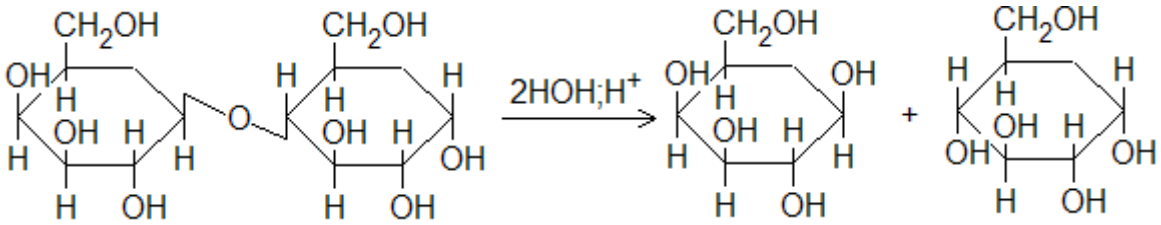
9.1. Write the structure of galactose and the scheme of its hydrolysis. What compounds are the reductors in this reaction?

9.2. Write the structure of disaccharide fragment of glucose and show the bond type.

9.3. Write the structure of completely acetylated disaccharide fragment of amilose.

Answers.

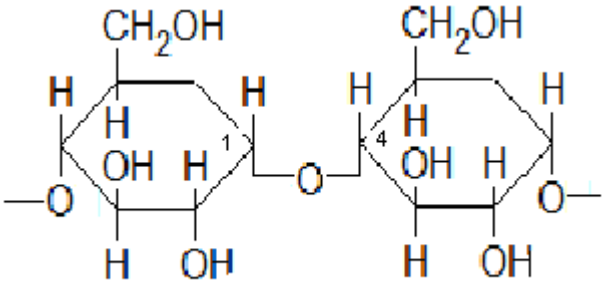
9.1.



Lactose ***galactose*** ***glucose***

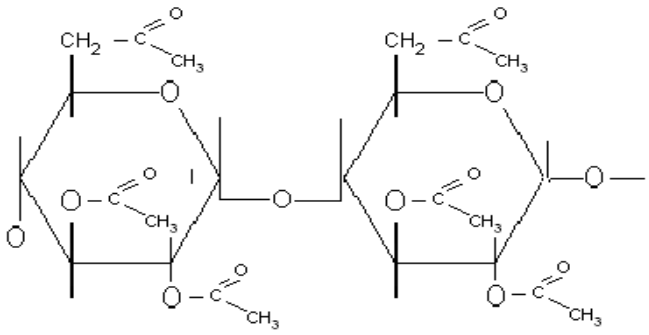
Lactose,glucose and galactose are the reductors.

9.2.



α-1,4-glucoside bond

9.3.



10. The algorithm of the experiments:

10.1. Demonstration of the presence of hydroxyle groups in saccharose.

10.2. Demonstration of absence of reductive abilities in saccharose.

10.3. Demonstration of saccharose hydrolysis.

10.4. Presence of reductive abilities in lactose.

10.5. Acidic hydrolysis of starch.

11. Detailed description of experiment:

11.1. Demonstration of the presence of hydroxyle groups in saccharose.

Put 1 drop of saccharose solution and 6 drops of NaOH solution, 5-6 drops of water and 1 drop of copper sulfate solution into the test-tube. Mark the results,write the reaction equation and make conclusions.

11.2. Demonstration of absence of reducing properties in saccharose.

The solution that was received in the first experiment must be heated until boiling. Mark the results, make the conclusions.

11.3. Demonstration of saccharose hydrolysis.

Put 1 drop of saccharose solution and 1 drop of HCl solution, 6drops of water into a test-tube and boil for 1 min. Hydrolysed solution put into two test-tubes. Add 6 drops of NaOH solution, 4-5 drops of water and 1 drop of $CuSO_4$ solution into the first one and heat until boiling. Put the resorcinol crystal, 2 drops of HCl concontrated into the second one and heat untiol boiling. Mark the results,write the scheme and make the conclusions.

11.4. The reducing abilities of lactose.

Put 1 drop of lactose solution, 4 drops of NaOH solution, 1 drop of $CuSO_4$ solution and heat until boiling. Mark the results, write the reaction equations and make conclusions.

11.5. Acidic hydrolysis of starch.

Put 1 drop of starch gleu, 2 drops of sulfuric acid inte the test-tube and put the test-tube into the boiling water. After 20 and 40 min. Make the qualitative reaction on the starch with one drop of hydrolysed solution. Mark the results, write the scheme of starch hydrolysis and make conclusions.

TOPIC 12: Heterocyclic compounds, their classification, structure and chemical properties.

1. Actuality of the topic: Structures of heterocycles are the base of such biologically important molecules as vitamines, koenzymes, nitrogen bases of nucleic acids etc. They are the components of medicines. The knowedge of their properties is neccesary for understanding of biological processes.

2. General aim: improve the knowledge of the structure and chemical properties of physiologically active heterocyclic compounds.

3. Actual aims and abilities:

- make conclusions about biological activity of heterfunctional compounds according to their structure and chemical character.

- make the qualitative reactions for determination of nicotinic acid, antipyrine, absence of phenol hydroxyde in acetylsalicylic acid.

4. Literature:

4.1. Lecture.

4.2. Zurabyan S.E., Fundumentals of bioorganic chemistry, Moscow, 2004, pp. 225-238.

5. Main questions of the topic:

5.1. Pentamerous heterocycles with one heteroatom (pyrrole). Benzopyrrole (indole) as a part of tryptophan and its metabolites (tryptamine, serotonin) and toxis compounds (skatole, indole).

5.2. Pentamerous heterocycles with two heteroatoms (pyrazole). Pyrazole derivatives as medical preparations.

5.3. Hexamerous heterocycles with one (pyridine) and two (pyrimidine) heteroatoms, their main properties. Pyrimidine nitrogen bases and their tautomery.

5.4. Heterocyclic compounds (purine) and its derivatives (nitrogen bases of nucleic acids, uric acid). Main properties, tautomerism.

6. The questions for individual learning:

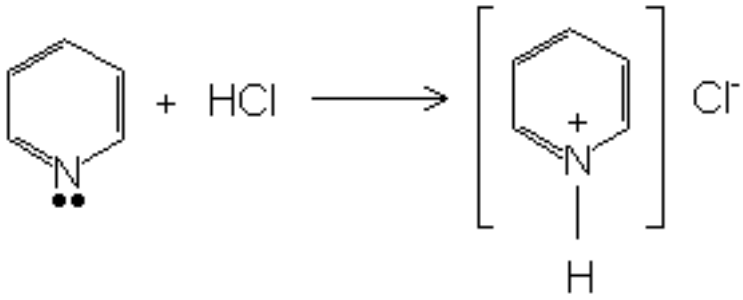
6.1. Heterocycles classification according to the cycle size, quantity and the nature of heteroatoms.

7. Examples of tasks:

7.1. Explian the main properties of nitrogen atoms in pyridine.

Answer.

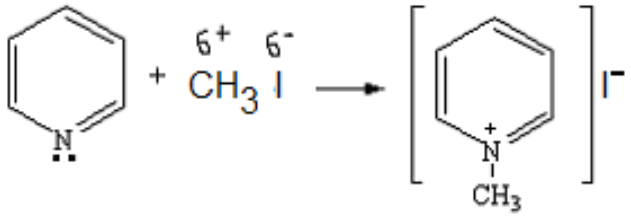
In pyridine the free electron pair of nitrogen atom does not take part in π-electronic density that is why nitrogen has basic properties.



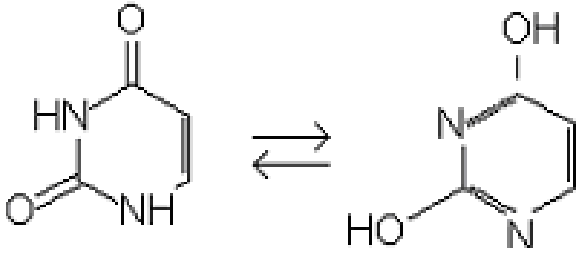
7.2. Explain the nucleophyllic character of pyridine.

Nitrogen atom in pyridine shows nucleophyllic properties because of the presence of free electron pair, for example in reactions with halogenalcanes:

Answer.



7.3. Write the lactim-lactam form of uracil.



lactam ***lactim***

8. Homework (must be performed in the laboratory notebook)*:*

8.1. Write the tautomeric forms of uric acid, what functional group forms salts?

8.2. Write the chemical scheme of NAD action.

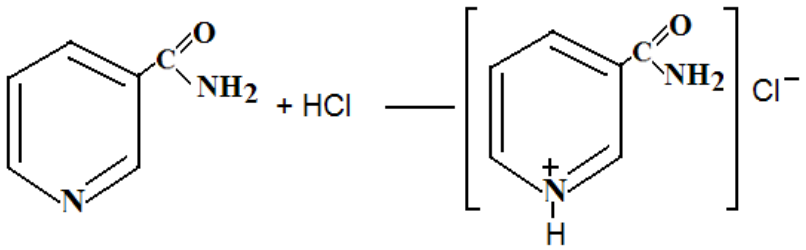
9. Example of control test:

9.1. Write the equation of pyridinium salt appearance during nicotinamide and hydrochloric acid interaction.

9.2. Name purine's biologically active derivative.

Answers:

9.1.



9.2. Uric acid, adenine, guanine, caffeine, toephylline, teobromine.

10. The algorithm of the experiments:

10.1. Quantitative reaction for nicotinic acid determination (PP vitamine).

10.2. Antipyrine and amidopyrine with ferrum (III) chloride.

11.Detailed description of experiment:

11.1. Quantitative reaction for nicotinic acid determination (PP vitamine).

Put 1ml of nicotinic acid solution into the test-tube and heat, add 6-7 drops of $CuSO_4$ solution and 0,5ml NH_4SCN solution. Mark the result of the reaction. Write the formulas of nicotinic acid and nicotinamide.

11.2. Antipyrine and amidopyrine with iron (III) chloride reaction.

Put several crystals of antipyrine in one test-tube, several crystals of amidopyrine in another one, add 2 drops of water and 1 drop of $FeCl_3$ solution into each of them. Mark the result of the reaction. Write the formulas of antipyrine and amidopyrine.

TOPIC 13: Nucleic acids, composition, structure and biological significance.

1. Actuality of the topic:

Nucleic acids are the main carriers of the genetic information in the organism. The knowledge of the structure and chemical properties of nucleic acids and their monomers (nucleotides) is necessary for understanding of chemical principles of structural organisation of nucleic acid macromolecules and nucleotide coenzymes for next learning of biochemistry and biology.

2. General aim: to fix the knowledge about the principles of the structure and learn about the principles of the biopolymer-cell components of the primary and secondary structures, that is usefull for understanding of their biological role.

3. Actual aims and abilities:

- to analyse the meanibg of nucleotides for the construction of nucleic acids and the action of nucleotide coenzyme.
- to interprete the action of vitamins in the formation of coenzymes catalysing the biochemical reactions in organism.

4. Literature:

4.1. Lecture.

4.2. Zurabyan S.E., Fundumentals of bioorganic chemistry, Moscow, 2004, pp. 225-238.

5. The main questions of the seminar:

5.1. Structural components of nucleic acids, chemical properties. Qualitative reaction.

5.2. Nucleosides: definition, structure, types of linkages, nomenclature, properties.

5.3. Nucleotides: difinition, structure, types of linkages, nomenclature, properties.

5.4. Nucleoside phosphate, the meaning of ATP. The role of nucleotides in the formation of coenzymes.

5.5. RNA and DNA: structure, types, types of linkages, complementary pairs. Biological significance of nucleic acids.

5.6. DNA duplex (Double spiral of DNA). Complementary pairs.

6. The questions for individual learning:

6.1. Qualitative reaction on carbohydrate component and phosphoric acid.

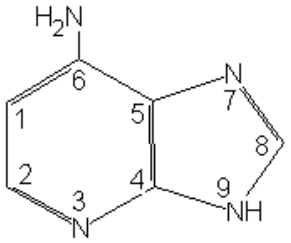
6.2. Formation of N-glicosidic and ester bonds.

6.3. The mechanism action of coenzyme NAD^+.

7. Examples of tasks:

7.1. Write the structural formula of adenine and point the pyrrol and pyridine nitrogen atoms.

Answer:

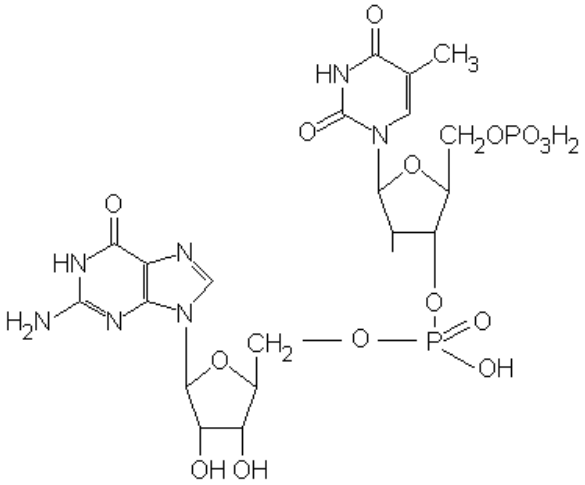


1,3,7 – pyridine nitrogen atom

9 – pyrrol nitrogen atom

7.2. Write the stracture of DNA-TG fragment.

Answer.



8. Homework (must be performed in the laboratory notebook)

8.1 Write the structure of cytidine, deoxyguanosine. Point the lactim-lactam tautomerization.

8.2. Write the structure of adenilic and thymidylic acid, point the types of linkages.

8.3. Write the structure of the dinucleotides DNA: T-G.

9***. Example of control test:***

9.1. Write the structure of lactim-lactam tautomerization of uracyl..

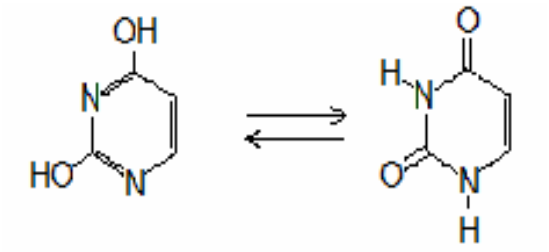
9.2. Write the hydrolysis of cytidine.

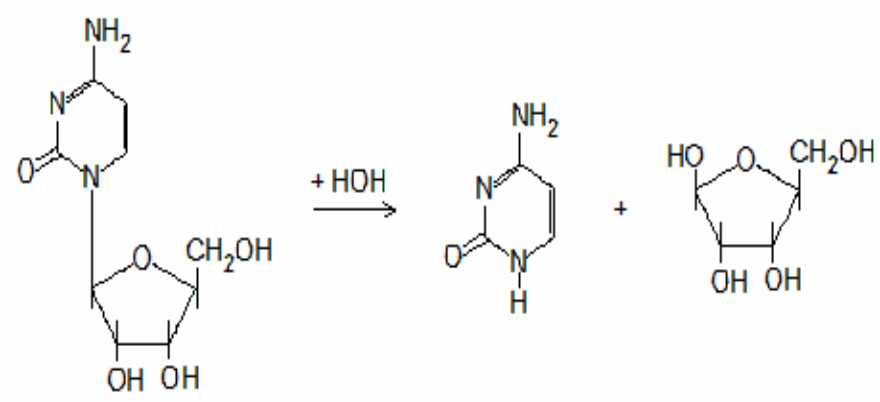
9.3. Write the structure of the dinucleotides RNA: guanine - cytosine

Answers.

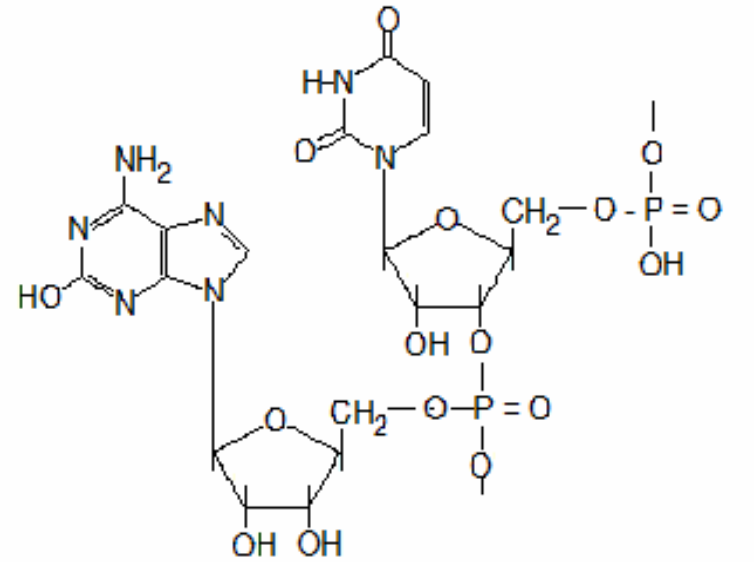
9.1.

9.2.





9.3.



10. The algorithm of the experiments:

10.1. Benedict's reaction of carbohydrate skeleton detection

10.2. Molybdenic probe for the phosphoric acid residue.

10.3. Dragendorff probe.

11. Detailed description of experiment

11.1. Benedict's reaction of carbohydrate skeleton detection.

In the test tube add the aquaous solution of yeast, 6 drops of NaOH and 2 drops of copper sulafte. Heat the mixture. Note the result, write the reaction equation, and make a conclution.

11.2. Molybdenic test for the phosphoric acid residue.

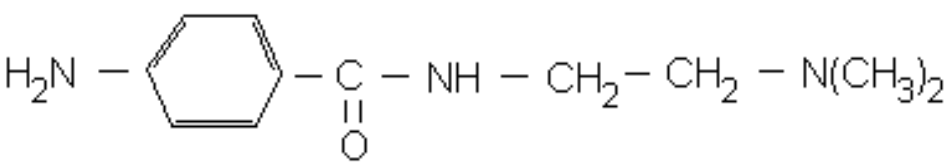
In the test tube add 5 drops of the aquous solution of yeast and molybdenic probe ($(NH_4)_2MoO_4$ in nitric acid).The mixture must be boiled for 5 min. Note the result, write the reaction equation, make conclutions.

11.3. Dragendorff`s test.

In the test tube add 2 drops of the aqueous solution of yeast and 5-6 drops of Dragendorff`s reagent (BiI_3 + KI). Note the result, write the reaction equation, make conclutions.

PRACTICAL ABILITIES AND SITUATION TASKS SOLUTION ON THE TOPIC: «TEORETICAL BASIS OF STRUCTURE AND REACTIVITY OF BIOORGANIC COMPOUNDS »

1. What is the difference between the stearin and paraffin candles?
2. How can we differentiate the mixture of phenol, acetic acid, benzine and ethanol? Write the reaction equations.
3. There are three liquids in the three test-tubes: benzene, toluene, stearene. Identify the substances in each test-tube. Write the reaction equations.
4. There are three liquids in the three test-tubes without labels: acetic acid, formic acid and pentane. Identify the substances in each test-tube. Write the reaction equations.
5. There are three liquids in the three test-tubes without labels: carbon tetrachloride, oktane, brominoethane. Identify the substances in each test-tube. Write the reaction equations.
6. There are different gases in three closed ampules: butene-1, methylamine and acetylamide. Identify the substances in each test-tube. Write the reaction equations.
7. There are five different liquids in the glass amoules: toluene, oleic acid, fomic acid, acetaldehyde and methanol. Identify the substances in each test-tube. Write the reaction equations.
8. How can we separate each gas from the mix of ammonia, methane propene and propine? Write the reaction equations.
9. How can we differentiate the mixture of aniline, phenol and benzene?
10. Kolamine (2 – aminoethanol - 1) takes part in the kefaline biosynthesis. Show the structure, configuration and different conformations of kolamine.
11. The bladder cancer is result of aminobenzine action. Explain the mutual action of aminogroup and benzene nucleus in the molecule.
12. Sulfosalicyllic acid is used for determination of protein in boiliquids in clinical laboratory diagnostics. Mark the type and sign of lectron effects in sulfosalicylic acid molecule.
13. Novocainamide as hydrochloride is used for curing of heart arrhythmia. Determine the protonation in novocainamide molecule



QUESTIONS FOR BIOORGANIC CHEMISTRY MODULE

1. Aldehyde and keton reactivity.
The electronic structure of oxogroup. The mechanism of nucleophylic addition in aldehydes and ketons. Interaction between aldehydes and alcohols, amines, aldol condensation reaction. Biological meaning of these reactions.

2. **Reactivity of carbon acids and their derivatives**.
The electronic structure of carboxygroup and mechanism of nucleophyllic substitution. Mechanism of interaction of carbon acids and alcohols, hydrolysis of esters in acidic and basic medium, interaction between halogenanhyride and ammonia. Biological meaning of these reactions. Acetylsalicylic acid, properties, determination of high quality.

3. Hydrocarbons.
Monosaccharides: glucose, fructose, ribose, desoxyribose. Structure, isomery, properties: O-, N-glycosides formation, alkilation, acetylation of oxygroups, qualitative reactions.

4. Hydrocarbons.
Olygosaccharides: saccharose, lactose. Structure, bond types, spatial structure, chemical properties: alkilation, acetylation of oxygroups, reductive properties, biological meaning.

5. Hydrocarbons.
Polysaccharides: starch (amylose, amylopectin), glycogen, cellulose. Contents, structure, bond types, spacial structure, chemical properties: alkilation, acetylation of oxygroups; qualitative ereaction for starch determination, biological meaning.

6. Aminoacids as structural components of peptides and proteines
The structure of carboxy and aminogroups, isomery, chemical properties of aminoacids: acid base properties, IES, IEP; qualitative and quantitave reactions in aminoacid analysis. Aminoacid transformation in human organism: decarboxylation, oxydesamination, intramolecular desamination. Serine`s methabolism in human organism.

7. **Peptides and proteins**.
Methods of extraction, separation, purification, determination of homogenety of proteins. The analysis of amino acid order in peptides and proteins by Edman. Main stages of protein synthesis.

8. Nucleic acids.
The structural components of nucleic acids: nitrogen basis, hydrocarbons, phosphoric acid. Chemical properties, qualitative reactions.
Nucleotides: structure, bond type, nomenclature, properties.
Mononucleotides: structure, bond types, nomenclature, properties.

RNA and DNA. The secondary structure of DNA, complementary bases. Biological meaning of nucleic acids.
ATP, structure, bond types, biological meaning.

9. Saponifiable lipids.
Fats (triacylglycerides). Higher fatty acids: saturated and unsaturated, spacial structure of unsaturated acids, chemical properties (hydrolysis, iodine number, peroxide oxidation).
Phosphoglycerols: composition, structure of phosphatidylcholine, phosphatidylcolamine, phosphatidylserine and their biological meaning.