MINISTRY OF HEALTH OF THE REPUBLIC OF UZBEKISTAN

TASHKENT PHARMACEUTICAL INSTITUTE

ORGANIC CHEMISTRY

Training manual
for implementation of laboratory work
for bachelors in the direction of
5510500-Pharmacy (by types), 5111000-Professional education
(5510500-pharmacy (pharmaceutical business)
(part 2 – 18 classes)

Tashkent-2021

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«CONFIRM»
Vice Rector of Academic Affairs
_____Z.A.Yuldashev
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INTRODUCTION

Organic chemistry is one of the main fundamental academic disciplines in the system of higher pharmaceutical education and plays an important role in teaching the basics of organic chemistry in the classes of organic compounds and their reactivity. Therefore, the chemical education of the future pharmacist is of great importance for professional training, since many organic compounds are used in the preparation of medicines and have an important biological value.

The purpose of studying the module "Organic Chemistry" is to form knowledge of the laws of chemical behavior of the main classes of organic compounds in relation to their structure, to perform qualitative reactions to functional groups, to obtain individual representatives of different classes of organic compounds, to conduct characteristic reactions with them. During the training, students will independently synthesize organic substances used as medicines.

This manual includes laboratory work on organic compounds that have important biological significance and are used as medicines-heterofuctional acids (oxy -, phenolo -, oxo-and amino acids), biologically active heterocyclic compounds and carbohydrates.

Before starting the laboratory work on the synthesis of organic compounds, the student will have to provide a protocol for its implementation, corresponding to the following plan:

1. Lab number.
2. Name and formula of the synthesized substance.
3. The literature used (author, year of issue, page).
4. Starting materials and their quantity.
5. Reagents for synthesis.
6. The equation of the main synthesis reaction.
7. Equations of side reactions of synthesis.
8. Calculation of the amount of starting materials, determination of the redundancy coefficient.
9. Description of the synthesis.
10. Picture of the installation for the synthesis.
11. Calculation of the yield of the obtained substance.
12. Physical constants of the obtained substance.
13. Conclusions.

Having issued the protocol after performing the synthesis, the student defends the work.

Laboratory work on the chemical properties of organic compounds is made out in the form of a table:

№	Name of the Experience	Reaction scheme	Reaction conditions (heating, catalyst, etc.)	The observed result of the experiment (color change, gas release, sediment appearance)	Conclusion
1	2	3	4	5	6

Systematic implementation of laboratory work in the course of studying organic chemistry is the key to successful knowledge of subsequent modules such as "Biological Chemistry", "Pharmaceutical Chemistry", "Toxicological Chemistry", "Pharmacognosy", "Technology of dosage forms".

Recommended literature

1. Shernyukh V.P., Shemchuk L.A. Organic Chemistry. Basic lecture course: The study guide for students of higher schools / edited by V.P.Chernyukh. – 4 ed., rev. and enl. – Kharkiv: NUPh; Original, 2011. – 440 p.

2. John McMurry. Organic Chemistry. – 9th ed. – ISBN: 978-1-305-63871-6, Boston, MA 02210, USA, 2016. – 1518 p.

3. Michael B. Smith. March’s Advanced Organic Chemistry: Reactions, mechanisms, and Structure. – 7th ed. – Published by JohnWiley & Sons, Inc., Hoboken, New Jersey, Canada. 2013. – 2075 p.

4. Paula Yurkanis Bruice. Organic Chemistry. – Pearson Education, ISBN 13: 978-0-321-69768-4, America, 2011. – 1263 p.

LESSON №1

Theme: Methods of purification and identification of liquid organic substances. Simple distillation of technical chloroform.

The purpose of the lesson: Develop knowledge of cleaning methods, identification of liquid organic substances, and the chemical utensils used in these methods.

Objectives: by the end of the lesson, the student should know:

1. basic rules for the organization of work in the purification of liquid organic substances;
2. principles of assembly of devices for working with liquid organic substances.
3. methods of purification of liquid organic substances;
4. methods of identification of liquid organic substances.

Basic training questions.

1. Organization of work in the purification of liquid organic substances.
2. Chemical utensils and auxiliary devices used in the performance of work on the purification of liquid organic substances.
3. The method of purification of liquid organic substances – distillation.
4. Types of distillation – simple, fractional, with water vapor, vacuum.
5. The use of simple distillation to separate a mixture of two components, the disadvantages of the method.
6. Fractional distillation (rectification), the purpose and method of its implementation. Deflegmators and their types.
7. Distillation with water vapor, devices. Purpose and method of implementation, precautions. Advantages of the method.
8. Low-pressure distillation (vacuum distillation), devices. Purpose and method of implementation, precautions. Advantages of the method.
9. Drying of purified liquid substances (vacuum drying and drying with drying agents).
10. Assessment of the purity and identification of liquid organic substances.
11. The use of simple distillation to identify substances.
12. Determination of the boiling point by the semimicrometer method of Sivolobov.
13. Density, refractive index-constants that characterize purity and identity.
14. Modern physical methods used for the purification and identification of liquid organic substances.
15. Spectral methods for establishing the identities of liquid organic substances.

Laboratory work. Simple distillation of technical chloroform, benzene.

Self-study (performed in preparation for the lesson).

The method of purification of liquid organic substances is extraction.

METHODS OF ISOLATION, PURIFICATION AND IDENTIFICATION OF LIQUID AND SOLID ORGANIC SUBSTANCES

Organic substances obtained during synthesis, as a rule, contain a certain amount of impurities: starting substances that have not reacted, by-products, solvents, etc. To purify organic substances from them, various methods of their purification and isolation are used. These methods are quite diverse and depend mainly on the aggregate state of the connection.

For the separation of liquid or volatile substances, the distillation method is used.

Distillation is the process of separating multicomponent liquid mixtures into separate fractions that differ in composition. Distillation is applicable only when the distilled substance is stable at the boiling point.

Depending on the conditions of the process, there are simple, fractional distillation, distillation with water vapor and under vacuum.

Simple distillation is effective in cases where the boiling points of the substances included in the mixture differ significantly (by at least 800C). A typical device for simple distillation at atmospheric pressure consists of a round-bottomed long-necked flask with a tap (Wurtz flask), a straight refrigerator, an allonzh and a receiver flask (Fig. 1.).

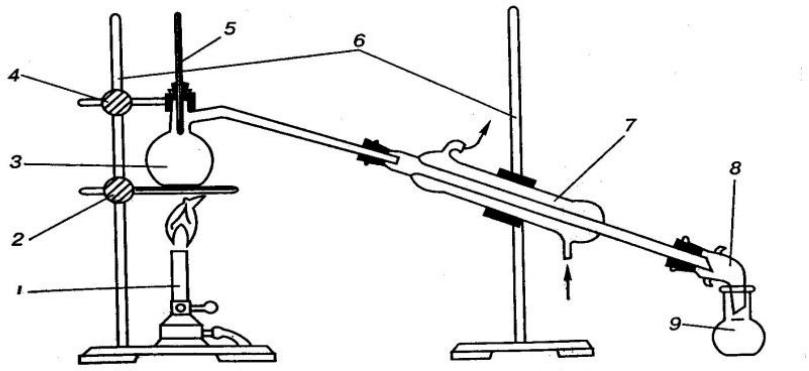


Fig. 1. Device for simple distillation of liquid substances: 1) Bunsen burner, 2) ring with clip and asbestos mesh, 3) distillation flask (Wurtz flask), 4) foot with clip, 5) thermometer, 6) tripods, 7) Liebig refrigerator, 8) allonge, 9) receiving flask

Fractional distillation is used to separate mixing liquids that boil at different temperatures.

Fractional distillation is carried out in a device that is essentially the same as the device for simple distillation, but equipped with a deflegmator (Fig.2)

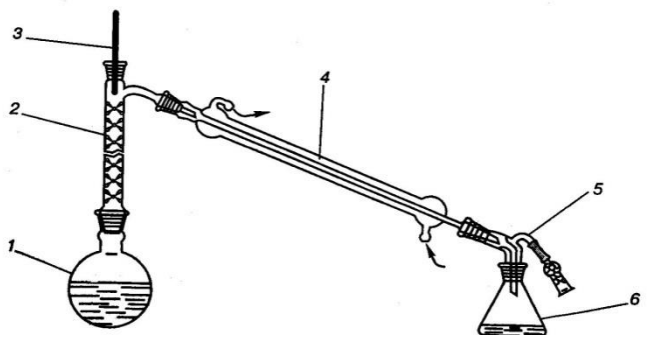


Fig. 2. Device for fractional distillation: 1) distillation flask, 2) deflegmator, 3) thermometer, 4) refrigerator, 5) allong with a chlorocalcium tube, 6) receiver

Distillation with water vapor is based on the fact that high-boiling substances that do not mix or do not mix much with water, when water vapor is passed through them, volatilize and condense together in the refrigerator. The distillate collected in the receiver in the form of two layers of immiscible liquids is then separated in a dividing funnel. With the help of steam distillation, it is possible to distill substances boiling significantly higher at a temperature of 100^0C.

Distillation with water vapor is carried out in a device consisting of a vaporizer, a distillation flask, a refrigerator and a receiver (Fig. 3).

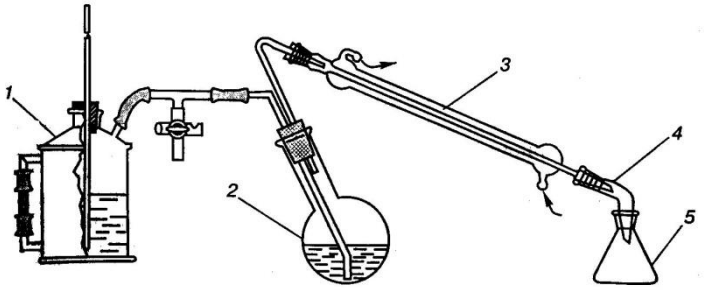


Fig. 3. Steam distillation device: 1) steam generator, 2) distillation flask, 3) refrigerator, 4) allong, 5) receiver

When it is necessary to lower the boiling point to reduce the risk of decomposition of the distilled substance, it is advisable to carry out distillation in a vacuum. To approximate the boiling point of a substance in a vacuum, the following rule is followed: when the external pressure is halved, the boiling point of the substance decreases by 15-20^0C.

The device for vacuum distillation (Fig. 4) differs from the device for simple distillation in that a flask with a Kleisen nozzle, equipped with a capillary with a very small internal diameter, is used as a distillation flask. Through this capillary, air enters the evacuated system in a thin trickle, bubbling through the liquid in the distillation flask, and thus the capillary performs the same role as the boilers in simple distillation. The capillary should reach almost to the bottom of the flask. On top of it, a piece of rubber vacuum hose with a thin wire inserted is put on, equipped

with a Hoffmann screw clip for subtly adjusting the speed of air bubbles passing through it.

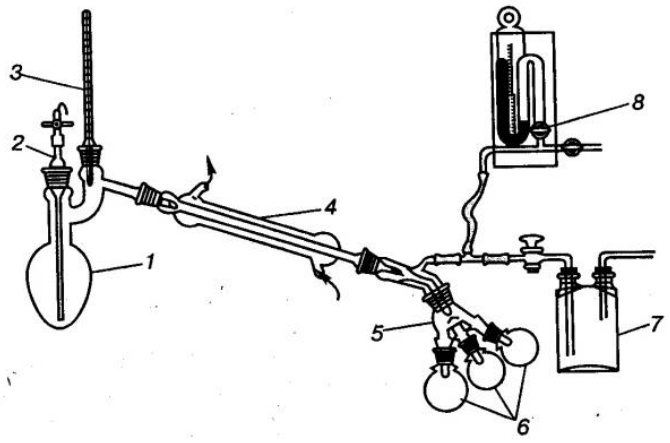


Fig. 4. Device for distillation in vacuum: 1) distillation flask, 2) capillary, 3) thermometer, 4) refrigerator, 5) allong ("spider"), 7) safety flask, 8) pressure gauge

Simple distillation technique. A simple distillation unit is assembled, as shown in Figure 1. A

Thermometer is inserted into the throat of the Wurtz flask so that the mercury ball of the thermometer is 0,5 cm below the opening of the outlet tube of the Wurtz flask. Depending on the boiling point of the liquid, water (up to 110-120^{0}C) or air (above 120^{0}C) refrigerators are used.

The liquid to be distilled is introduced into the Wurtz flask through a funnel, the spout of which should be lower than the outlet of the Wurtz flask. In this case, the distillation flask is filled with no more than 2/3 of the volume. In order to avoid overheating and the liquid boils evenly, so - called "boiling water" is added to the distillation flask-small pieces of unglazed plate or capillaries, lowered with the open end down.

The choice of heating device depends on the boiling point of the distilled liquid, its flammability and explosion hazard. For uniform heating, it is best to place the distillation flask in the appropriate bath. Distillation is carried out at such a speed that within a second no more than two drops of distilled liquid (distillate) flow into the receiver. The distillation can not be carried out dry, There should always be at least 2-3 ml of liquid in the flask.

During the entire distillation of the individual substance, the vapor temperature must remain constant. If the temperature rises during the distillation, it means that a mixture of substances is distilled. At the initial moment of distillation, the temperature is usually lower than expected. This may be due either to the inertia of the mercury thermometer, or to the fact that more volatile impurities are driven off at the first moment. Therefore, the first portions of the distillate (until a constant distillation temperature is reached) are collected separately and discarded. After the

temperature is established, the main fraction of the substance is collected. As soon as the temperature begins to rise again, the receiver is changed to collect another fraction.

LABORATORY WORK

Simple distillation of technical chloroform

Reagents: chloroform

Equipment and chemical utensils: Bunsen burner, ring with clip and asbestos mesh, distillation flask (Wurtz flask), foot with clip, thermometer, tripods, Liebig refrigerator, allonzh, receiving flask.

Getting the job done:

1. Assemble the unit for simple distillation: using the presser foot, the distillation flask is mounted on a tripod, followed by a straight Liebig refrigerator, an allong and a receiver flask.

2. The chloroform to be distilled is introduced into the Wurtz flask through a funnel, the spout of which should be below the outlet of the Wurtz flask. In this case, the distillation flask is filled with no more than 2/3 of the volume.

3. In order to avoid overheating and the liquid boils evenly, "boiling pots" (small pieces of an unglazed plate or capillaries lowered with the open end down) are introduced into the distillation flask.

4. Insert a thermometer into the throat of the Wurtz flask so that the mercury ball of the thermometer is 0,5 cm below the opening of the outlet tube of the Wurtz flask.

5. Connect the refrigerator to the tap, open the water.

6. Under the Wurtz flask, use the ring foot to cover the asbestos paper and start heating.

7. The distillation is carried out at such a speed that within a second no more than two drops of the distilled liquid (distillate) flow into the receiver.

8. During the entire distillation, the vapor temperature must remain constant. If the temperature rises during the distillation, it means that a mixture of substances is distilled. At the initial moment of distillation, the temperature is usually lower than expected.

9. The first portions of the distillate (until a constant distillation temperature is reached) are collected separately and discarded.

10. After the temperature is established, the main fraction of the substance is collected. As soon as the temperature begins to rise again, the receiver is changed to collect another fraction.

11. Distillation should not be carried out dry, there should always be at least 2-3 ml of liquid in the flask.

Control questions

1. What chemical utensils are used for cleaning liquid organic substances?
2. What methods of cleaning organic compounds do you know?
3. What are the main methods of cleaning liquid organic substances?
4. Define decantation and explain the essence of this method.
5. What is filtering? What filtering methods do you know?
6. What are the basic principles of simple filtering?
7. What method can be used to separate mixtures of liquid and solid substances that differ in density?
8. What organic substances can be separated using a dividing funnel?
9. What is distillation? What types of distillations do you know?
10. What is the principle of conducting a simple distillation? What are its disadvantages?
11. What is the principle of steam distillation? What are its advantages and disadvantages?
12. When is it advisable to conduct vacuum distillation? Its advantages and disadvantages?
13. What parameters are related to the physical constants of organic matter?

Task: Define simple distillation operations and specify their correct order.

Operation Name	Student's answer	Correct answer
A thermometer is inserted into the throat of the distillation flask		
Monitor the thermometer readings		
A simple distillation unit is assembled, which consists of a round-bottomed, long-necked flask with a tap (Wurtz flask), a straight refrigerator, an allong and a receiver flask		
Through the funnel, the liquid to be distilled is introduced into the distillation flask, while the distillation flask is filled with no more than 2/3 of its volume		
"Boiling water" is added to the distillation flask»		
Collect the first portions of the distillate (until a constant distillation temperature is reached)		
A simple distillation unit is assembled, which consists of a flat-bottomed long-necked flask with a tap (Wurtz flask), a return refrigerator, an allonzh and a receiver flask		
Through the funnel, the liquid to be distilled is introduced into the distillation flask, while the distillation flask is filled with no more than 1/2 of its volume		

Change the receiver to collect another fraction (as soon as the distillation temperature begins to increase again)		
A simple distillation unit is assembled, which consists of a round-bottomed, long-necked flask with a tap (Wurtz flask), a deflegmator, a direct refrigerator, an allonzh and a receiver flask		
Through the funnel, the liquid to be distilled is introduced into the distillation flask, while the distillation flask is filled with water.		
Heat the distillation flask		
Collect the main fraction of the substance (after the distillation temperature has been established)		

LESSON №2

Theme: Methods of purification and identification of solid organic substances. Recrystallization of benzoic acid.

The purpose of the lesson: To develop knowledge about the methods of purification and identification of solid organic substances.

Objectives: by the end of the lesson, the student should be able to:

1. basic rules for the organization of work in the purification of solid organic substances;
2. principles of assembly of devices for working with solid organic substances.
3. methods of purification of solid organic substances;
4. methods of identification of solid organic substances.

Basic training questions.

1. Organization of work in the purification of solid organic substances.
2. Chemical utensils and auxiliary devices used in the performance of work on the purification of solid organic substances.
3. The method of purification of solid organic substances – crystallization.
4. Solvent selection.
5. Removal of colored and resinous impurities.
6. Crystal extraction.
7. Separation of fallen crystals.
8. Drying of crystals: in the air, in the desiccator, in the drying cabinet.
9. Sublimation – sublimation) - theoretical foundations and advantages of the method.
10. Assessment of the identity and purity of solid organic substances.
11. Melting point-the criterion of identity and purity of the substance.

Laboratory work. Recrystallization of benzoic acid.

Self-study. (performed in preparation for the lesson).

The method of purification of solid organic substances is chromatography.

METHODS OF PURIFICATION AND IDENTIFICATION OF SOLID ORGANIC SUBSTANCES.

Filtering

The simplest way to separate the liquid from the solid particles in it is decantation-draining the liquid from the settled sediment. However, it is difficult to separate the completely liquid phase from the solid phase in this way. This can be achieved by filtering-passing the liquid with the sediment through the filter material. There are different filter materials and different filtration methods.

The most common filter material in the laboratory is filter paper. Paper filters are made from it. The size of the filter is determined by the mass of the sediment, not by the volume of the filtered liquid. The filtered sediment should not occupy more than half of the filter volume. Before starting work, the filter is wetted with the solvent to be filtered. During filtration, the liquid level should be slightly lower than the upper edge of the paper filter.

A simple filter is made from a square piece of filter paper (Fig. 1) The filter must fit snugly to the inner surface of the glass funnel. The folded filter has a larger filter surface, filtering through it is faster. If the solution contains strong acids or other organic substances that destroy the paper, glass crucibles with a porous glass bottom or glass funnels with porous glass plates soldered into them are used for filtration. Glass filters are numbered according to the pore size: the larger the filter number, the smaller the pore cross-section and the finer the sediments can be filtered on it.

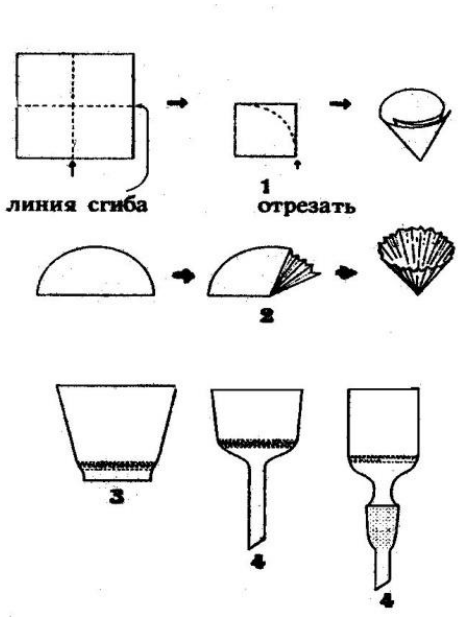


Fig. 1. Filters:
1) production of a simple filter,
2) production of a folded filter,
3) a filter crucible with a porous plate, 4) funnels with glass with a porous plate

In the laboratory, several filtration methods are used: simple, in a vacuum, hot.

Simple filtration is reduced to the use of a glass funnel with a paper filter embedded in it (Fig. 2).The funnel is inserted into the ring, a glass or a flat-bottomed flask is placed under it to collect the filtered liquid (filtrate). The funnel spout should be slightly lowered into the receiver and touch its wall. The filtered liquid is transferred to the filter by a glass rod.

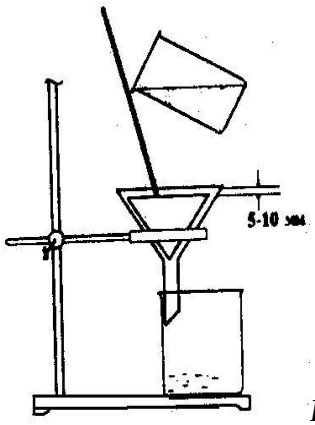


Fig. 2. Simple filtering

To accelerate and more completely separate the sediment from the filtrate, vacuum filtration is resorted to. In a flat-bottomed thick-walled Bunsen flask, a porcelain Buchner funnel is inserted with a rubber stopper (Fig. 3), which has a flat perforated partition, on which a paper filter is placed. The filter is cut out according to the size of the bottom of the funnel. The vacuum is created by a water jet pump. If the pressure in the water supply system is weakened, water from the pump can get into the device. To avoid this, install a safety flask.

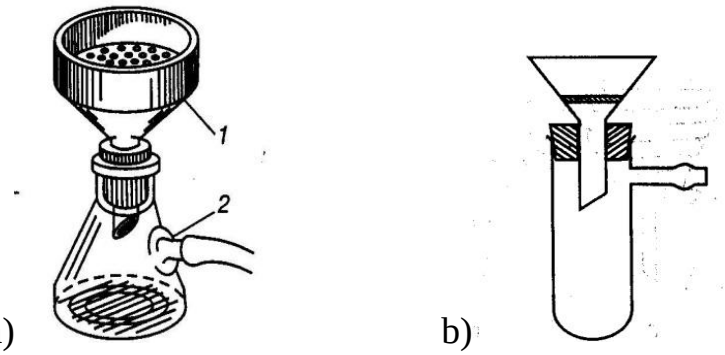


Fig. 3. Filtration a) in vacuum: 1) Bunsen flask, 2) Buchner funnel; b) small amounts of substances

When performing filtration in a vacuum, certain rules must be observed: 1) connecting the water jet pump and connecting it to the system, 2) wetting the filter with a small amount of the solvent that is supposed to be filtered, 3) applying the filter liquid. The sediment collected on the filter is squeezed out with a glass stopper until the mother liquor stops dripping from the funnel. If a whistling sound occurs during filtering, this indicates that the filter is loosely placed or has broken through, in which case the filter should be replaced. If the sludge on the Buchner funnel needs to be washed, then using a three-way tap, first connect the Bunsen flask to the

atmosphere, then the sludge is impregnated with a washing liquid and filtered, re-connecting the vacuum. After the end of filtration, first disconnect the entire system from the vacuum, then turn off the water jet pump.

One of the main methods that are used in laboratory practice for the purpose of purification, identification of solid organic substances, are:

- crystallization;
- sublimation (sublimation).

Crystallization is one of the most important methods of purification and separation of solid substances in laboratory and industrial conditions. The method is based on the process of crystal formation from a melt, solution, or gas phase. But the substance obtained as a result of crystallization is not always clean enough, so the resulting product is subjected to further purification, which is called recrystallization. The contaminated substance is dissolved in a suitable solvent when heated and a saturated solution is obtained. The hot solution is filtered, freeing it from insoluble impurities, then the filtrate is cooled. When the saturated solution is cooled, the solubility of the substances decreases. Part of the dissolved substance falls out in the form of a precipitate, which contains less impurities than the original substance. The method is applicable for substances in which the solubility increases significantly with increasing temperature.

The result of crystallization depends more on the choice of solvent (Table 1). The substance to be cleaned should be poorly dissolved in the selected solvent in the cold and well-at its boiling point. The contaminants must be difficult to dissolve or insoluble in the solvent. The solvent must not react with the solute. It should cause the formation of stable crystals and be easily removed from the surface of the crystals during washing and drying.

Table 1.

Solvents used in recrystallization

Properties	Class of compounds	Solvents
Hydrophobic	Hydrocarbons, halogen-derived hydrocarbons, esters	Hydrocarbons, ether, halogen-derived hydrocarbons
	Amines, esters, nitro compounds	Esters
	Nitriles, ketones, aldehydes	Alcohols, dioxane, acetic acid
	Phenols, amines, alcohols, carboxylic acids, sulfonic acids	Alcohol, water
Hydrophilic	Salt	Water

When the solvent is selected, the substance is heated with it to a boil, observing all precautions. First, the solvent is taken in a smaller amount than is necessary for the complete dissolution of the substance.

If necessary, the solution is discolored by adding an adsorbent (crushed activated carbon, finely torn filter paper). Before adding adsorbents, the solution should be cooled slightly, as these substances can increase the boiling process, which will lead to a vigorous release from the flask. The mixture of the dissolved substance with the adsorbent is reheated to a boil and filtered hot using a conical funnel and a folded filter. The flask with the filtrate is left to cool. Gradually, crystals of the test substance fall out of the filtrate. Slow cooling of the filtrate allows you to get large crystals, fast – small ones.

Solid organic substances during the distillation of solvents can be released in the form of oily liquids, which makes it difficult to crystallize them. This can be avoided by adding a few pure crystals of the crystallized substance. The friction of the glass rod against the vessel walls also facilitates the crystallization process.

Sublimation (sublimation) is the process of evaporation of a solid substance, followed by condensation of its vapors directly into the solid, bypassing the liquid phase. Sublimate is used to purify those organic substances whose crystallization is difficult.

To sublimate a small amount of the substance at atmospheric pressure, it is placed in a porcelain cup and covered with a circle of filter paper with small holes made with a needle. An overturned glass funnel is placed on top, the spout of which is tightly closed with a cotton swab (Fig. 5). The cup is carefully heated. The vapors of the sublimating substance pass through the holes on the filter and condense on the inner walls of the funnel. The partition protects the crystals of the pure substance from falling into the heating zone.

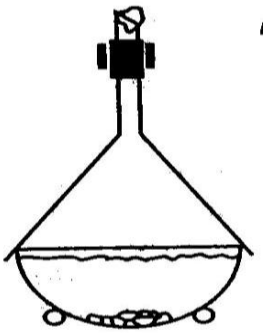


Fig. 5. Device for sublimation at atmospheric pressure.

As with any evaporation, the rate of sublimation is proportional to the area of the evaporated surface, so the substance must be thoroughly ground before sublimation and not allow it to melt.

The disadvantages of sublimation are the relatively long duration of the process and the limited use. However, this method of purification differs favorably from recrystallization by the absence of contact of the substance with the solvent and a high final yield.

LABORATORY WORK

Experiment 1. Recrystallization of benzoic acid

Reagents: benzoic acid, water

Equipment and chemical utensils: a conical flask (glass) with a capacity of 100 ml, a ring with a clip and an asbestos mesh, a simple funnel, a filter, a gas burner.

Getting the job done:

1. In a conical flask (glass) with a capacity of 100 ml, place 1 g of benzoic acid and 50 ml of water.

2. The mixture is heated to a boil – the benzoic acid is completely dissolved.

3. If the solution is colored, then an adsorbent – crushed activated carbon-is added to discolor the solution. Before adding the adsorbent, the solution should be cooled slightly, since the adsorbent can increase the boiling process, which can lead to a vigorous ejection from the flask.

4. The mixture of the dissolved substance with the adsorbent is reheated to a boil.

5. The hot solution is quickly filtered through a folded filter using a conical funnel and a folded filter.

6. The filtrate is equally poured into two flasks.

7. The contents of one flask are quickly cooled under running tap water or in ice and shaken. Benzoic acid falls out in the form of small crystals.

8. The solution in another flask is kept at room temperature for 20-25 minutes. There is a slow precipitation of shiny large lamellar crystals of benzoic acid.

9. The resulting crystals are filtered out using a Buchner funnel and a Bunsen flask (Fig. 3).

10.The crystals are dried.

Experience 2. Anthraquinone (naphthalene) sublimation)

Reagents: anthraquinone (naphthalene)

Equipment and chemical utensils: porcelain cup, ring with clip and asbestos mesh, simple funnel, filter, gas burner.

Getting the job done:

1. A porcelain cup is placed on the ring with a clip.

2.Anthraquinone (naphthalene) is placed in a porcelain cup.

3. The porcelain cup is covered with a circle of filter paper with small holes made with a needle.

4. An overturned glass funnel is placed on top, the spout of which is tightly closed with a cotton swab (Fig. 5).

5.The cup is carefully heated.

6. The vapors of the sublimating substance pass through the holes on the filter and condense on the inner walls of the funnel. The partition protects the crystals of the pure substance from falling into the heating zone.

Control questions

1. What chemical utensils are used in cleaning solid organic substances?
2. What methods of cleaning solid organic compounds do you know?
3. What are the main methods of cleaning solid organic substances?
4. Define crystallization and explain the essence of this method.
5. What is the essence of recrystallization?
6. How is the solvent selected for recrystallization?
7. What is recrystallization? Explain the essence of this method.
8. What is sublimation? The essence of this method.
9. What methods of identification of solid organic substances do you know?
10. What parameters are related to the physical constants of solid organic matter?
11. What method can be used to separate mixtures of liquid and solid substances that differ in density?

LESSON №3

Theme: Oxy-acids. Properties of lactic, tartaric, and citric acids.

The purpose of the lesson: To form knowledge about the reactivity of oxy-acids in relation to their structure.

Objectives: by the end of the lesson, the student should be able to:

1. apply the knowledge of nomenclature, isomerism, and stereoisomerism to the class of oxyacids;
2. write reactions for the production of oxy-acids;
3. write reactions due to the presence of a hydroxyl group;
4. write reactions due to the presence of a carboxyl group;
5. determine the type and mechanism of transformations occurring during heating, associated with the mutual influence of functional groups, depending on their relative location in the oxy-acids.

Basic training questions.

1. Stereoisomerism of hydroxy acids with one and two centers of chirality. D,L- and R,S-configuration notation systems. Enantiomers, diastereomers, racemates.

2. Acidic properties of oxy-acids: a) in comparison with the corresponding carboxylic acids, b) in comparison with α -, β -, and γ-hydroxyacids.

3. Reactions occurring in the carboxyl group: formation of salts (with ammonia, sodium hydroxide, sodium carbonate), esters.

4. Reactions going on the hydroxyl group (with hydrogen bromine, acetic anhydride, acetic acid).

5. Reactions characteristic of both the carboxyl and hydroxyl groups (with sodium, thionyl chloride, and phosphorus (V) chloride).

6. Specific properties of hydroxyacids. Cleavage in an acidic environment.

7. The reaction that distinguishes α -, β -, and γ-hydroxyacids is heating.

8. Redox reactions of oxy-acids.

Laboratory work. Properties of lactic, tartaric, and citric acids.

Self-study (performed in preparation for the lesson).

Stereoisomerism of oxy-acids, methods of their preparation.

LABORATORY WORK

Experience 1. Evidence of lactic acid structure

Reagents: lactic acid, concentrated sulfuric acid.

Equipment and chemical utensils: test tubes, a plug with a gas outlet tube, a gas burner.

Getting the job done:

1.0,5 ml of lactic acid is placed in a dry test tube.

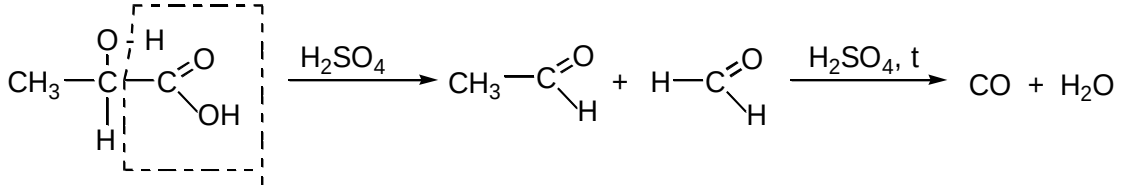
2. Carefully pour 0,5 ml of concentrated sulfuric acid.

3. The opening of the test tube is closed with a stopper with a gas outlet tube.

4. The contents of the test tube are carefully heated in the flame of the burner.

5. The liquid in the test tube darkens and foams.

6. Lactic acid, when heated in the presence of concentrated sulfuric acid, decomposes to form acetic aldehyde and formic acid, which under these conditions decomposes to carbon monoxide (II) and water.



7. When igniting the gas released from the exhaust pipe, a blue color of the flame is observed, which indicates the release of carbon monoxide (II).

Experience 2. Obtaining tartaric acid salts

Reagents: tartaric acid, 10% sodium hydroxide solution, 5% potassium hydroxide solution

Equipment and chemical utensils: test tubes, glass rod.

Getting the job done:

1.0,1 g of tartaric acid is placed in a test tube.

2. Add 1 ml of water.

3. Carefully, drop by drop, add a 5% solution of potassium hydroxide, rubbing a glass stick on the walls of the test tube.

4. There is a white crystalline precipitate of the acidic potassium salt of tartaric acid, which is poorly soluble in water.

$$HOOC\text{-}CHOH\text{-}CHOH\text{-}COOH + KOH \longrightarrow KOOC\text{-}CHOH\text{-}CHOH\text{-}COOH + H_2O$$

5.The resulting sediment is divided into two parts.

6. Drop by drop, pour the excess potassium hydroxide into the first test tube.

$$KOOC\text{-}CHOH\text{-}CHOH\text{-}COOH + KOH \longrightarrow KOOC\text{-}CHOH\text{-}CHOH\text{-}COOK + H_2O$$

7. The second tube is filled with 0.5 ml of sodium hydroxide.

$$KOOC\text{-}CHOH\text{-}CHOH\text{-}COOH + NaOH \longrightarrow KOOC\text{-}CHOH\text{-}CHOH\text{-}COONa + H_2O$$

8. In both test tubes, the precipitate of the acidic potassium salt of tartaric acid is dissolved to form medium well-soluble salts.

The solution is used for the following reaction.

Experiment 3. Preparation of the Fehling solution and study of its properties

Reagents: potassium-sodium tartaric acid (from previous experience), 5% copper sulfate solution, 10% sodium hydroxide solution, formalin

Equipment and chemical utensils: test tubes, glass rod.

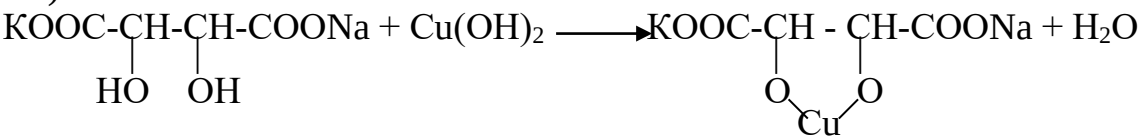
Getting the job done:

1. Pour 0,5 ml of copper sulfate solution into the test tube.

2. Add about 0,5 ml of 10% sodium hydroxide solution dropwise until a blue copper hydroxide precipitate is formed.

3. solution of the potassium-sodium salt of tartaric acid is added to the precipitate (previous experience).

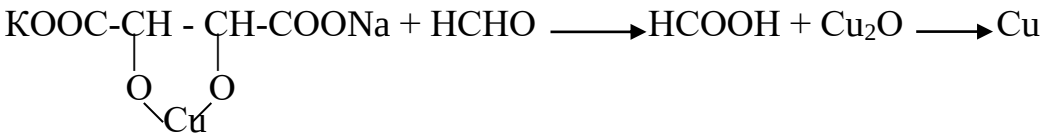
4. The blue precipitate dissolves to form a bright blue solution (Fehling solution).



5.Pour 1 ml of Fehling solution into the test tube.

6. Add a dilute formalin solution and heat.

7.Red copper oxide (I) precipitate or free copper precipitates.



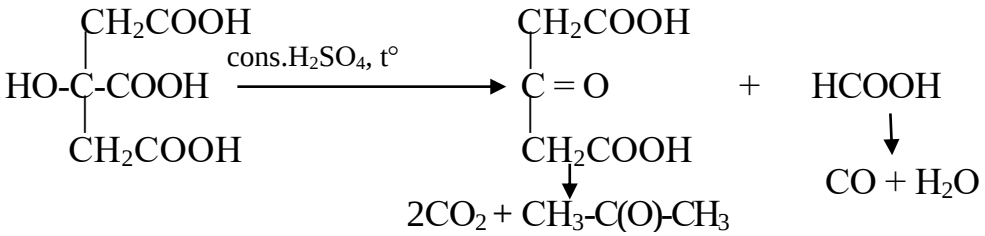
Experiment 4. Decomposition of citric acid

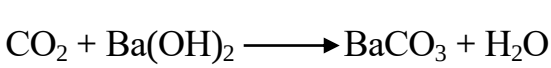
Reagents: citric acid crystals, concentrated sulfuric acid, barite water

Equipment and chemical utensils: test tubes, a glass rod, a stopper with a gas outlet tube.

Getting the job done:

1. Crystal citric acid is placed in a dry test tube at a height of 5 mm.
2. Carefully pour 1 ml of concentrated sulfuric acid.
3. The test tube is closed with a stopper with a gas outlet tube.
4. The end of the exhaust pipe is lowered into a test tube with 1 ml of barite water.
5. The initial mixture is heated in a burner flame.
6. Observe the rapid release of gas bubbles.
7. The formation of a white precipitate of barium carbonate indicates the release of carbon monoxide (IV).





8. When igniting the gas released from the exhaust pipe, a blue color of the flame is observed, which indicates the release of carbon monoxide (II).

Control questions

1. What compounds are called oxy-acids? Their classification.
2. Describe the stereoisomerism of oxy-acids.
3. How is the optical activity of oxy-acids determined?
4. What compounds are called "enantiomers"," diastereomers"," mesoform"," racemate"?
5. What are the main methods for producing oxy-acids?
6. Explain the acidic properties of oxy-acids in relation to carboxylic acids.
7. How to change the acidic properties of oxyacids in a series of α-, β-, γ-oxyacids?

8. With the help of some reactions can be distinguished α-, β-, γ-hydroxy acid from each other?

9. What compounds are formed by heating α-oxyacids in the presence of sulfuric acid?

10. What reactions it is possible to prove the existence of hydroxyl groups in the oxyacids?

11. What is the quality reagent for the carboxyl group of oxy-acids?

12. What reactions are characteristic of both the hydroxyl group and the carboxyl group of hydroxyacids?

13. The sequence of which reactions allows you to get a Fehling reagent from tartaric acid?

Task: Fill in the table ("Assessment").

Oxy-acids

TEST	**PROBLEM SITUATION**
1. How many stereoisomers does this compound have? CH_2OH-CHOH-CHOH-CHOH-COOH A. 4 B. 6 C. 8 D. 10 2. Which of the compounds forms a non-dilute acid when heated? A. Lactic acid B. α-hydroxyisobutyric acid C. β -oxybutyric acid D. γ -oxybutyric acid	An organic substance of the molecular formula $C_4H_8O_3$, when heated, forms a substance of the molecular formula $C_4H_6O_2$, which attaches bromine to form a dibromo derivative, and when oxidized, forms a mixture of acetic and oxalic acids. Determine the structure of organic matter and name it according to all possible nomenclatures.
GLOSSARY **1. Optical activity - …** **2. Mesoform - …**	**PRACTICAL SKILLS** Specify the reagents with which the hydroxyacids interact only with the hydroxyl group. 1. HC1 2. Na 3. $NaHCO_3$ 4. $PC1_5$ 5. $(CH_3CO)_2O_6$. [O] Write the corresponding reaction equations.

LESSON №4

Theme: Phenolic acids. Properties of salicylic acid, synthesis of aspirin and salol, their distinctive reactions.

The purpose of the lesson: To form knowledge about the reactivity of phenolic acids in relation to their structure.

Objectives: By the end of the lesson, the student should be able to:

1. apply the knowledge of nomenclature, isomerism to the class of phenolic acids;
2. write reactions for obtaining phenolic acids;
3. write reactions due to the presence of a hydroxyl group;
4. write reactions due to the presence of a carboxyl group;
5. determine the type and mechanism of transformations occurring during heating, associated with the mutual influence of functional groups, depending on their relative location in phenolic acids;
6. distinguish salicylic acid from its derivatives – aspirin and salol.

Basic training questions.

1. Phenolic acids-structure, nomenclature.
2. Industrial method for producing salicylic acid. The Kolbe method.
3. Acidic properties of phenolic acids. Comparison of the acidic properties of salicylic acid with benzoic and p-hydroxybenzoic acids.
4. Reactions characteristic of phenolic hydroxyl (interaction with acid anhydrides). Preparation of acetylsalicylic acid.
5. Reactions following the carboxyl group: with sodium carbonate, alcohols. Preparation of sodium salicylate, phenylsalicylate, and methyl salicylate.
6. Reactions taking place both on the phenolic hydroxyl and on the carboxyl group (with sodium hydroxide, phosphorus chloride (V)).
7. Electrophilic substitution reactions on the benzene ring.
8. Preparation of p-aminosalicylic acid by carboxylation of m-aminophenol.
9. o-Hydroxycinnamic acids (cis - and trans -). Coumarin o-coumaric acid.
10. Decarboxylation of gallic acid.

Laboratory work. Properties of salicylic acid, synthesis of aspirin and salol, their distinctive reactions.

Self-study (performed in preparation for the lesson).

Salicylic acid, aspirin, phenylsalicylate, phenol-distinctive reactions.

LABORATORY WORK

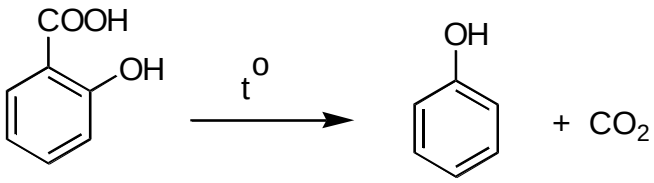
Experiment 1. Decomposition of salicylic acid by heating

Reagents: salicylic acid, barite water

Equipment and chemical utensils: test tubes, stopper with gas outlet tube, gas burner

Getting the job done:

1. Salicylic acid is placed in a dry test tube at a height of 5 mm.
2. The test tube is closed with a stopper with a gas outlet tube.
3. The end of the exhaust pipe is lowered into a test tube with barite water.
4. The contents of the first test tube are heated.
5.White crystals are collected on the walls of the test tube.
6. Salicylic acid decomposes into phenol and carbon dioxide when heated.
7. Carbon dioxide is detected by the turbidity of barite water, phenol-by the characteristic smell.



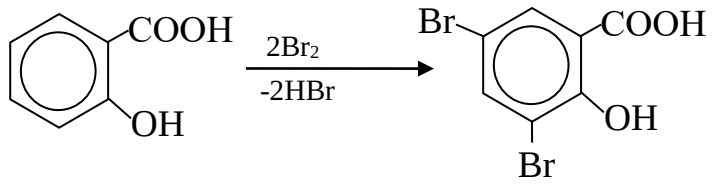
Experience 2. Interaction of salicylic acid with bromine

Reagents: salicylic acid, benzoic acid, bromine water

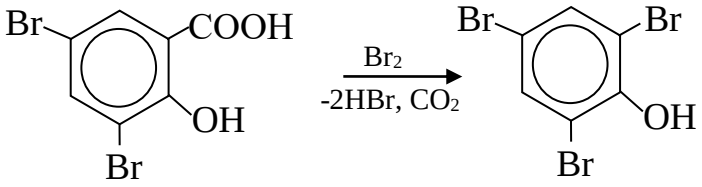
Equipment and chemical utensils: test tubes, pipette

Getting the job done:

1. Take two test tubes.
2. Several crystals of salicylic acid are placed in one test tube, and benzoic acid is placed in the other.
3. Pour 5-10 drops of distilled water into both test tubes.
4. The crystals of salicylic and benzoic acid are dissolved.
5. Pour 2-3 drops of bromine water.
6. In a test tube with salicylic acid, a precipitate is formed, the bromine water solution is discolored.



7. There are no changes in the test tube with benzoic acid.
8.Bromine water is added to the test tube with salicylic acid.
9. A yellow precipitate is observed, which indicates the decarboxylation of 3,5-dibromosalicylic acid, 2,4,6-tribromophenol is formed.



10. The test tube is carefully heated for 1 minute.

11. The precipitate dissolves, 2,4,6-tribromophenol forms 2,4,4,6-tetrabromocyclohexadiene-2,5-one.

This reaction is used in pharmaceutical practice to detect salicylic acid by the bromatometric method.

Experience 3. Interaction of salicylic acid with sodium bicarbonate

Reagents: salicylic acid, phenol, 5% sodium bicarbonate solution

Equipment and chemical utensils: test tubes, spatula, pipette

Getting the job done:

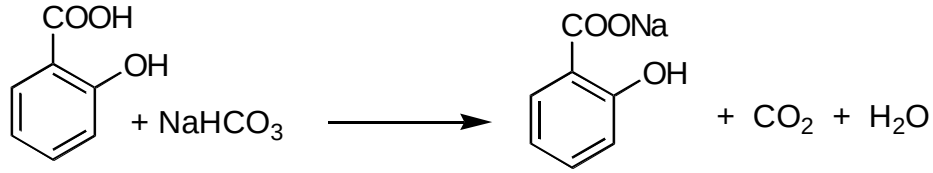
1.Pour 1 ml of 5% sodium bicarbonate solution into two test tubes.

2.Salicylic acid is added to one tube at the tip of the spatula, and the same amount of phenol is added to the other.

3. Shake the contents of the test tubes.

4. In a test tube with salicylic acid, the release of gas bubbles is observed.

5. In a test tube with phenol, no visible changes are observed, since phenols do not displace carbonic acid from its salts.



Experiment 4. Detection of phenolic hydroxyl in salicylic acid

Reagents: salicylic acid, 1% solution of iron (III) chloride)

Equipment and chemical utensils: test tubes, pipette

Getting the job done:

1.Several crystals of salicylic acid are placed in a dry test tube.

2. Add 1 ml of distilled water.

3. To add 1-2 drops of iron (III) chloride solution.

4. The solution is colored purple.

$o\text{-}C_6H_4(OH)COOH + FeCl_3 \longrightarrow [o\text{-}C_6H_4(OH)COO]_3Fe + 3HCl$

The formed complex is stable. When an equal amount of alcohol is added, the color of the complex is preserved.

Experiment 5. Hydrolysis of acetylsalicylic acid (aspirin)

Reagents: aspirin, 1% solution of iron (III) chloride)

Equipment and chemical utensils: test tubes, gas burner, pipette

Getting the job done:

1.Several crystals of acetylsalicylic acid are placed in a dry test tube.

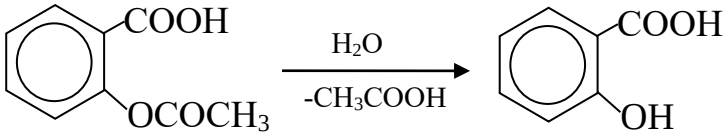
2. Add 5 ml of distilled water.

3. Acetylsalicylic acid dissolves.

4. The solution is divided into two parts.

5. To the first add a few drops of iron (III) chloride. Purple staining is not observed.

6. The second part of the solution is boiled for 5 minutes, acetic acid is detected by the smell.



7. The test tube is cooled and a few drops of iron (III) chloride solution are added.

8. A characteristic purple staining is observed, indicating the presence of phenolic hydroxyl.

There is no free phenolic hydroxyl in acetylsalicylic acid. As an ester, acetylsalicylic acid is easily hydrolyzed when boiled with water, forming salicylic acid, which in turn gives a characteristic staining with iron (III) chloride.

The reaction with iron (III) chloride is used to determine the quality of acetylsalicylic acid. If stored improperly, it can decompose into acetic acid, detectable by opening the flask by smell, and salicylic acid, detectable by iron (III) chloride.

Control questions

1. What compounds are called phenolic acids?

2. What are the main methods of obtaining phenolic acids?

3. Explain the acidic properties of phenolic acids in relation to carboxylic acids and oxy-acids.

4. How do the acidic properties of phenolic acids change in the series of o -, m -, p-oxybenzoic acids?

5. What compounds are formed when phenolic acids are heated?

6. What reactions can be used to prove the presence of a hydroxyl group in phenolic acids?

7. What is the quality reagent for the carboxyl group of phenolic acids?

8. What reactions are characteristic of both the hydroxyl group and the carboxyl group of phenolic acids?

9. What are the derivatives of salicylic acid?

10. What reactions can distinguish salicylic acid from benzoic acid and phenol?

11. What reactions can distinguish salicylic acid from aspirin and salol?

12. What reaction can determine the purity of aspirin?

LESSON №5

Theme: Oxoacids. Reactions confirming the structure of the acetoacetic ether.

The purpose of the lesson: To form knowledge about the reactivity of oxoacids depending on their structure and the ability to plan the synthesis of acids and ketones based on acetoacetic ether.

Objectives: By the end of the lesson, the student should be able to:

1. apply the knowledge of nomenclature, isomerism to the class of oxoacids;

2. write reactions for the production of oxoacids;

3. write the chemical properties of oxoacids as heterobifunctional compounds.

4. explain the keto-enol tautomerism and the factors of stabilization of the enol form of acetoacetic ether;

5. write the reactions characteristic of the keto-and enol forms of acetoacetic ether;

6. plan the synthesis of acids and ketones based on acetoacetic ether.

Basic training questions.

1. Oxoacids-structure, nomenclature.

2. Methods for producing oxoacids.

3. Acidic properties of oxoacids.

4. Chemical properties of oxoacids as heterobifunctional compounds.

5. Specific properties of glyoxalic acid (disproportionation, decarboxylation, decarbonylation reactions, easy oxidability).

6. Decarboxylation of acetoacetic acid at room temperature.

7. Acetoacetic ether.

8. Preparation-Kleisen condensation, mechanism.

9. Keto-enol tautomerism. Reasons for the stabilization of the enol form of acetoacetic ether.

10. Reactions characteristic of the ketone form of acetoacetic ether (interaction with potassium cyanide, sodium hydrosulfite, hydrazine, hydroxylamine, reduction).

11. Reactions characteristic of the enol form of acetoacetic ether (color reaction with iron (III) chloride, enolate formation, bromination, interaction with phosphorus chloride, acylation).

12. Ketonic and acid cleavage of acetoacetic ether.

13. Preparation of carboxylic acids and ketones from acetoacetic ether.

Laboratory work.

Reactions confirming the structure of the acetoacetic ether.

Self-study (performed in preparation for the lesson).

Isomerism, the nomenclature of oxoacids. Syntheses based on acetoacetic ether.

LABORATORY WORK

Experiment 1. Reaction of acetoacetic ether with iron (III) chloride)

Reagents: acetoacetic ether, 1% solution of iron (III) chloride)

Equipment and chemical utensils: test tubes, pipette.

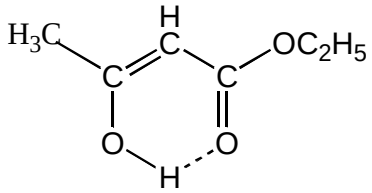
Getting the job done:

1.10 drops of acetoacetic ether are added to the test tube.

2. Add 2 drops of 1% iron chloride solution.

3. The appearance of a red-purple staining is observed, which proves the presence of an enol form of acetoacetic ether.

4. The enol form of acetoacetic ether is stable due to the formation of an intramolecular hydrogen bond:



Experiment 2. Reaction of acetoacetic ether with bromine water

Reagents: acetoacetic ether, bromine water

Equipment and chemical utensils: test tubes.

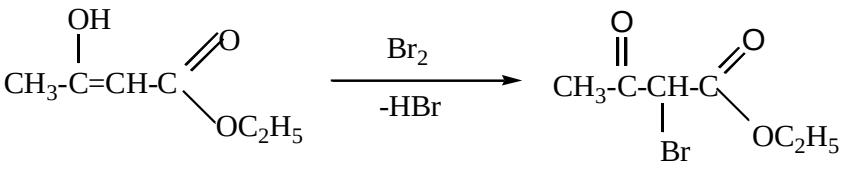
Getting the job done:

1.10 drops of acetoacetic ether are added to the test tube.

2. Add 1 drop of saturated bromine water.

3. Observe the discoloration of bromine water, which occurs with the participation of the enol form.

The addition of bromine leads to the formation of α-bromoacetoacetic ether, which does not contain enol hydroxyl:



Experiment 3. Decomposition of acetoacetic ether

Reagents: acetoacetic ether, 10% solution of sulfuric acid, barite water, solution of iodine in potassium iodide, 10% solution of sodium hydroxide

Equipment and chemical utensils: test tubes, a plug with a gas outlet tube, a gas burner.

Getting the job done:

1.10 drops of acetoacetic ether are added to the test tube.

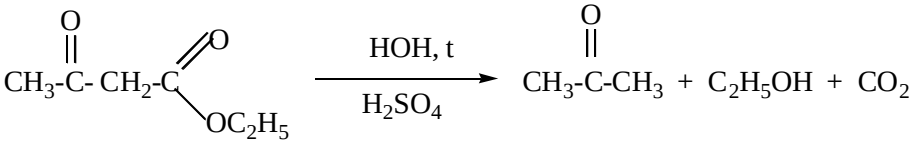
2. Add 1 ml of 10% sulfuric acid solution.

3. The test tube is closed with a stopper with a gas outlet tube.

4. The end of the exhaust pipe is lowered into a test tube with 1 ml of barite water.

5. The reaction mixture is heated.

6. Turbidity of the barite water solution is observed, which indicates the release of carbon monoxide (IV) (decarboxylation).



7. Without stopping heating, the end of the gas outlet tube is lowered into a test tube with 1 ml of a solution of iodine in potassium iodide, previously discolored by the drip addition of a 10% solution of sodium hydroxide.

8. Observe the formation of a light yellow precipitate and feel the specific smell of iodoform, which confirms the formation of acetone and ethanol.

Control questions

1. What compounds are called oxoacids?

2. What are the main methods of obtaining oxoacids?

3. Explain the acidic properties of oxoacids in relation to oxy-acids.

4. What products are formed when heating α - and β-oxoacids?

5. What explains the instability of acetoacetic acid.

6. What reactions can be used to prove the presence of a carbonyl group in oxoacids?

7. What reactions can distinguish glyoxalic acid from other oxoacids?

8. Why does glyoxalic acid, unlike aliphatic aldehydes, form a stable hydrate form?

9. What is the mechanism of the Kleisen condensation reaction?

10. What is the keto-enol tautomerism of acetoacetic ether?

11. Specify the reasons for the stabilization of the enol form of acetoacetic ether.

12. What reactions can be used to prove the presence of the enol form of acetoacetic ether?

13. Under what conditions is ketone and acid cleavage of acetoacetic ether carried out?

14. Explain the scope of application of acetoacetic ether in the synthesis of carboxylic acids and ketones.

Task: 1. Enter the products that are formed when the corresponding compounds interact.

Training«Turntable»

Reagent	Compound		
	glyoxalic acid	pyruvic acid	acetoacetic ether
NaOH (cons.)			
$NaHCO_3$			
CH_3COC1			
C_2H_5OH			
NH_3 (t)			
$FeCl_3$			
PCl_5			
t^0			
Br_2			
Ag_2O (NH_3)			
H_2O (t^0)			

2. Specify the correct sequence of reagents, with which you can get from the acetoacetic ether a) butyric acid and b) pentanone.

“Blitz Survey”

Preparation of butyric acid (a) and pentanone (b) from acetoacetic ether

Reagent	a		b	
	student's answer	correct answer	student's answer	correct answer
C_2H_5OH				
C_2H_5Cl				
CH_3Cl				
t^0, H_2O				
cons. NaOH				
C_2H_5ONa				
H_2O				
t^0				
HC1				

LESSON №6

Theme: Amino acids, amides of acids. Properties of glycocol and urea.

The purpose of the lesson: To form knowledge about the reactivity of amino acids, amides and ureides of acids in relation to their structure, the ability to conduct qualitative reactions to amino acids.

Objectives: By the end of the lesson, the student should be able to:

1. apply the knowledge of nomenclature, isomerism, and stereoisomerism to the class of amino acids;
2. write reactions for obtaining amino acids;
3. write reactions due to the presence of amino-and carboxyl groups;
4. write methods of preparation and chemical properties of amides and ureides of acids;
5. be able to conduct high-quality reactions of amino acids and acid amides.

Basic training questions.

1. Amino Acids-structure, classification, nomenclature.
2. Acid-base properties of amino acids.
3. Reactions of amino acids due to the nucleophilicity of the amino group (alkylation, acylation, reactions with nitric acid, aldehydes, phenylisothiocyanate, chloroform in an alkaline medium).
4. Reactions of amino acids caused by the mutual influence of two functional groups depending on their location (specific reactions of □-, □-, □-amino acids).
5. Comparative characterization of amino acids and carboxylic acid amides-distinctive properties.
6. Carbonic acid amides-preparation, properties.

Laboratory work. Properties of glycocol and urea.

Self-study (performed in preparation for the lesson).

Stereoisomerism and methods for obtaining amino acids. Amides and ureides of carboxylic acids.

LABORATORY WORK

Experiment 1. Formation of a copper complex salt of glycocol

Reagents: 1% glycocol solution, 5% copper sulfate solution, 10% sodium hydroxide solution

Equipment and chemical utensils: test tubes, pipette

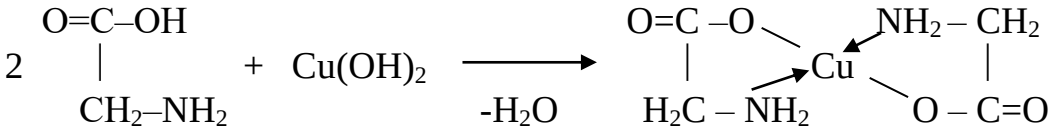
Getting the job done:

1.Pour 1 ml of copper sulfate solution into the test tube.

2. Add an equal volume of 10% sodium hydroxide solution.

3.Pour 1-2 ml of glycocol solution into the resulting solution.

4. The blue precipitate dissolves and a characteristic intense staining of the solution appears.



Glycocol, as a α-amino acid, easily forms a complex cyclic compound with copper, colored in blue. Copper in such intra-complex compounds does not have an ionic character, so there is no precipitation of $Cu(OH)_2$ in the alkaline solution).

Experience 2. Interaction of glycocol with formaldehyde

Reagents: 1% glycocol solution, formalin, 10% sodium hydroxide solution, 1% alcohol solution of phenolphthalein

Equipment and chemical utensils: test tubes, pipette

Getting the job done:

1.Pour 5 ml of 1% glycocol solution into the test tube.

2. Add a drop-by-drop tinted solution of alkali until a non-fading color appears, which happens quite quickly.

3. In another test tube, add the same alkali to the mixture of 1 ml of formalin and 3-4 ml of water also until the color appears.

4. Both colored liquids are mixed and discoloration of the mixture is observed, that is, the appearance of an acid reaction as a result of mixing alkaline solutions.

5. With further gradual addition of the colored alkali solution to the mixture, the color of phenolphthalein continues to disappear.

The glycocol derivative formed due to the amino group already shows pronounced acidic properties. After the addition of formaldehyde, the main properties disappear due to the blocking of the amino group.

Experiment 3. The effect of nitric acid on amino acids

Reagents: 1% glycocol solution, 5% sodium nitrite solution, 8% hydrochloric acid solution

Equipment and chemical utensils: test tubes, pipette

Getting the job done:

1.Pour 1 ml of 5% sodium nitrite solution into the test tube.

2. Add 1 ml of 1% glycocol solution.

3. Add an 8% solution of hydrochloric acid drop by drop (to an acidic medium).

4. When the reaction mixture is shaken, gas bubbles are released:

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

$$NH_2\text{-}CH_2\text{-}COOH + HONO \longrightarrow HO\text{-}CH_2\text{-}COOH + N_2\uparrow + H_2O$$

By determining the amount of nitrogen released, you can find out the number of amino groups in amino acids.

Experience 4. Determination of urea structure

Reagents: urea, barite water, red litmus paper

Equipment and chemical utensils: test tubes, pipette, gas burner

Getting the job done:

1. Urea is placed in a test tube at a height of 5 mm.

2. Carefully, without wetting the top of the test tube, add 10 drops of barite water.

3. The contents of the test tube are heated.

4. Observe the release of gas bubbles and the formation of a white precipitate of barium carbonate.

5. The released vapors turn the red litmus paper blue, which indicates the release of ammonia.

$$H_2NC(O)NH_2 + 2HOH \xrightarrow{t^o} CO_2\uparrow + H_2O + 2NH_3\uparrow$$

$$CO_2 + Ba(OH)_2 \longrightarrow BaCO_3 + H_2O$$

Urea (carbonic acid diamide) is easily hydrolyzed in the presence of acids, alkalis, and water (when boiled) to form ammonia and carbonic acid. The ability of acid amides to easily undergo hydrolysis sharply distinguishes them from amino acids, in which the amino group is strongly bound to the radical and does not hydrolyze.

Experience 5. Decomposition of urea by nitrous acid

Reagents: 1% urea solution, 5% sodium nitrite solution, concentrated sulfuric acid

Equipment and chemical utensils: test tubes, pipette

Getting the job done:

1.Pour 2 ml of urea solution into the test tube.

2. Add an equal volume of sodium nitrite solution and 1 ml of sulfuric acid solution.

3. Shake the contents of the test tube.

4. Observe the rapid release of gas bubbles:

$$NaNO_2 + H_2SO_4 \longrightarrow HNO_2 + Na_2SO_4$$

$$H_2NC(O)NH_2 + 2HONO \longrightarrow CO_2\uparrow + 2N_2 + 3H_2O$$

This reaction is used to quantify urea by measuring the volume of nitrogen released.

Experiment 6. Decomposition of urea when heated (biuret formation)

Reagents: urea, red litmus paper, 10% potassium hydroxide solution, copper sulfate

Equipment and chemical utensils: test tubes, pipette, gas burner

Getting the job done:

1.About 1 g of urea is placed in a dry test tube.

2. The test tube is heated.

3. First, the urea melts.

4. Then there is an abundant release of ammonia, which is detected by the blueness of the red litmus paper.

5. The melt gradually thickens and hardens again, despite the continued heating.

6.A slight white coating settles on the upper cold parts of the test tube.

7. After cooling the test tube, add 1-2 ml of warm water to it, shake and drain the liquid into another test tube.

8. To the resulting biuret solution, add 3-4 drops of alkali (until transparent) and 1 drop of copper sulfate.

9.There is a beautiful characteristic pink-purple coloring.

When heated above the melting point, urea breaks down with the release of ammonia. At 150-160°, 2 urea molecules cleave 1 ammonia molecule and give a biuret that is well soluble in warm water:

$$H_2NCONH_2 + H_2NCONH_2 \longrightarrow NH_3 + H_2NCONHCONH_2$$

Biuret is characterized by the formation of a complex compound in an alkaline solution with copper salts, which has the following composition in a solution of potassium hydroxide: $(H_2NCONHCONH_2)_2 \cdot KOH \cdot Cu(OH)_2$.

Control questions

1. What organic compounds are called amino acids? Their classification.
2. What are the main methods of obtaining amino acids in the laboratory?
3. How will solutions of alanine, lysine, and aspartic acid act on litmus?
4. In what reactions do amino acids exhibit amphoteric properties?
5. What properties are characteristic of amino acids in the carboxyl group?
6. What properties are characteristic of amino acids by amino group?
7. What compounds are formed when heating α-, β -, and γ-amino acids?
8. What is a peptide and a peptide bond?

9. By what chemical reactions can glycine and anthranilic acid be distinguished? Give the corresponding reaction equations.

10. What compounds are called carboxylic acid amides? Their methods of obtaining them.

11. How do the acidic-basic properties in the series of amino acids and amides of carboxylic acids change?

12. What chemical reactions can distinguish between glycine and acetamide? Give the corresponding reaction equations.

13. What qualitative reactions to amino acids do you know?

14. Explain the biological significance of amino acids.

15. What are the amides of carbonic acid called? Bring their structure.

16. What properties are characteristic of urea?

17. Give the reactions of urea cleavage.

18. What compounds are called ureides? Their methods of obtaining them.

Task: Enter the products that are formed when the corresponding compounds interact.

Training "Turntable"

Reagents	Compound		
	Alanine	Acetamide	Urea
HCl			
NaOH			
HNO_2			
CH_3Cl			
CH_3OH			
CH_3COCl			
$CuSO_4$+NaOH			
alanine			
heating			
NaOBr			
HNO_3			
$H_2C=O$			
$CHCl_3$, alcho.NaOH			

LESSON №7

Theme: Heterofunctional acids. Synthesis of acetylsalicylic acid (aspirin).

The purpose of the lesson: To consolidate knowledge about the mechanism of acylation reactions on the example of the synthesis of acetylsalicylic acid and on the

reactivity of heterofunctional acids (oxy -, phenolo -, oxo -, amino acids), amides and ureides of acids in relation to their structure.

Objectives: By the end of the lesson, the student should know:

1. nomenclature, isomerism, and stereoisomerism of heterofunctional acids;
2. methods for obtaining heterofunctional acids;
3. reactions caused by the presence of a carboxyl group;
4. reactions caused by the presence of hydroxyl, oxo - and amino groups;
5. specific reactions of heterofunctional acids;
6. methods of preparation and chemical properties of amides and ureides of acids;
7. acylation reactions, their mechanism;
8. the method of synthesis of acetylsalicylic acid.

Basic training questions.

1. The main chemical utensils used in the synthesis of acetylsalicylic acid, the principles of its assembly.
2. Calculation of the number of initial and received products.
3. The type and mechanism of the ongoing chemical reaction of organic synthesis.
4. The course of synthesis and purification of the raw product.
5. Nomenclature, isomerism, preparation and chemical properties of heterofunctional acids.

Laboratory work. Synthesis of acetylsalicylic acid (aspirin).

Self-study. Students:

1. perform the synthesis of acetylsalicylic acid;
2. draw up a protocol with records of the experiment, observations, and conclusions.
3. pass research papers on the topic: “Heterofunctional acids”;
4. independently answer individual questions.

LABORATORY WORK

Organic synthesis is the production of organic matter of a given composition and structure from simpler compounds.

Before proceeding with organic synthesis, you should carefully study the methodology, prepare reagents, chemical utensils, and assemble the necessary devices. Special attention should be paid to the issues of safe operation.

The resulting compounds contain impurities, after the synthesis is always carried out purification, determine the physical constants of the resulting substance. The

established physical constants are compared with reference data. The results of the experimental work are recorded in the laboratory journal as follows:

1-§._____
job number

2 -§. Synthesis_____
name and structural formula of the synthesized substance

3-§. Literature_____

4 -§: Starting materials_____
name and quantity

5-§. Auxiliary reagents_____
name and quantity

6-§. Basic reaction_____

7-§. Adverse reactions_____

8-§. Calculation of the amount of starting materials and determination of the redundancy factor_____

9-§. Synthesis method_____
a description of the method of synthesis of

10-§is given. Drawing_____
drawing of devices and devices used in the synthesis of

11 -§. Calculation of product yield_____

12-§. Physical constants_____
density, boiling point, temp, solubility

13 -§. Conclusion_____

Synthesis of acetylsalicylic acid (aspirin)

Reagents: salicylic acid, acetic anhydride, concentrated sulfuric acid, toluene, distilled water

Equipment and chemical utensils: round-bottomed flask with a capacity of 100 ml, forstoss, dividing funnel, thermometer, Liebig refrigerator, gas burner, water bath, Buchner funnel, Bunsen flask, glass with a capacity of 250 ml.

Getting the job done:

1. Salicylic acid weighing 3 g is placed in a round-bottomed flask.
2. Then pour 3 ml of acetic anhydride.
3. Add 3 drops of concentrated sulfuric acid.
4. The mixture is slightly heated and stirred.
5. The flask is closed with a reverse refrigerator.
6. The reaction mixture is heated for an hour in a water bath at a temperature of 60ºC.

7. Then the temperature of the bath is increased to 900C and continues heating for another hour.

8. After that, the reaction mass, periodically stirring with a glass rod, is cooled first in air, and then in the crystallizer with cold water and ice.

9. Shiny needle-like crystals fall out.

10. The crystals are filtered out on the Buchner funnel.

11. Wash with ice water, and then with a small amount of toluene.

12. Synthesis yield ≈ 3.5 g.

Description of the final product

Acetylsalicylic acid (aspirin) is a colorless crystalline substance, soluble in ethyl alcohol, diethyl ether, difficult to dissolve in water, tpl=136.5^0 S.

Control questions

1. Name the methods for obtaining acetylsalicylic acid.

2. What is the method of synthesis of acetylsalicylic acid in the laboratory?

3. Dishes used in the synthesis of acetylsalicylic acid and the principles of their assembly.

4. The main reaction of synthesis, its mechanism.

5. What side reactions can occur during the synthesis of acetylsalicylic acid?

6. Write the main and side reactions of the synthesis.

7. What purification methods can be used in the synthesis of acetylsalicylic acid?

8. What are the methods of identification of acetylsalicylic acid?

Task: Answer individual questions.

Individual questions

1. Which of the following oxy-acids are optically active: a) 2-hydroxypropanoic acid, b) 4-hydroxybutanoic acid, c) 2-hydroxy-2-methylpropanoic acid. For an optically active acid, give the reaction reactions with a) NaOH, b) $PC1_5$.

2. Give the reaction of obtaining lactic acid from the corresponding a) halocarboxylic acid, b) aldehyde and write the reaction of its interaction with: 1) $CH_3OH(H^+)$, 2) PCl_5, 3) $(CH_3CO)_2O$, 4) conc. H_2SO_4, t^o.

3. The sequence of reactions that can be obtained from malic acid from succinic acid. Give the stereoisomers of malic acid and write the reactions of its interaction with a) NaOH (H_2O), b) $3(CH_3)_2CHOH$, c) $2PCl_5$, d) HCl.

4. Compare the acidic properties ofα-, β-, γ- oxybutyric acids, give the reactions of their heating, name the resulting compounds.

5. What compounds are formed when the following acids are heated: a) α-hydroxyisobutyric acid, b) β- oxy-α-methylbutyric acid, c) 4-hydroxybutanoic acid. Give the corresponding reaction equations.

6. Obtain 2-hydroxy-2-methylpropanoic acid from aldehyde using HCN, is the resulting acid optically active? Write the reaction reactions of this acid with the following reagents: a) NaOH, b) CH_3OH (H^+), c) $(CH_3CO)_2O$, d) $KMnO_4$ (H^+), e) t^o, H^+.

7. Give the reaction of obtaining 3-oxybutanoic acid from the corresponding halocarboxylic acid and write the reaction of its interaction with: 1) $CH_3OH(H^+)$, 2) PCl_5, 3) $(CH_3CO)_2O$, 4) t^o, conc. H_2SO_4, 5) Na, 6) NaOH (H_2O).

8. Give the sequence of reactions for obtaining salicylic acid from phenol and write the reactions of its interaction with: a) Br_2, b) CH_3COCl, c) $NaHCO_3$, d) CH_3OH, e) PCl_5.

9. According to the Kolbe method, get salicylic acid. Give the synthesis reactions from salicylic acid a) acetylsalicylic acid, b) phenylsalicylate. With the help of which reactions it is possible to distinguish the obtained compounds from salicylic acid, give the corresponding reaction equations.

10. Compare the acidic properties of salicylic acid with its para-and meta-isomers. Write a scheme of qualitative reactions that allow you to distinguish salicylic acid from a) phenol, b) benzoic acid, c) acetylsalicylic acid, d) phenylsalicylate.

11. Give a scheme for obtaining salicylic acid by the Kolbe method and write the reactions of its interaction with the following reagents: a) Br_2, b) CH_3COCl, c) $NaHCO_3$, d) CH_3OH, e) PCl_5.

12. Give the reaction for producing glyoxalic acid from the corresponding alcohol, and write the reaction of her interactions with: 1) $Ag_2O(NH_3)$, 2) $NaHSO_3$, 3) KOH (60%), 4) CH_3OH, 5) HCN, 6) $C_6H_5NH\text{-}NH_2$.

13. Give 3 method for producing pyruvic acid reaction and write its interaction with the following reagents: a) $NaHSO_3$, b) $NH_2\text{-}NH_2$, c) NH_2OH, g) $NaHCO_3$, d) PCl_5.

14. Keto-enol tautomerism of acetoacetic ether. Write the reactions of its interaction with a) $NaHSO_3$, b) bromine water, c) HCN, d) Na, e) CH_3COCl, k) $PC1_5$, l) $FeCl_3$, m) Na.

15. Write the structural formulas of the following esters: methylacetoacetic, diethylacetoacetic, methylisopropylacetoacetic. Which of the above compounds can be represented in the keto-enol form? Write the equations of chemical reactions that prove the presence of the enol form of the ether.

16. Write the structural formulas of the following acids, name them according to the international nomenclature: a) pyruvic acid, b) β-ketopropionic acid. Explain their

relation to a) heating and b) oxidation by the corresponding reaction equations. Write the reaction of pyruvic acid with 1) sodium hydrosulfite, 2) phenylhydrazine.

17. By what sequence of reactions can acetoacetic ether be obtained from acetic acid? Give the corresponding equations and write the reactions of the interaction of acetoacetic ether with the following reagents: a) Na, b) Br_2, c) CH_3COC1.

18. Write the structural formulas of the following acids and name them according to the rational nomenclature: a) 2-aminopropanoic acid, b) 2-amino-2-methylpropanoic acid, c) 4-aminobutanoic acid, d) 2-amino-3-methylbutanoic acid. Specify the acids that have optical isomers, and give their projection formulas. Define the concepts "enantiomer, diastereomer, racemate".

19. Obtain 2-amino-3-methylpropanoic acid from the corresponding halic acid. Is the resulting amino acid an optically active compound? Write the reactions of its interaction with the following reagents: a) $NaHCO_3$, b) HONO, c) CH_3COCl, d) PCl_5.

20. Give all possible isomers of 3-aminobutanoic acid, name them according to rational and international nomenclature. What reaction can distinguish 2-, 3 -, 4-aminobutanoic acids from each other? Give the corresponding reaction equations.

21. Get 2-aminopropanoic acid from the corresponding halocarboxylic acid, give its stereoisomers. Write the reaction of its interaction with the following reagents: a) $CuSO_4$+NaOH, b) HNO_2, c) $(CH_3CO)_2O$, d) t^o, e) $CHCl_3$, NaOH (alcohol).

22. Which of the above amino acids is optically active? A) 2-aminopropane, b) 4-aminobutane, c) 2-amino-2-methylpropane. Write the reaction of the optically active acid with a) $Cu(OH)_2$, b) CH_2O, c) HCl, d) HNO_2.

23. Give the formula of the intramolecular salt of 2-amino-3-methylbutanoic acid and write the reaction of its interaction with the following reagents: a) $Cu(OH)_2$, b) CH_2O, c) $NaNO_2$+HCl, d) t^o, e) alanine.

24. Amphoteric properties of amino acids: write the reaction equations of the interaction of α - aminobutyric acid with a) NaOH (H_2O), b) HCl, c) $(CH_3CO)_2O$, d) CH_3I, e) ($NaNO_2$+HCl).

25. Urea (urea) – preparation. Write the reactions of its interaction with the following reagents: a) HONO, b) NaOBr, c) HNO_3, d) t^o, e) CH_3Cl.

26. Give the methods of obtaining acetamide and write the reaction of its interaction with a) NaOBr, b) HNO_2, c) HNO_3.

LESSON №8

Theme: Five-membered heterocyclic compounds with one heteroatom. Preparation of furan, pyrrole, furfural, properties of furfural.

The purpose of the lesson: To form knowledge about the laws and features of the chemical behavior of five-membered heterocyclic compounds with one heteroatom in relation to their structure.

Objectives: By the end of the lesson, the student should be able to:

1. name heterocyclic compounds according to the international nomenclature;
2. write reactions for the production of five-membered heterocyclic compounds;
3. explain the electronic structure of five-membered heterocyclic compounds;
4. compare the acid-base properties of the studied compounds;
5. to compare the reactivity of five-membered heterocyclic compounds in electrophilic substitution reactions;
6. conduct qualitative reactions to pyrrole, furan and thiophene and their derivatives;
7. show the use of five-membered heterocyclic compounds for the synthesis of medicinal substances.

Basic training questions.

1. Heterocyclic compounds-classification, nomenclature.
2. Five-membered heterocyclic compounds with one heteroatom: furan, pyrrole, thiophene.
3. Methods for producing five-membered heterocyclic compounds with a single heteroatom: cyclocondensation of 1,4-dicarbonyl compounds, mutual transformations of five-membered heterocyclic compounds (Yuryev cycle), obtaining furfural from pentosanes, obtaining furan by decarbonylation of furfural in the presence of zinc and manganese chromites.
4. Electronic structure of furan, pyrrole, and thiophene.
5. Aromaticity. π-redundant systems. Comparison of the reactivity of pyrrole, furan, and thiophene in electrophilic substitution reactions.
6. Acid-base properties. Acidic properties of pyrrole, comparison with aliphatic amines.
7. Acidophobia of pyrrole and furan. Absence of acidophobic properties in the presence of electron-acceptor substituents in the pyrrole and furan nuclei. The absence of acidophobia in thiophene.
8. Features of the electrophilic substitution reactions of pyrrole, furan and thiophene, related to the nature of the heteroatom. Reactions of halogenation, nitration, sulfonation, their conditions. The reaction of the azo combination of pyrrole.
9. Hydrogenation. Hydrogenation of pyrrole with hydrogen at the time of isolation.
10. Diene synthesis reaction: interaction of furan with maleic anhydride.

11. Furfural. Reactions of nucleophilic addition, addition-cleavage, oxidation, reduction, croton condensation with ethyl acetate. No acidophobia. Electrophilic substitution reactions. Preparation of furacillin.

Laboratory work. Preparation of furan, pyrrole, furfural, properties of furfural.

Self-study (performed in preparation for the lesson).

Indole and its derivatives.

LABORATORY WORK

Experience 1. Obtaining and detecting furan

Reagents: slime acid, concentrated hydrochloric acid, pine splinter

Equipment and chemical utensils: test tubes, gas burner, tripod, pipette

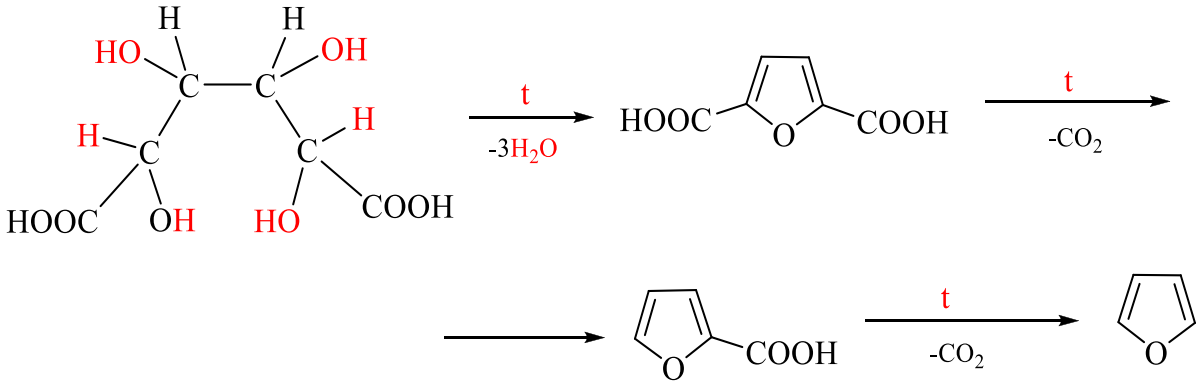
Getting the job done:

1.About 0,5 g of slime acid is placed in a dry test tube.

2. Heat the test tube with slime acid until decomposition.

3. Furan vapors released during the decomposition of slime acid are detected using a pine splinter moistened with concentrated hydrochloric acid.

4. In the furan pairs, the pine splinter is colored green.



Experience 2. Obtaining and detecting pyrrole

Reagents: slime acid, concentrated ammonia solution, glycerin, concentrated hydrochloric acid

Equipment and chemical utensils: test tubes, tripod, gas burner, pipette

Getting the job done:

1.About 0,5 g of slime acid is placed in a dry test tube.

2. Add 1 ml of concentrated ammonia solution.

3. Then pour 0,5 ml of glycerin.

4. The test tube with the reaction mixture is fixed almost horizontally in the tripod holder.

5. Carefully warm up the lower part of the test tube in the flame of the burner.

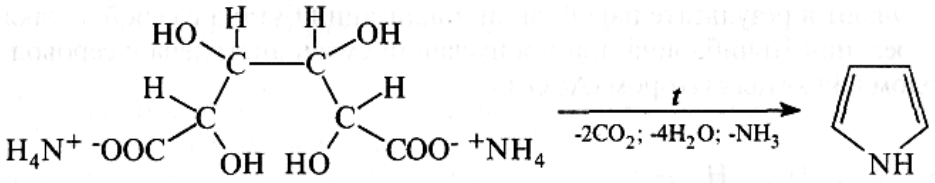
6. First, water vapor is released, then the mixture foams.

7. The resulting volatile products have an unpleasant specific smell.

8. Continuing heating, a pine splinter moistened with concentrated hydrochloric acid is introduced into the test tube.

9. The released pyrrole vapors paint the splinter in a bright red color.

$$HOOC\text{-}(CHOH)_4\text{-}COOH + 2NH_3 \longrightarrow H_4NOOC\text{-}(CHOH)_4\text{-}COONH_4$$



Experience 3. Obtaining furfural from pentosans

Reagents: sawdust, 1% solution of iron (III) chloride, concentrated hydrochloric acid

Equipment and chemical utensils: test tubes, pipette, gas burner, water bath, filter paper moistened with a mixture of aniline and glacial acetic acid (1:1)

Performance of the work:

1.About 1 g of vegetable raw materials (sawdust, bran, sunflower husk or crushed corn cobs) are placed in a test tube.

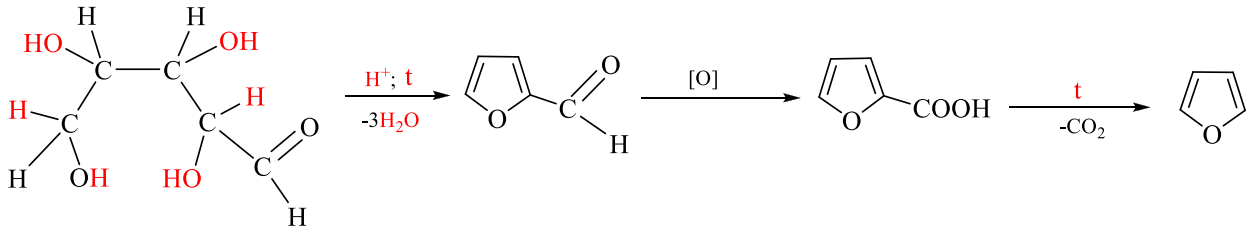
2. Add 2 ml of concentrated hydrochloric acid.

3. Then pour 2 ml of water and 2-3 drops of 1% solution of iron (III) chloride.

4. The test tube with the reaction mass is placed in a water bath and h6 is heated.

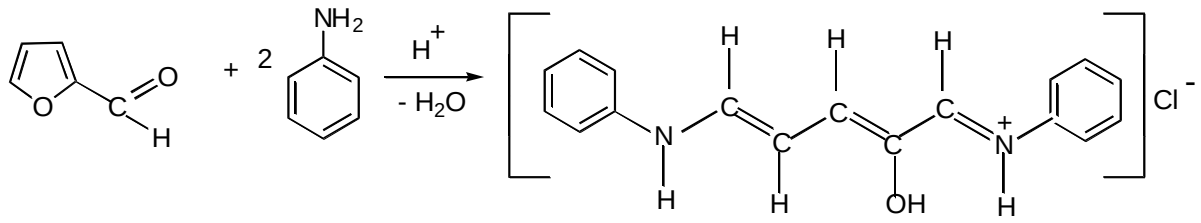
5. Vegetable raw materials contain polysaccharides-pentosans of the general formula $(C_5H_8O_4)$ n, which, when heated in an acidic medium, hydrolyze to form pentoses of the composition $C_5H_{10}O_5$, more often aldopentoses-xylose and arabinose.

The resulting aldopentoses undergo intramolecular dehydration to form furfural:



6. To detect furfural, a strip of filter paper moistened with a mixture of aniline and glacial acetic acid (1:1) is lowered into the test tube.

7. In the vapors of the released furfural, the strip of filter paper turns pink-red, which is explained by the formation of the product of condensation of furfural with aniline, accompanied by the opening of the furan cycle.



Control questions

1. What organic compounds are called heterocyclic? Their classification and nomenclature.

2. What is the aromaticity of heterocyclic compounds?

3. Explain the π-redundancy of five-membered heterocyclic compounds.

4. Give general and specific methods for the production of pyrrole, furan and thiophene.

5. What are the chemical properties of pyrrole, furan and thiophene?

6. What is the comparative reactivity of pyrrole, furan and thiophene in electrophilic substitution reactions? Explain the reasons.

7. What is acidophobia, for which compounds is it characteristic?

8. How do the acidophobic properties of pyrrole, furan affect their ability to undergo electrophilic substitution reactions – nitration and sulfonation?

9. Explain the acidic properties of pyrrole and give reactions confirming the acidic properties of pyrrole.

10. How does the aldehyde group in furfural affect the acidophobia of the furan ring? Explain the reasons.

11. What reactions are characteristic of furfural?

12. By what sequence of reactions can furfural be obtained from furacilin?

13. What are the main derivatives of furan, pyrrole and thiophene used as medicines?

Task: To conduct a comparative characterization of five-membered heterocyclic compounds with one heteroatom.

Technique "Cinquain"

Option 1

Representatives	Structure	The main common feature	The main difference
Pyrrol			
Thiophene			

Option 2

Representatives	Structure	The main common feature	The main difference
Furan			
Thiophene			

LESSON №9

Theme: Five-membered heterocyclic compounds with two heteroatoms. Qualitative reactions of antipyrine, amidopyrine, and analgin.

The purpose of the lesson: To form knowledge about the laws and features of the chemical behavior of five-membered heterocyclic compounds with two heteroatoms in relation to their structure.

Objectives: By the end of the lesson, the student should be able to:

1. write reactions for the production of five-membered heterocyclic compounds with two heteroatoms;
2. explain the electronic structure of five-membered heterocyclic compounds with two heteroatoms;
3. compare the acid-base properties of the studied compounds;
4. to compare the reactivity of five-membered heterocyclic compounds with two heteroatoms in electrophilic substitution reactions;
5. conduct qualitative reactions to antipyrine, amidopyrine, analgin;
6. show the use of five-membered heterocyclic compounds with two heteroatoms for the synthesis of medicinal substances.

Basic training questions.

1. Nomenclature of five-membered heterocyclic compounds with two heteroatoms (azoles).
2. Preparation of azoles: imidazole from glyoxal, formaldehyde and ammonia, pyrazole from diazomethane and acetylene, pyrazole homologues from 1,3-diketones and hydrazine.
3. Electronic structure of pyrazole, imidazole. The structure of pyrrole and pyridine nitrogen, their contribution to the formation of a sextet of π-electrons.
4. Aromaticity and π-excess of azoles.
5. Acid-base properties of azoles. Comparison of the main properties of imidazole and pyrazole. No acidophobia. Associates of imidazole and pyrazole.
6. Azoles as nucleophiles. The alkylation reaction.

7. Reactivity of azoles in electrophilic substitution reactions, comparison with five-membered heterocycles with one heteroatom. Reactions of halogenation, nitration, and sulfonation at position 4.

8. Pyrazolone-5, tautomeric transformations. Pyrazolone-5 derivatives as medicinal products. Preparation of 3-methyl-1-phenylpyrazolone-5 from acetoacetic ether and phenylhydrazine. Preparation of antipyrine. Preparation of amidopyrine from antipyrine. Qualitative reactions.

9. Histidine, histamine. Comparison of acid-base properties.

Laboratory work. Qualitative reactions of antipyrine, amidopyrine, and analgin.

Self-study (performed in preparation for the lesson).

Pyrazolone-5 and its derivatives: antipyrine, amidopyrine, analgin. Benzimidazole.

LABORATORY WORK

Experience 1. Qualitative reactions to antipyrine

Reagents: antipyrine, 1% solution of iron (III) chloride, 10% solution of sodium nitrite, dilute sulfuric acid

Equipment and chemical utensils: test tubes, pipette

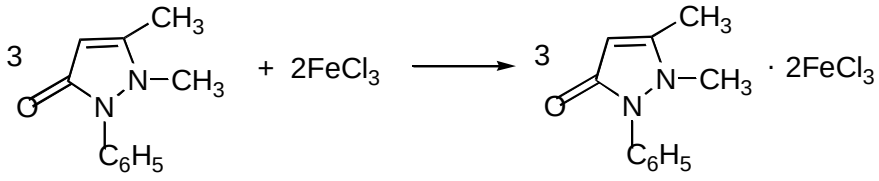
Getting the job done:

1.In two test tubes, several crystals of antipyrine are dissolved in 4 drops of water.

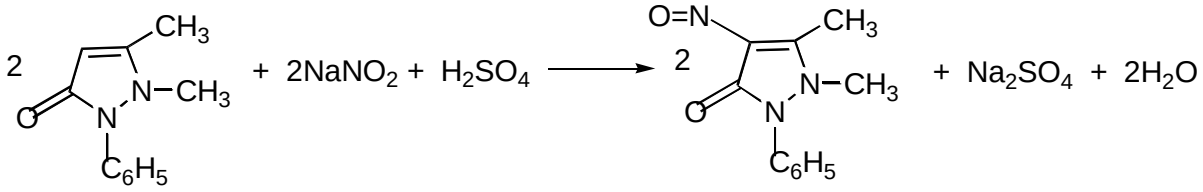
2.Add 1 drop of 1% iron (III) chloride solution to one test tube.

3. In the second test tube, add 1 drop of 10% sodium nitrite solution and 3 drops of dilute sulfuric acid.

4. In the first test tube, the appearance of an intense orange color is observed, due to the formation of a complex compound – ferropyrin.



5. In the second test tube, an emerald-green staining is observed due to the formation of 4-nitrozoantipyrin:



Experience 2. Qualitative reactions to amidopyrine

Reagents: amidopyrine, 1% solution of iron (III) chloride, dilute hydrochloric acid, freshly prepared solution of potassium hexacyanoferrate (III)

Equipment and chemical utensils: test tubes, pipette

Getting the job done:

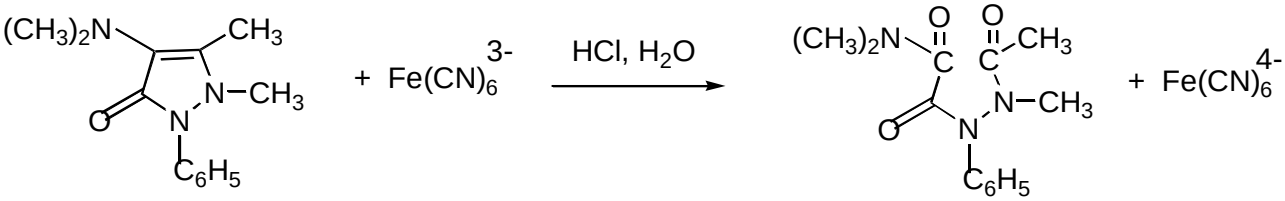
1.In two test tubes, several crystals of amidopyrine are dissolved in 4 drops of water.

2. Add 1 drop of 1% iron (III) chloride solution to one tube.

3.Add 10 drops of freshly prepared potassium hexacyanoferrate (III) solution and 1 drop of 1% iron (III) chloride solution to the second tube.

4. In the first test tube, a blue, rapidly disappearing color appears, 3 more drops of 1% iron (III) chloride solution are added to the test tube – a flaky brown precipitate is formed. Upon subsequent acidification of the contents of the test tube with 2 drops of dilute hydrochloric acid, the precipitate dissolves, and the solution acquires a non-disappearing intense blue-violet color (a distinctive reaction of amidopyrine from analgin).

5. In the second test tube, the appearance of a dark blue staining of the solution due to the formation of Prussian blue (a distinctive reaction of amidopyrine from antipyrine) is observed.



$$3Fe(CN)_6 + 4Fe^{3+} \longrightarrow Fe_4[Fe(CN)_6]_3$$

Experience 3. Qualitative reactions to analgin

Reagents: analgin, 1% solution of iron (III) chloride, 10% solution of hydrochloric acid

Equipment and chemical utensils: test tubes, pipette, water bath, gas burner

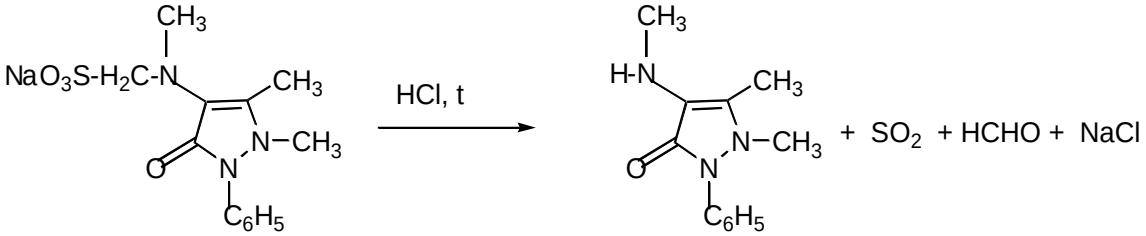
Getting the job done:

1. In two test tubes, several analgin crystals are dissolved in 4 drops of water.

2. In one test tube, add 1 drop of 1% solution of iron (III) chloride, in the second-4 drops of 10% solution of hydrochloric acid.

3. In the first test tube, the appearance of a dark blue staining is observed, turning into a dark green, and then into yellow.

4. In the second tube when heated for 2 minutes in a water bath feel the sharp smell of sulfur oxide (IV) and formaldehyde:



5. Then in the test tube to the cooled solution was added to 2 drops of 1% ferric chloride (III).

6. See the gradual appearance of a yellow-red color (for distinctive reaction of dipyrone from other drugs of the group of pyrazolones-5)

Control questions

1. What organic compounds are called five-membered heterocyclic compounds with two heteroatoms? Their classification and nomenclature.

2. Explain the aromaticity of heterocyclic compounds with two heteroatoms.

3. Explain the types of nitrogen in pyrazole, their effect on the acid-base properties of heterocycles.

4. Give the methods for obtaining pyrazole and imidazole.

5. What are the chemical properties characteristic of pyrazole?

6. What is the comparative reactivity of pyrrole and pyrazole in electrophilic substitution reactions? Explain the reasons.

7. Is acidophobia characteristic of five-membered heterocyclic compounds with two heteroatoms?

8. Explain the acid-base properties of pyrazole and imidazole. Give a method for obtaining antipyrine and amidopyrine. By what reactions can they be distinguished from each other?

9. Explain the azole tautomerism in pyrazole?

10. What tautomeric forms are characteristic of pyrazolone-5?

LESSON №10

Theme: Nitrogen-containing six-membered heterocyclic compounds with one heteroatom. Properties of pyridine and quinoline.

The purpose of the lesson: To form knowledge about the laws and features of the chemical behavior of six-membered heterocyclic compounds with one heteroatom in relation to their structure.

Objectives: By the end of the lesson, the student should be able to:

1. explain the electronic structure of six-membered heterocyclic compounds with one heteroatom.

2. write reactions for the production of six-membered heterocyclic compounds with one heteroatom;

3. compare the acid-base properties of the studied compounds;

4. to compare the reactivity of six-membered heterocyclic compounds with one heteroatom in electrophilic and nucleophilic substitution reactions;

5. show the use of six-membered heterocyclic compounds for the synthesis of medicinal substances.

Basic training questions.

1. Six-membered heterocyclic compounds with one heteroatom: pyridine, quinoline, isoquinoline.

2. Classification, nomenclature.

3. Methods of preparation: pyridine (by condensation of acetylene with prussic acid), α-picoline (by condensation of acrolein with ammonia), quinoline (by Scraup synthesis).

4. Electronic structure of pyridine, quinoline. Aromaticity. π- insufficient systems.

5. Reactions of pyridine and quinoline as tertiary amines: basic properties (formation of salts), nucleophilic properties (interaction with alkyl halides), interaction with sulfotrioxide.

6. Comparison of the reactivity of pyridine and quinoline in electrophilic substitution reactions (nitration, sulfonation, halogenation).

7. Comparison of the reactivity of pyridine and quinoline in the reactions of nucleophilic substitution (hydroxylation, amination).

8. Attachment reactions. Hydrogenation of pyridine and quinoline.

9. Oxidation of quinoline.

10. Pyridine homologs-picolines. Oxidation.

11. Preparation of medicinal substances: vitamin PP, cordiamine, isoniazid, phytyvazyd, oxin, 5-NHQ.

Laboratory work. Properties of pyridine and quinoline.

Self-study (performed in preparation for the lesson).

Methods for the preparation of six-membered heterocyclic compounds. Pyridine-N-oxide.

LABORATORY WORK

Experience 1. Interaction of pyridine with iron (III) chloride

Reagents: water solution of pyridine, 1% solution of iron (III) chloride)

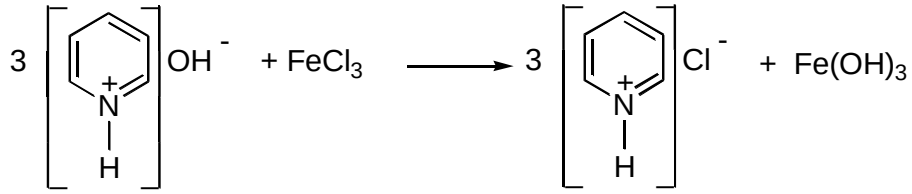
Equipment and chemical utensils: test tubes, pipette

Getting the job done:

1.1 ml of an aqueous solution of pyridine is placed in a test tube.

2. Pour 0,5 ml of 1% iron (III) chloride solution.

3. The formation of a brown-brown precipitate of iron (III) hydroxide is observed):



Experience 2. The effect of oxidizing agents on pyridine

Reagents: water solution of pyridine, 1% solution of potassium permanganate, 10% solution of sodium carbonate

Equipment and chemical utensils: test tubes, pipette, gas burner

Getting the job done:

1.A mixture of equal amounts of an aqueous solution of pyridine, 1% solution of potassium permanganate and 10% solution of sodium carbonate is placed in a test tube.

2. Shake the mixture thoroughly.

3. The discoloration of the potassium permanganate solution is not observed, the color of the solution does not disappear when the mixture is heated to a boil. Pyridine is resistant to oxidizing agents.

Experience 3. Interaction of pyridine with picric acid

Reagents: water solution of pyridine, saturated water solution of picric acid

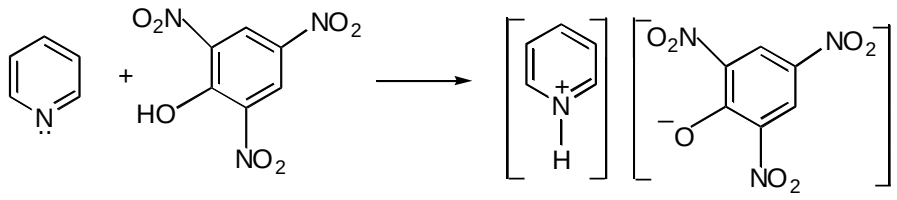
Equipment and chemical utensils: test tubes, pipette

Getting the job done:

1.1 drop of an aqueous solution of pyridine is placed in a test tube.

2. Add 2 drops of a saturated aqueous solution of picric acid.

3. The contents of the test tube are shaken and the formation of yellow needle-like crystals of pyridinium picrate is observed:



The resulting crystalline salt precipitate is soluble in an excess of pyridine.

Control questions

1. What organic compounds are called six-membered heterocyclic compounds with one heteroatom? Their classification and nomenclature.
2. Explain the aromaticity of six-membered heterocyclic compounds with one heteroatom.
3. Explain the type of nitrogen in pyridine, the acid-base properties of pyridine.
4. Give the methods for obtaining pyridine, picoline and pyridine carbonic acids.
5. What are the chemical properties characteristic of pyridine and quinoline?
6. What is the comparative reactivity of pyridine and quinoline in electrophilic and nucleophilic substitution reactions? Explain the reasons.
7. What are the main derivatives of pyrazole and imidazole used as medicines?

Task: To analyze the situational problem ("Case study").

Case " Unknown substance»

The content of the case. The first written description of this substance was made by the Scottish chemist Thomas Andersen in 1851. He discovered it when examining bone oil obtained by dry distillation of non-fat bones, among other substances, a colorless liquid with an unpleasant smell was obtained.

Questions. What substance was discovered by the Scottish chemist Thomas Andersen in 1851 in the study of bone oil?

What binds this substance to benzene? What is its structure?

What properties are characteristic of this substance?

Is it possible to obtain this substance by synthetic methods? Write the reaction equations.

Is it possible to use this substance as a starting reagent for the synthesis of drugs? If so, what kind of ones?

Name the important derivatives of this substance.

Additional information.

In 1869, Koerner, in a private letter to Cannizzaro, suggested that this substance could be considered as benzene containing a heteroate.

Problem	Solution	Result

2. Fill in the conceptual table.

Comparison features	Cyclic compounds and their characteristics		
	benzene	pyridine	quinoline
Structure, aromaticity, π-insufficiency			
Basic properties			
Alkylation and acylation			
Electrophilic substitution			
Nucleophilic substitution			
Oxidation			

LESSON №11

Theme: Nitrogen-containing six-membered heterocyclic compounds with two heteroatoms and condensed heterocyclic compounds. Properties of barbiturates and uric acid.

The purpose of the lesson: To form knowledge about the laws and features of the chemical behavior of six-membered heterocyclic compounds with two heteroatoms and condensed heterocyclic compounds in relation to their structure.

Objectives: By the end of the lesson, the student should be able to:

1. explain the electronic structure of six-membered heterocyclic compounds with two heteroatoms and condensed heterocyclic compounds.
2. write reactions for the production of six-membered heterocyclic compounds with two heteroatoms;
3. compare the acid-base properties of the studied compounds;
4. to compare the reactivity of six-membered heterocyclic compounds with two heteroatoms in electrophilic and nucleophilic substitution reactions;
5. show the use of six-membered and condensed heterocyclic compounds for the synthesis of medicinal substances.

Basic training questions.

1. Six-membered heterocyclic compounds with two heteroatoms-classification, nomenclature.
2. Electronic structure of pyridazine, pyrimidine, and pyrazine. π-insufficient aromatic systems.
3. Comparison of the reactivity in the reactions of electrophilic and nucleophilic substitution of diazines with benzene and pyridine.

4. Reactions of diazines as tertiary amines: basic properties (salt formation), nucleophilic properties (interaction with alkyl halides).

5. Reduction reactions of diazines.

6. Pyrimidine hydroxy derivatives: uracil, thymine, cytosine, barbituric acid.

7. Preparation of barbituric acid and barbiturates.

8. Tautomeric transformations of uracil, thymine, cytosine, and barbituric acid: lactim-lactam and keto-enol tautomerism.

9. Condensed heterocyclic compounds-purine, numbering, electronic structure, aromaticity.

10. Prototropic tautomerism of purine.

11. Hydroxy derivatives of purine: hypoxanthine, xanthine, uric acid.

12. Lactim-lactam tautomerism of purine hydroxy derivatives.

13. Acid-base properties of purine hydroxy derivatives.

14. Qualitative reaction of purine compounds (murexide reaction).

15. N-Methyl Derivatives of xanthine: theophylline, theobromine, caffeine. Tautomeric forms. Acid-base properties.

16. Aminopurines: adenine (6-aminopurine), guanine (2-amino-6-hydroxypurine). Tautomeric transformations. The action of nitrogenous acid.

Laboratory work. Properties of barbiturates and uric acid.

Self-study (performed in preparation for the lesson).

Barbituric acid and drugs based on it.

LABORATORY WORK

Experiment 1. Fusion of barbituric acid derivatives with sodium hydroxide

Reagents: barbital (5,5-diethylbarbituric acid), crystalline sodium hydroxide, dilute sulfuric acid

Equipment and chemical utensils: mortar, spatula, litmus paper, pipette

Getting the job done:

Experience working in a fume hood!

1.Place a spatula of barbital in the mortar.

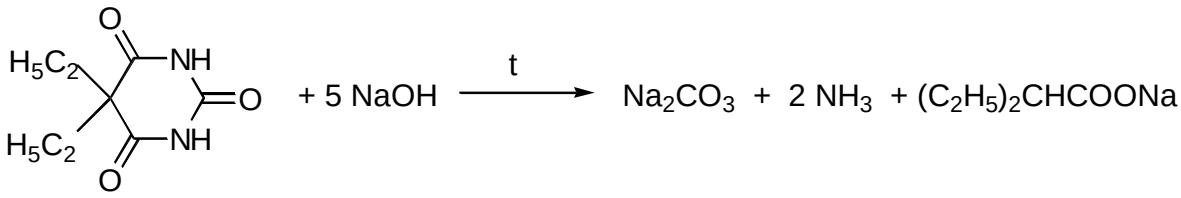
2. Add double the amount of crystalline sodium hydroxide.

3. The mixture is thoroughly ground.

4. Transfer to the crucible and fuse.

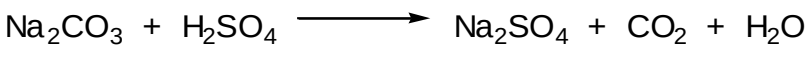
5. Feel the characteristic smell of ammonia.

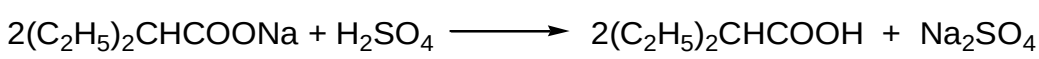
6. The released ammonia vapors turn the red litmus paper moistened with water blue:



7. The resulting alloy is dissolved in water and acidified with dilute sulfuric acid.

8. Observe the release of carbon monoxide (IV) gas bubbles and smell rancid oil (free diethylacetic acid):





This reaction confirms the structure of barbituric acid derivatives as cyclic ureides, which, when fused with crystalline sodium hydroxide, undergo cleavage.

Experience 2. Interaction of barbiturates with sodium hydroxide solution

Reagents: barbital, 10% sodium hydroxide solution

Equipment and chemical utensils: spatula, test tubes, pipette

Getting the job done:

1.Place the barbital in the test tube at the tip of the spatula.

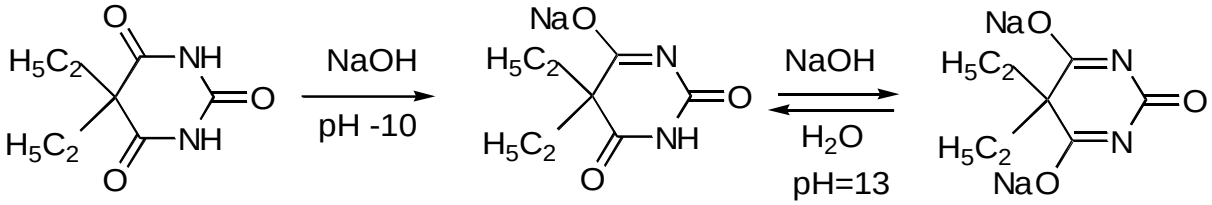
2. Add 1 ml of water.

3. Shake the contents of the test tube.

4.1 ml of 10% sodium hydroxide solution is added to the resulting suspension.

5. The solution becomes transparent, which is due to the formation of water-soluble mono -, disodium salts of 5,5-diethylbarbituric acid.

The disodium salt of 5,5-diethylbarbituric acid is hydrolyzed in an aqueous solution. The equilibrium in the reaction is shifted towards the formation of the monosodium salt of 5,5-diethylbarbituric acid:



Experience 3. Interaction of barbiturates with silver nitrate

Reagents: barbital, 10% sodium hydroxide solution, 2% silver nitrate solution

Equipment and chemical utensils: spatula, test tubes, pipette

Getting the job done:

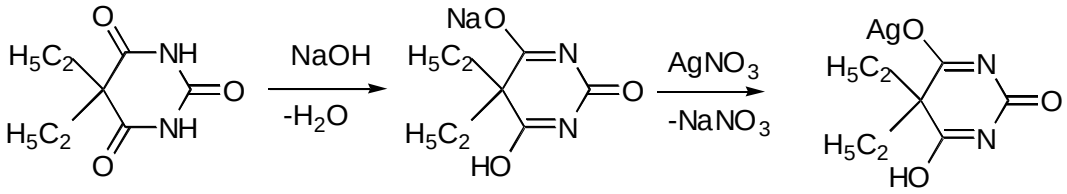
1.Place the barbital in the test tube at the tip of the spatula.

2. Add 2 ml of 10% sodium hydroxide solution.

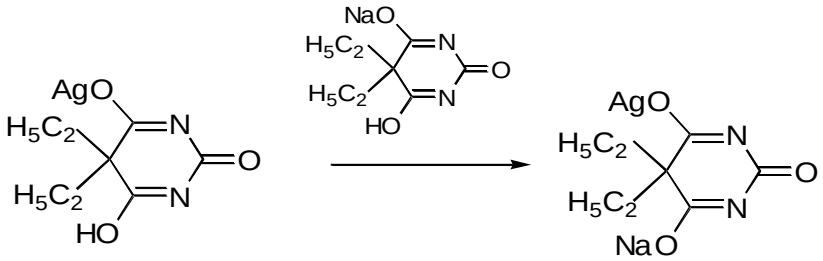
3. The mixture is vigorously shaken and filtered.

4. A 2% solution of silver nitrate is added to the resulting filtrate drop by drop.

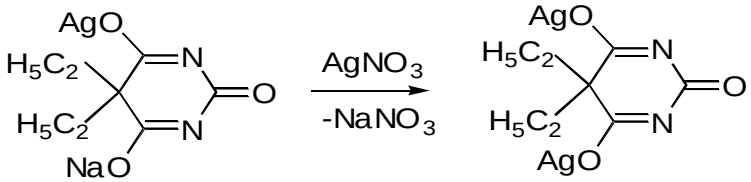
5. Observe the formation of a white precipitate of monosilver salt of barbital, which disappears when the solution is shaken:



Dissolution odnosemjannyj silver salt of Barbital due to the presence in the solution of monosodium salts and formation of soluble silver-sodium salt of Barbital:



Subsequent addition of 2% aqueous solution of silver nitrate observe the release of a white precipitate decerebrados salt of Barbital, which persisted in shaking:



This reaction is intra-group and allows you to confirm the authenticity of drugs derived from barbituric acid.

Experiment 4. Solubility of uric acid and its salts in water

Reagents: uric acid, 10% sodium hydroxide solution, saturated ammonium chloride solution

Equipment and chemical utensils: spatula, test tubes, pipette

Getting the job done:

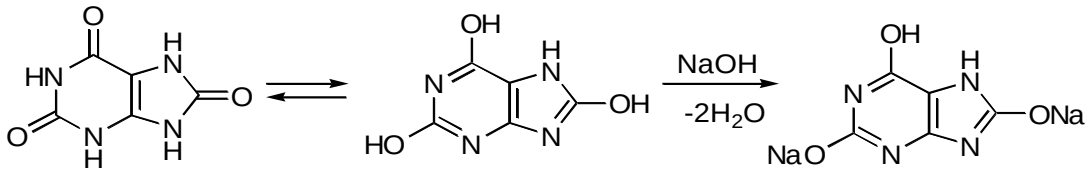
1.Uric acid is placed on the tip of the spatula in a test tube.

2.Add water drop by drop when shaking.

3. After adding 10 drops of water, poor solubility of uric acid is noted.

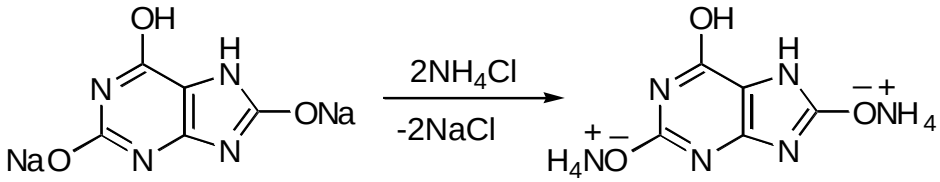
4.Add 1 drop of 10% sodium hydroxide solution to the resulting suspension.

5. The solution becomes transparent due to the formation of the disodium salt of uric acid, which is highly soluble in water:



6.Add 1 drop of saturated ammonium chloride solution to the resulting solution.

7. Observe the formation of a white precipitate of the diammonium salt of uric acid-ammonium urate:



Experiment 5. Murexide reaction

Reagents: uric acid, concentrated nitric acid, 10% ammonia solution

Equipment and chemical utensils: porcelain cup, spatula, gas burner, pipette

Getting the job done:

The experiment is performed in a fume hood!

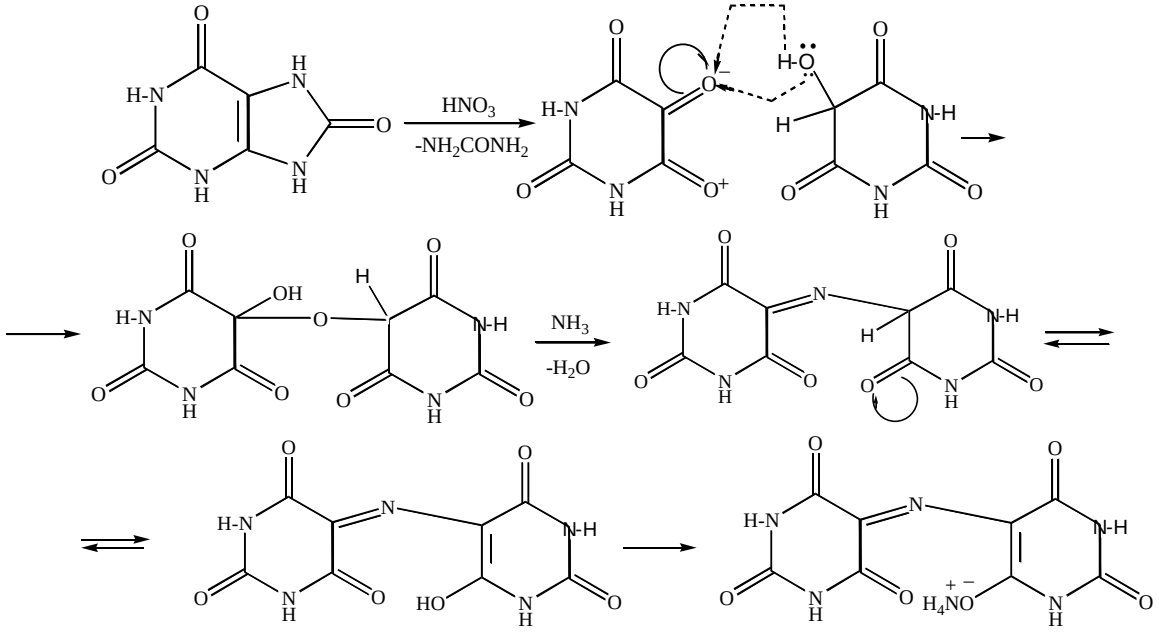
1. Place a few uric acid crystals in a porcelain cup.

2. Add 3-4 drops of concentrated nitric acid.

3. The resulting mixture is carefully evaporated over the flame of the burner to dry.

4. The resulting pink-red residue after cooling is moistened with 1-2 drops of 10% ammonia solution.

5. Observe the appearance of a purplish-purple color.



The murexide reaction is a group-wide reaction to purine and its derivatives.

Control questions

1. What organic compounds are called six-membered heterocyclic compounds with two heteroatoms?
2. Explain the aromaticity of six-membered heterocyclic compounds with two heteroatoms.
3. Describe the electronic structure of pyridazine, pyrimidine and pyrazine. Explain why these compounds, despite having two main centers, form salts with only one acid equivalent.
4. Write the methods for obtaining pyrimidine, pyridazine, pyrazine.
5. Compare the reactivity of pyrimidine and pyridine in electrophilic and nucleophilic substitution reactions.
6. What types of tautomerism are characteristic of barbituric acid?
7. What drugs are barbituric acid derivatives?
8. What heterocyclic compounds are called condensed?
9. Explain the numbering in the purine molecule.
10. Explain the types of nitrogen in the purine molecule.
11. What chemical properties are characteristic of purine?
12. Give the structure of the hydroxy derivatives of purine, explain their tautomerism.
13. Name the methyl derivatives of xanthine, explain their structure.

Task: To conduct a comparative characterization of heterocyclic compounds

Technique "Cinquain"

Option 1

Representatives	Structure	The main common feature	The main difference
Pyrazole			
Purine			

Option 2

Representatives	Structure	The main common feature	The main difference
Pyridine			
Pyrimidine			

LESSON №12

Theme: Heterocyclic compounds. Synthesis of 4-nitrozoantipyrine.

The purpose of the lesson: To consolidate the knowledge of heterocyclic compounds. To form knowledge on the mechanism of nitrosation on the example of the synthesis of 4-nitrozoantipyrine.

Objectives: By the end of the lesson, the student should know:

1. structure, aromaticity, π-redundancy and π-insufficiency of heterocyclic compounds;
2. methods for producing heterocyclic compounds;
3. reactivity of heterocyclic compounds in electrophilic and nucleophilic substitution reactions;
4. acid-base properties of heterocyclic compounds;
5. representatives of heterocyclic compounds used in the preparation of medicines;
6. nitrosation reactions, their mechanism;
7. methods and principles of the synthesis of 4-nitrozoantipyrine.

Basic training questions.

1. The main chemical utensils used in the synthesis of 4-nitrozoantipyrine, the principles of its assembly.
2. Calculation of the number of initial and received products.
3. The type and mechanism of the ongoing chemical reaction of organic synthesis.
4. The course of synthesis and purification of the raw product.
5. Structure, aromaticity, π-redundancy, π-insufficiency, methods of preparation, chemical properties of heterocyclic compounds.

Laboratory work. Synthesis of 4-nitrozoantipyrine.

Self-study. Students:

1. perform the synthesis of 4-nitrozoantipyrine;
2. draw up a protocol with records of the experiment, observations, and conclusions;
3. pass essays on the topic: "Derivatives of five-and six-membered heterocyclic compounds used in medicine»;
4. answer individual questions independently.

LABORATORY WORK

Synthesis of 4-nitrozoantipyrine

Reagents: antipyrine-1.9 g, 25% solution of sulfuric acid-2 ml, sodium nitrite-0.8 g, iodine starch paper

Equipment and chemical utensils: conical flasks of 100 ml – 2 pcs., Bunsen flask, Buchner funnel, thermometer, measuring cylinder

Getting the job done:

1. In a flask with a capacity of 100 ml, 1.9 g of antipyrine is placed.

2. Add 10 ml of water.

3.Add 2 ml of 25% sulfuric acid solution to the obtained antipyrine solution.

4. Add crushed ice to the flask.

5. The reaction mixture is cooled to 2-30C.

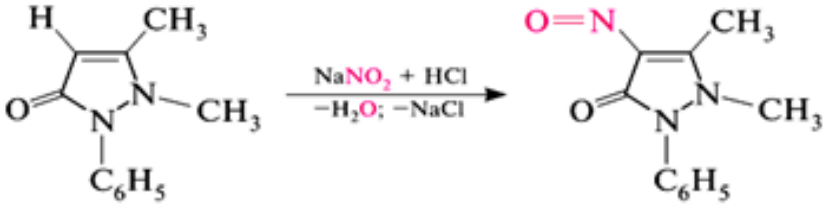
6. In the second flask, 0.8 g of sodium nitrite is dissolved in 10 ml of water.

7.In the first flask, gradually, with constant shaking, add a solution of sodium nitrite. The temperature of the reaction mixture should not exceed 2-30C.

8. The end of the reaction is determined using iodine-starch paper (a drop of the solution should give a blue spot on the paper that does not disappear for 10-15 minutes).

9. The resulting precipitate is filtered out on a Buchner funnel, washed with water and dried.

10. Synthesis yield ≈1.8 g (84%).



Description of the final product

4-nitrozoantipyrin is an emerald-green crystalline substance that is soluble in water and organic solvents.

Control questions

1. Write a diagram of the interaction of antipyrine with nitric acid.

2. What is the significance of this reaction in pharmaceutical analysis?

3. Why does the nitrosation reaction proceed according to position 4?

4. What role does sulfuric acid play in this reaction?

5. What is the nitrosating reagent?

6. Why should the temperature regime be strictly adhered to when obtaining 4-nirozoantipyrine from antipyrine?

7. How is the end of the nitrosation reaction controlled?

Individual questions

1. Give the structural formulas of the following compounds: a) α-methylfuran, b) N-ethylpyrrol, c) thiophene-2-sulfonic acid, d) β-acetylthiophene, e) pyrrolidine, e) 2,5-dimethylfuran, k) 2,5-dimethyl-2,5-dihydrofuran, l) α- bromothyophene, m) α, α'-dimethylpyrrol.

2. Aromaticity and its features in a series of five-membered heterocycles with one heteroatom (furan, pyrrole, thiophene). Electrophilic substitution by the example of sulfonation and nitration of pyrrole and thiophene. Name the resulting connections.

3. The reaction of the mutual transition of furan, pyrrole, thiophene (Yuryev reaction). Compare their aromaticity, their relation to mineral acids. Give the corresponding reaction equations.

4. Explain the ratio of furfural to the action of mineral acids and give the reactions of its interaction with the following reagents: a) Ag_2O (NH_3), b) H_2, c) CH_3COONO_2, d) KOH (60%), e) NH_2NH_2.

5. Furan – aromaticity, preparation. Write for furan the reactions of a) sulfonation, b) hydrogenation, c) oxidation, d) with maleic anhydride. Name the products you received.

6. Explain whether furfural is an acidophobic compound? Explain the reasons. Write the reaction diagrams of furfural with the following reagents: a) $NaHSO_3$, b) $NH_2NHC_6H_5$, c) HNO_3, then semicarbazide. Name the resulting reaction products.

7. Pyrrole-aromaticity, methods of preparation. Give the reaction equations confirming the weak acidic properties of pyrrole. Name the resulting connections.

8. Explain the aromaticity of pyrrole and its relation to mineral acids. Write the reaction reactions of pyrrole with the following reagents: a) $NaNH_2$, b) H_2 (Pt), c) CH_3COONO_2. Name the products you received.

9. Thiophene-aromaticity, π-redundancy. Give the reactions of halogenation, nitration, sulfonation, and reduction for thiophene.

10. Give three ways to obtain thiophene. Compare its aromaticity with benzene, write its reactions a) alkylation, b) nitration, c)

11. Write the structure of the following compounds: a) 4-aminopyrazole, b) 2,4-dimethylthiazole, c) imidazole-4-sulfonic acid, d) 4-nitro-5-methyloxazole, e) 1,2-diazole, e) 1,3-thiazole, g) 1,2-oxazole, h) 2,3-dimethyl-1-phenylpyrazolone-5.

12. Pyrazolone-5-tautomeric forms. With the help of which reactions you can get an antipyrine, give the corresponding reaction equations.

13. Pyrazole-aromaticity, amphoteric properties. Give the reactions of alkylation and acylation of pyrazole, name the resulting reaction products.

14. Explain the effect on the chemical properties of the "pyridine" type nitrogen atom in the pyrazole molecule with pyrrole. Give the reaction reactions of pyrazole with a) HCl, b) CH_3Cl, c) CH_3COCl. Name the resulting connections.

15. Give the sequence of reactions by which you can get amidopyrine from antipyrine. How do I distinguish the resulting compounds? Explain the answer.

16. Prototropic (azole) tautomerism of imidazole. Give the reactions of nitration, sulfonation, halogenation, alkylation and acylation of imidazole, name the resulting reaction products.

17. Write the reaction equations for the interaction of imidazole with the following reagents: a) HCl, b) KOH, c) CH_3I, d) CH_3COCl, e) conc. HNO_3, e) Cl_2. Name the products you received.

18. Write the structure of the following compounds: a) 3-methylpyridine, b) 2-aminopyridine, c) N-pyridine oxide, d) pyridinium hydrosulfate, e) γ-picoline, e) 5-vinyl-2-methylpyridine, k) 2-methylquinoline, l) N-acetylpyridinium chloride.

19. Pyridine-aromaticity, π - insufficiency. Write and name the products formed by the interaction of pyridine with the following reagents: a) Br_2, SO_3, t, b) CH_3COC1, c) $NaNH_2$, d) C_2H_5Br.

20. Give the methods for obtaining pyridine and 2-, 3-, 4-methylpyridines. Write the oxidation reactions of the resulting compounds. Name the resulting connections.

21. Give a scheme for obtaining N-pyridine oxide. Compare the ratio of pyridine and pyridine N-oxide to the action of electrophilic reagents, write their nitration and sulfonation schemes. Explain the answer.

22. Barbituric acid-preparation, its tautomeric forms. Give the sequence of reactions by which pyrimidine can be obtained from barbituric acid.

23. Preparation of pyrimidine from malon ether and urea. Compare the reactivity of pyrimidine and pyridine in electrophilic substitution reactions. Write the reaction of pyrimidine with: a) CH_3Cl, b) CH_3COCl, c) $NaNH_2$, d) $H_2SO_4 + SO_3$, $HgSO_4$.

24. Preparation of quinoline by the Scraup method. Give the reactions of sulfonation, oxidation, nitration, halogenation, reduction and amination.

25. The sequence of reactions from aniline can be obtained quinoline (Skraup method). Give the reactions of oxidation and reduction of quinoline and name the products obtained.

26. Suggest a scheme for the synthesis of 5-NHQ (8-hydroxy-5-nitroquinoline) from quinoline. Give the reactions of oxylation and reduction of quinoline. Name all the resulting reaction products.

27. Six-membered heterocyclic compounds with one nitrogen atom: pyridine, quinoline, acridine-the main properties. Give the sulfonation, nitration, and halogenation reactions for pyridine.

28. Compare the main properties of quinoline and pyridine. Write the reactions of the interaction of quinoline with the following reagents: a) HCl, b) H_2SO_4 (in the cold), c) CH_3I, d) $NaNH_2$, e) KOH. Name the products.

29. Write the reaction diagrams of nicotinic acid with the following reagents: 1) HCl, 2) CH_3I, 3) NaOH (H_2O), 4) C_2H_5OH (H^+), 5) $SOCl_2$, 6) t^0 . Name the products.

30. Purine-aromaticity, preparation. Give the reactions that confirm the acidic-basic properties of purine.

31. Purine-structure, nomenclature, acid-base properties. Write the reactions of the interaction of perin with the following reagents: a) CH_3Cl, b) CH_3COCl.

32. N-methylated xanthines - caffeine, theophylline, theobromine. Give their structure, name them according to the international nomenclature. Explain their acidic properties.

33. Xanthine and hypoxanthine – their tautomeric forms. With the help of which reactions it is possible to prove the amphoteric nature of xanthine and hypoxanthine, give the appropriate reaction equations.

34. Uric acid-tautomeric forms, acidic properties. Give a sequence of reactions that can be used to obtain purine from uric acid.

LESSON №13

Theme: Monosaccharides. Properties of glucose.

The purpose of the lesson: To form knowledge of the stereochemical structure, tautomeric forms and laws of the reactivity of monosaccharides.

Objectives: by the end of the lesson, the student should know:

1. Classification of monosaccharides;
2. stereoisomerism of monosaccharides and the basic concepts of “D,L-configuration”, “enantiomers”, “diastereomers”, “epimers”;
3. cyclo-oxotautomerism of monosaccharides and the phenomenon of mutarotation;
4. Rules for the transition from Colli-Tollens projection formulas to Heuors formulas;
5. methods for obtaining monosaccharides;
6. reactivity of monosaccharides;
7. qualitative reactions of monosaccharides.

Basic training questions.

1. Monosaccharides-classification, nomenclature.
2. Stereoisomerism of monosaccharides. Assignment to the D,L-stereochemical series. Enantiomers, diastereomers, epimers.
3. Cyclic structure of monosaccharides. Rules for the transition from Colli-Tollens projection formulas to Heuors formulas. Unnomers.
4. Cyclo-oxotautomerism of monosaccharides. The phenomenon of mutarotation.
5. Methods for obtaining monosaccharides.
6. Chemical properties of monosaccharides.

6.1. reactions involving open forms (oxidation and reduction reactions, epimerization in an alkaline medium, addition and addition-cleavage reactions);

6.2. reactions involving cyclic forms (reactions of semi-acetal hydroxyl-formation of glycosides; reactions of alcohol groups-formation of esters and esters, their relation to hydrolysis; interaction with copper hydroxide at room temperature).

Laboratory work. Properties of glucose.

Self-study (performed in preparation for the lesson).

Methods for obtaining monosaccharides.

LABORATORY WORK

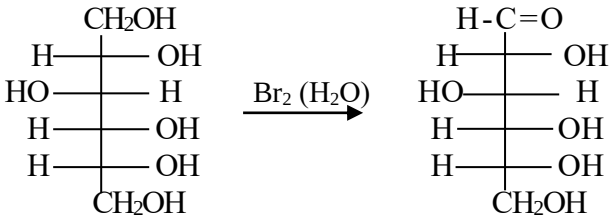
Experiment 1. The formation of monose during the oxidation of polyatomic alcohol

Reagents: mannitol (sorbitol), saturated bromine water, 10% sodium hydroxide solution, copper (II) sulfate solution)

Equipment and chemical utensils: spatula, test tubes, pipette, water bath, gas burner

Getting the job done:

1. In a test tube, 0,1-0,2 g of mannitol (sorbitol) is dissolved in 2 ml of water.
2. Add 8-10 ml of bromine water.
3. Heat in a boiling water bath until discolored. If the color does not disappear, continue heating in the burner flame.
4. An alkali solution and a few drops of copper (II) sulfate solution are added to the cooled colorless solution.
5. The resulting blue precipitate of copper (II) hydroxide dissolves when shaken, forming a blue solution.
6. The solution is heated.
7. A red precipitate falls out, which is explained by the appearance of an aldehyde group in the products:



Experience 2. Oxidation of monosaccharides with bromine water

Reagents: 1% glucose and fructose solutions, bromine water

Equipment and chemical utensils: test tubes, pipette, water bath, gas burner

Getting the job done:

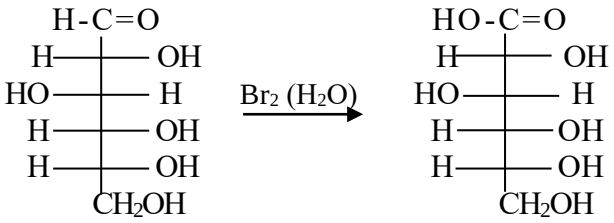
1. In one test tube, pour 1 ml of 1% glucose solution, in the second-1% fructose solution.

2.Add 5 ml of bromine water to each tube.

3. The mixture is heated in a boiling water bath for 15 minutes.

4. The glucose solution with bromine water is discolored, which indicates the process of glucose oxidation to form gluconic acid.

5. Fructose solution with bromine water does not change the color.



Experiment 3. Evidence for the presence of an α-glycol fragment in glucose

Reagents: 0,5% glucose solution, 10% sodium hydroxide solution, 2% copper (II) sulfate solution)

Equipment and chemical utensils: test tubes, pipette, gas burner

Getting the job done:

1.6 drops of a 10% solution of sodium hydroxide and 1 drop of a 2% solution of copper (II) sulfate are placed in a test tube.

2. The formation of a blue precipitate of copper (II) hydroxide is observed.

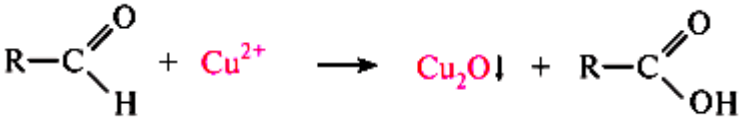
3. When 1 drop of 0,5% glucose solution is added, the precipitate quickly dissolves to form a transparent blue solution. This reaction confirms the presence of an α-glycol fragment in the glucose molecule.

4. To the resulting solution of copper (II) saccharate of blue color, add a few drops of water so that the height of the liquid in the test tube is 20 mm.

5. Hold the test tube obliquely and carefully heat the upper part of the solution in the flame of the burner.

6. Observe the transition of the blue color of the solution to green, and then its discoloration.

7. At the same time, a yellow precipitate of copper (I) hydroxide appears, which turns into a red-brown precipitate of copper (I) oxide.



Experiment 4. The effect of fuchsin sulfuric acid on glucose

Reagents: 1% glucose solution, formalin, saturated fuchsin sulfuric acid solution

Equipment and chemical utensils: test tubes, pipette

Getting the job done:

1. In two test tubes, pour 1 ml of a solution of fuchsin sulfuric acid.

2.Formalin is added to the first test tube, and glucose solution is added to the second.

3. Soon, a pink-purple staining appears in the first test tube, while the second remains colorless.

Glucose, like other monosaccharides, is an equilibrium mixture of several tautomeric forms in solution, in which the open form is contained in a small amount. Therefore, glucose does not give some characteristic reactions to the aldehyde group (it does not form bisulfite derivatives, does not give a reaction with fuchsin sulfuric acid).

Experience 5. The effect of Fehling's solution on glucose

Reagents: 5% glucose solution, copper (II) sulfate, ferrotic salt, 10% sodium hydroxide solution

Equipment and chemical utensils: test tubes, pipette

Getting the job done:

1.2 drops of an aqueous solution of copper (II) sulfate and 2 drops of an alkaline solution of a ferrotic salt – the potassium-sodium salt of tartaric acid-are placed in a test tube.

2. The release of a blue precipitate of copper (II) hydroxide is observed, which forms a water-soluble blue complex with the ferrotic salt.

3. Then 3 drops of 5% glucose solution are added to the test tube and the mixture is heated to a boil. A gradual discoloration of the solution and the formation of a red-brown precipitate of copper (I) oxide are observed.

Experiment 6. Selivanov's reaction to ketoses

Reagents: 1% solutions of glucose, fructose, Selivanov reagent (0,01 g of resorcinol in a mixture of 10 ml of water and 10 ml of conc. hydrochloric acid)

Equipment and chemical utensils: test tubes, pipette, water bath, gas burner

Getting the job done:

1.2 ml of freshly prepared Selivanov reagent is placed in two separate test tubes.

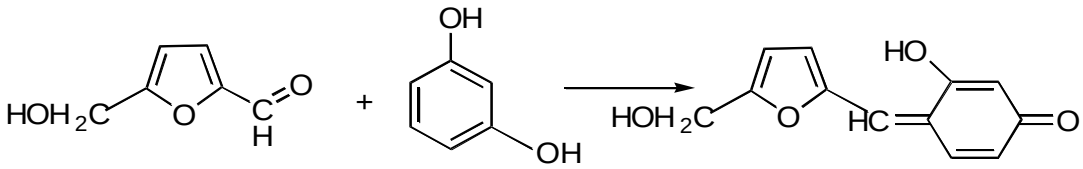
2. Add 0,5 ml of glucose solution to one of the test tubes, and 0,5 ml of fructose solution to the other.

3. The test tubes are placed for 2 minutes in a boiling water bath.

4. In a test tube with fructose, in contrast to glucose, a rapid appearance of red staining of the solution is observed.

5. When the test tubes are subsequently heated in the burner flame to a boil, the colored solution becomes turbid and a precipitate is released.

The reaction is caused by the formation of 5-hydroxymethylfurfural, which under the influence of concentrated hydrochloric acid condenses into a colored substance.



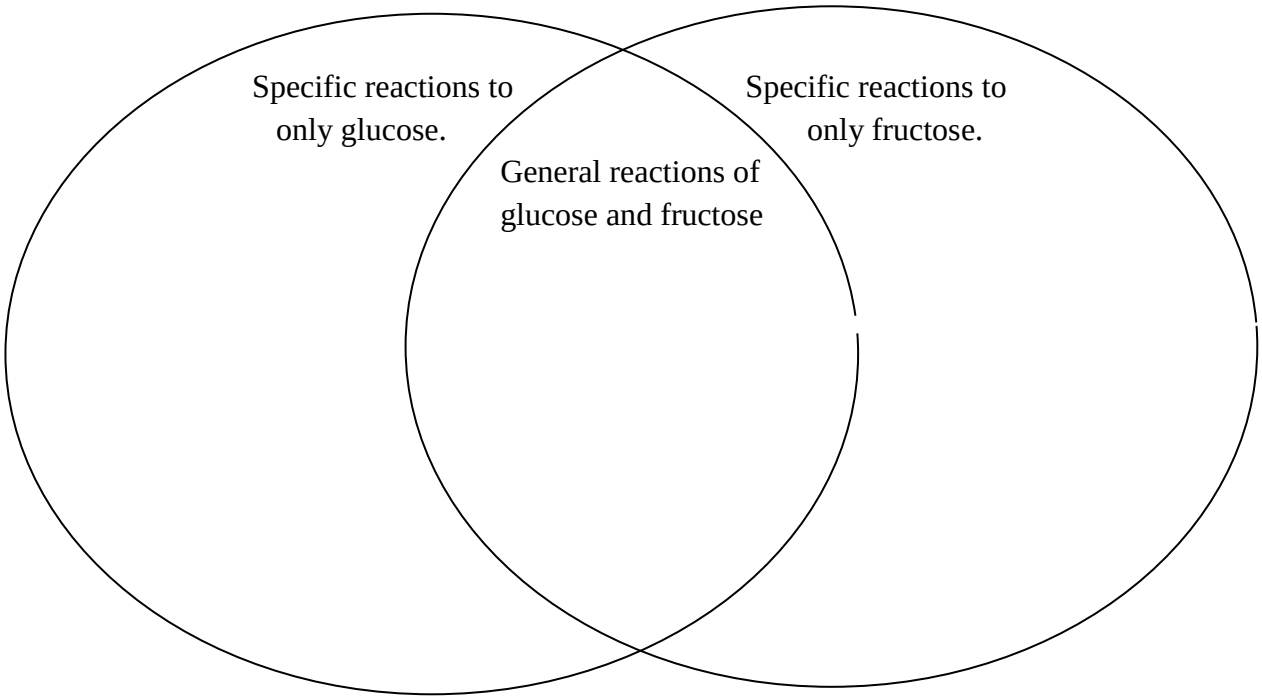
Ketoses in the experimental conditions are converted to 5-hydroxymethylfurfural 15-20 times faster than aldoses, which causes the rapid appearance of color and its intensity in the fructose solution. Under these conditions, aldohexoses only acquire a weak pink color when boiled for a long time.

Control questions

1. What organic compounds are called carbohydrates?
2. What groups are carbohydrates classified into?
3. What are monosaccharides?
4. What is the different structure of glucose and fructose molecules?
5. In what forms can monosaccharides exist?
6. Explain the rules for the transition from the projection formulas of Fischer, Colli-Tollens to the Heuors formulas.
7. What is mutarotation? What is the cause of it?
8. Explain the stereoisomerism of monosaccharides. Define "enantiomers", "diastereomers", "epimers", "anomers".
9. The cyclic structure of monosaccharides. Rules for the transition from Colli-Tollens projection formulas to Heuors formulas. Unnomers.
10. What methods of obtaining monosaccharides do you know?
11. What chemical properties are characteristic of monosaccharides?
12. What reactions can be used to prove the presence of a carbonyl group in monosaccharides?
13. What reactions can distinguish glucose from fructose?
14. Why does fructose, being ketohexose, react as a "silver mirror"?
15. What reaction can be used to prove that there are five hydroxogroups in a glucose molecule?
16. What is observed when glucose interacts with a freshly prepared solution of copper (II) sulfate under normal conditions and when heated? Explain the answer.

Task: Create a Venn diagram of the properties of glucose and fructose.

Venn diagram»



LESSON №14

Theme: Disaccharides. Properties of reducing (lactose) and non-reducing (sucrose) disaccharides.

The purpose of the lesson: To form knowledge of the stereochemical structure, tautomeric forms and laws of the reactivity of disaccharides.

Objectives: by the end of the lesson, the student should know:

1. classification of disaccharides;
2. cyclo-oxotautomerism of reducing disaccharides and the phenomenon of mutarotation;
3. chemical properties specific only to reducing disaccharides;
4. general chemical properties of reducing and non-reducing disaccharides;
5. the phenomenon of inversion.

Basic training questions.

1. Classification, nomenclature of disaccharides.
2. General chemical properties of reducing and non-reducing disaccharides.

2.1. Hydrolysis of lactose, cellobiose, maltose, sucrose.

2.2. Inversion, invert sugar.

2.3. Alkylation and acylation reactions.

2.4. Interaction with copper (II) hydroxide in the cold.

3. Chemical properties of reducing disaccharides.
4. Cyclo-oxotautomerism of lactose, cellobiose, maltose. Mutarotations.

5. Oxidation reactions with bromine water, Fehling solution, Tollens reagent, copper (II) hydroxide under heating.

6. Addition reactions (with hydrogen, hydrogen cyanide, etc.).

7. Addition-cleavage reactions with hydroxylamine, phenylhydrazine. Formation of ozazones.

Laboratory work. Properties of reducing (lactose) and non-reducing (sucrose) disaccharides.

Self-study (performed in preparation for the lesson).

Cyclo-oxotautomeria of disaccharides.

LABORATORY WORK

Experience 1. Proof of the presence of hydroxyl groups in disaccharides and their reducing ability

Reagents: 1% solutions of lactose and sucrose, 2% solution of copper (II) sulfate, 10% solution of sodium hydroxide aqueous solution of pyridine, 1% solution of iron (III) chloride)

Equipment and chemical utensils: test tubes, pipette, gas burner

Getting the job done:

1. In one of the test tubes, put 1 drop of 1% sucrose solution, in the other-lactose.

2.Add 4 drops of 10% sodium hydroxide solution and 1 drop of 2% copper (II) sulfate solution to both test tubes.

3. In both test tubes, the release of a bright blue precipitate of copper (II) hydroxide is observed, which dissolves during subsequent shaking of the test tube.

4. A clear blue solution of the complex copper (II) salt with lactose is formed in one test tube and a solution of the complex copper (II) salt with sucrose:

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

lactose + $Cu(OH)_2$ $\longrightarrow$ complex salt of copper (II) with lactose + H_2O

sucrose + $Cu(OH)_2$ $\longrightarrow$ complex salt of copper (II) with sucrose + H_2O

5. In the complex salts of copper (II)with lactose and sucrose, pour 2 ml of water.

6. The test tubes are shaken and gently heated.

7. In a test tube with lactose, the formation of a precipitate is observed, the color of which changes from yellow to red-brown, in the second test tube with a complex salt of sucrose and copper, no visible changes occur, since sucrose does not have reducing properties.

Experience 2. Obtaining calcium saccharate

Reagents: 20% sucrose solution, lime milk

Equipment and chemical utensils: test tubes, measuring cylinder, ordinary funnel, filter paper, gas burner

Getting the job done:

1.Pour 5 ml of 20% sucrose solution into the test tube.

2. Add 5 ml of lime milk.

3. The test tube is shaken (part of the lime should remain undissolved).

4. The solution is filtered.

5. When boiling the filtrate, the hardly soluble tricalcium saccharate $C_{12}H_{22}O_{11}\cdot 3CaO\cdot 3H_2O$

Experiment 3. Sucrose hydrolysis

Reagents: 2% sucrose solution, 10% sulfuric acid solution, Fehling solution, concentrated hydrochloric acid, resorcinol

Equipment and chemical utensils: test tubes, pipette, water bath, gas burner, litmus paper

Getting the job done:

1.Pour 2-3 ml of a 2% solution of beet sugar into a test tube.

2. Add 2-3 drops of dilute sulfuric acid.

3. The solution is heated in a boiling water bath for 5-10 minutes.

4. Then cool.

5. Bring to a slightly alkaline reaction (litmus test).

6. The contents of the test tube are divided into 2 test tubes.

7. A solution of Fehling is added to one test tube-the formation of a red precipitate of copper (I) oxide is observed.

8. A resorcinol crystal, 1 ml of hydrochloric acid is added to the second test tube and heated to a boil – a reddish staining appears, indicating the formation of fructose.

Sucrose consists of two monosaccharides – glucose and fructose, linked by a glycosidic bond, which is easily broken down during hydrolysis to form free glucose and fructose.

Control questions

1. What carbohydrates are called disaccharides?

2. What groups are disaccharides classified into? Their nomenclature.

3. What is the difference between regenerating and non-regenerating disaccharides from each other?

4. In what forms can there be reducing disaccharides?

5. What are the general chemical properties of disaccharides?

6. What products are formed during the hydrolysis of disaccharides?

7. What is inversion? What is its cause?

8. What chemical properties are characteristic only of reducing disaccharides?

9. What reactions can be used to prove the presence of hydroxyl groups in disaccharides?

10. What reactions can be used to prove the presence of a carbonyl group in reducing disaccharides?

11. What are the main ways to isolate disaccharides?

Task: To analyze the situational problem ("Case study").

"Food for the brain". Sucrose is one of the most common disaccharides. It is extremely important in a person's life. The famous Soviet scientist P. M. Zhukovsky highly appreciated the role of sugars in the development of human civilization: "In the development of human culture on earth, sugar plays a huge role, of course, not directly, but through its physiological effect on the entire human body. From early childhood to old age, we have a deep need for sugar. Where you need to put a lot of physical and mental energy, where you need to keep a good memory, sugar is indispensable." Throughout the world, sucrose is usually obtained from sugar cane or sugar beet. Ancient Bengal was the birthplace of sugar cane. In Russia, sugar was originally sold in pharmacies. In Russia, the first beet sugar-producing enterprises appeared in 1801-02. At the beginning of the 20th century, a person ate 2 kg of sugar for a year, now – 40 kg.

Task.

1. Read carefully the text of the paragraph on sucrose. Make a list of plants that contain sucrose.

2. Outline a method for extracting sucrose from beets or other plants. Make a diagram that shows the process of obtaining sugar.

3. Conduct an experiment proving the composition and structure of sucrose:

a) reaction with copper (II) hydroxide without heating and when heated;

b) reaction with "lime milk".

4. Analyze the structure of sucrose and make a list of the main properties of sucrose in terms of the relationship of properties with the structure as a representative of disaccharides. Suggest an experiment plan that allows you to distinguish sucrose from other carbohydrates.

5. Based on additional information, evaluate the importance of sucrose for modern humans.

6. Express critical opinions about the name of sugar by nutritionists "white death", agree or refute. Make recommendations in the form of advertising for the proper use of sugar by a person.

LESSON №15

Theme: Polysaccharides. Properties of starch and cellulose.

The purpose of the lesson: To form knowledge about the laws and features of the chemical behavior of polysaccharides in relation to their structure.

Objectives: by the end of the lesson, the student should know:

1. Classification of polysaccharides;
2. structure of starch and cellulose;
3. hydrolysis of polysaccharides;
4. cellulose derivatives – xanthogenate, acetylcellulose, nitrocellulose, carboxymethylcellulose.

Basic training questions.

1. Polysaccharides-definition, classification.
2. Starch, the components of starch (amylose, amylopectin). Glycogen. Chemical properties of starch (reactions of exhaustive methylation, acetylation). Stepwise hydrolysis of starch.
3. Cellulose-structure, relation to hydrolysis.
4. The effect of alkali on cellulose.
5. Preparation of esters with nitric acid, acetic anhydride. Preparation of cellulose xanthogenate.
6. Production of carboxymethylcellulose, diethylaminoethyl cellulose.
7. Heteropolysaccharides.

Laboratory work. Properties of starch and cellulose.

Self-study (performed in preparation for the lesson).

Heteropolysaccharides – hyaluronic acid, heparin, chondroitin sulfate.

LABORATORY WORK

Experience 1. Obtaining starch paste

Reagents: starch

Equipment and chemical utensils: test tubes, glass rod, gas burner, glass with a capacity of 50 ml

Getting the job done:

1. Pour about 1 g of dry starch into the test tube.

2. Add 5-6 ml of water and shake.

3. Allow the mixture to settle and drain the water.

4. Repeat washing the starch with new portions of water 2-3 more times.

5. Add the last portion of water and shake the mixture well, pour the starch suspension into a glass with 50 ml of water heated to a boil.

6. An almost transparent, slightly opalescent starch paste is formed.

7. Cool the solution and use it for subsequent reactions.

Experience 2. Qualitative reaction to starch

Reagents: 0,5% starch paste solution, iodine solution in potassium iodide

Equipment and chemical utensils: test tubes, pipette, gas burner

Getting the job done:

1.5 drops of 0,5% starch paste solution (from previous experience) are placed in a test tube.

2. Add 1 drop of iodine solution in potassium iodide.

3. Observe the appearance of an intense blue color of the solution.

4. When heating the colored starch solution with iodine, the color disappears, and when cooling it appears again.

5. Starch is a mixture of two oligosaccharides – amylose (20%) and amylopectin (80%). Amylose molecules in complexes with iodine form a spiral around the iodine molecule, and when heated, the amylose spiral unwinds.

Experience 3. Interaction of starch with copper (II) hydroxide)

Reagents: 0,5% starch paste solution, 10% sodium hydroxide solution, 5% copper (II) sulfate solution)

Equipment and chemical utensils: test tubes, pipette, water bath, gas burner

Getting the job done:

1.Add a few drops of 10% sodium hydroxide solution and 1-2 drops of 5% copper (II) sulfate solution to 1-2 ml of paste.

2. The mixture is heated in boiling water for 2-3 minutes.

3. The solution remains almost unpainted, blue flakes of insoluble copper (II) hydroxide turn black when heated, red or yellow precipitate is not formed.

In very long chains of starch molecules, free glycoside hydroxyl groups are located only at the ends of the chain, that is, the relative number of them in the molecule is very small, so the starch does not react with alkali, does not reduce copper hydroxide.

Experiment 4. Acid hydrolysis of starch

Reagents: 0,5% starch paste solution, 10% sodium hydroxide solution, 5% copper (II) sulfate solution, iodine solution in potassium iodide

Equipment and chemical utensils: test tubes, pipette, water bath, gas burner, slide glass

Getting the job done:

1.1 ml of 0,5% starch paste solution is placed in a test tube.

2. Add 10 drops of 10% sulfuric acid solution.

3. Heat in a water bath for 20 minutes.

4. The solution becomes transparent.

5. A drop of the solution is applied to the slide and mixed with 1 drop of iodine in potassium iodide. The absence of intense blue staining indicates complete hydrolysis of starch

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{H^+} nC_6H_{12}O_6$$

The presence of glucose can be proved by the reaction of interaction with copper (II) hydroxide.

Control questions

1. What organic compounds are called polysaccharides?
2. What groups are polysaccharides classified into?
3. What is the difference between starch, glycogen and cellulose?
4. Explain the reactivity of starch and cellulose.
5. What products are formed during the hydrolysis of polysaccharides?
6. Are polysaccharide solutions capable of mutarotizing?
7. What reactions can be used to prove the presence of hydroxyl groups in polysaccharides?
8. What is the qualitative reaction to starch?
9. What reagents are able to dissolve cellulose?
10. Name the cellulose derivatives used in medicine.

Task: To conduct a comparative characterization of polysaccharides.

"Sinkwein" technology

Representatives	Structure	The main common feature	The main difference
Starch			
Cellulose			

LESSON №16

Theme: Carbohydrates. Synthesis of N-glycoside of white streptocide.

The purpose of the lesson: To form knowledge about the reactivity of glycosides and how to obtain them, to consolidate knowledge about carbohydrates.

Objectives: By the end of the lesson, the student should know:

1. glycoside formation reactions;
2. ratio of glycosides to hydrolysis;
3. types of glycosides;
4. chemical cookware used in organic synthesis and the principles of its assembly;
5. the synthesis reaction, its mechanism and conditions of its course;
6. methods of identification of the synthesized substance.

Basic training questions.

1. Carbohydrates, their classification.
2. Monosaccharides, structure, stereoisomerism.
3. Cyclic forms of monosaccharides, tautomerism.
4. Monosaccharide derivatives-glycosides, their classification.
5. Reactions of formation of glycosides.
6. The ratio of glycosides to hydrolysis.
7. Chemical utensils used in organic synthesis.
8. Principles of assembly of devices for work on organic synthesis.
9. Calculation of the number of initial and received products.
10. The type and mechanism of the ongoing chemical reaction of organic synthesis.
11. The course of synthesis and purification of the raw product.

Laboratory work. Synthesis of N-glycoside of white streptocide.

Self-study. Students:

1. perform the synthesis of N-glycoside of white streptocide;
2. draw up a protocol with records of the experiment, observations, and conclusions;
3. pass essays on the topic: "Carbohydrates»;
4. answer individual questions independently.

LABORATORY WORK

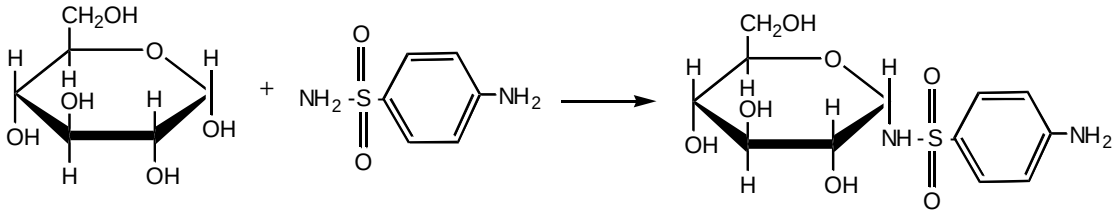
Synthesis of white streptocide N-glycoside

Reagents: glucose-2.5 g, white streptocide-2.4 g, concentrated hydrochloric acid HC1-1 drop, a mixture of diethyl ether and ethyl alcohol

Equipment and chemical utensils: glass with a capacity of 150 ml, conical flasks with a capacity of 50 ml – 2 pcs, Buchner funnel, Bunsen flask, water bath, crystallizer, gas burner

Getting the job done:

1. Pour 2.5 g of glucose into a glass with a capacity of 150 ml.
2. Pour in 25 ml of warm water.
3. The mixture is stirred until the glucose is completely dissolved.
4. Then, 2.4 g of white streptocide is added to the glucose solution in portions.
5. The reaction mixture is thoroughly mixed.
6. The reaction mixture is heated for 30 minutes in a water bath.
7. Add 1 drop of concentrated hydrochloric acid to the cooled reaction mixture.
8. White crystals are formed, which are filtered out on a funnel, washed with a mixture of diethyl ether and ethyl alcohol.
9. Output ≈ 18 g.



Description of the final product

N-glycoside of white streptocide is a colorless, odorless crystalline substance that does not dissolve in ethyl alcohol, diethyl ether, and is moderately soluble in water.

Control questions

1. What compounds are called carbohydrates? Their classification.
2. What carbohydrates are called monosaccharides? Their classification.
3. Explain the cyclic forms of monosaccharides, tautomerism.
4. What monosaccharide derivatives are called glycosides? Their classification.
5. When interacting with what reagents do monosaccharides form glycosides?
6. Explain the ratio of glycosides to hydrolysis.
7. What is formed when glucose interacts with white streptocide?
8. What is the significance of this reaction in pharmaceutical analysis?
9. What role does hydrochloric acid play in this reaction?

Individual questions

1. Write the structural formulas of the following compounds: a) L-fructose, b) D-fructose, c) L-glucose, d) D-glucose. Explain their relation to the D-and L-series. On their example, explain the concepts of "enantiomer", "epimer".

2. Give the tautomeric forms of D-glucose and write the reactions of its interaction with: a) HCN, b) CH_3OH, c) (CH_3CO_2) O, name the resulting reaction products.

3. Give the structure of the following compounds and explain their relationship to each other: L-xylose, D-arabinose, D-xylose, D-ribose. Define the terms "enantiomer", "diastereomer", "anomer", "epimer".

4. Monosaccharides-classification, stereoisomerism, methods of preparation.

5. Tautomeric forms of D-glucose, explain the phenomenon of mutorationation. Give the reactions of galactose interaction with a) CH_3OH (HCl dry.), b) $NH_2NHC_6H_5$.

6. Cyclo-oxo-tautomerism of D-mannose, the phenomenon of mutorationation. Define the concept of "anomer".

7. Tautomerism of D-fructose. Explain the phenomenon of mutoratation. Write the reaction reactions of D-fructose with a) C_2H_5OH (HC1), b) CH_3I and name the resulting products.

8. Explain the reasons why fructose, being ketose, reacts as a "silver mirror". Explain the answer with appropriate transformations.

9. Using the example of D-glucose, explain the conversion of monosaccharides in an alkaline medium (epimerization). Write the reactions of the interaction of D-glucose with a) HCN, b) CH_3OH (HC1), c) H_2.

10. Write the reactions of the interaction of D-glucose with the following reagents: 1) HNO_3, 2) $[Ag[NH_3]_2OH]$, 3) NH_2OH, 4) C_2H_5OH (HCl dry), 5) $(CH_3CO)_2O$ followed by hydrolysis. Name the resulting connections.

11. On the example of D-glucose, give the oxidation reactions of monosaccharides-the production of aldonic, aldaric and uronic acids.

12. Give the reactions of the interaction of D-mannose with the following reagents: 1) [H], 2) Br_2, H_2O, 3) NH_2OH, 4) C_2H_5OH (HCl dry), 5) CH_3I followed by hydrolysis. Name the resulting connections.

13. Define the concepts of "reducing" and "non-reducing" disaccharides, give examples, their distinctive reactions.

14. Tautomerism of maltose, the phenomenon of mutoratation. Write the reactions of the interaction of maltose with: a) Br_2 (H_2O), b) CH_3I, name the resulting compounds.

15. Give the reaction reactions of lactose with the following reagents: a) [H], b) Br_2, c) $C_6H_5NHNH_2$, d) CH_3I, followed by hydrolysis. Name the resulting connections.

16. Tautomeric forms of lactose, mutoratation. Give the reaction reactions of lactose with the following reagents: a) CH_3OH (HCl), b) CH_3I and name the resulting reaction products.

17. Tautomeric forms of cellobiosis, explain the phenomenon of mutoratation. Write the reactions of the interaction of cellobiose with: a) HCN, b) NH_2OH.

18. What reactions can be used to prove the reducing properties of maltose? Give the corresponding reaction equations.

19. Sucrose-structure, inversion. Write the reactions of alkylation and acylation of sucrose followed by hydrolysis. Name the resulting connections.

20. Sucrose-structure. Whether the phenomenon of mutoratation is typical for sucrose, explain the reasons. Give the reaction of sucrose with a) copper (II) hydroxide in the cold and b) alkylation followed by hydrolysis

21. What reactions can distinguish lactose from sucrose? Give the appropriate reaction equations.

22. Polysaccharides-classification. The components of starch-amylose and amylopectin, their relationship to hydrolysis.

23. Starch-structure, relation to hydrolysis. For the starch hydrolysis product, write the complete methylation reaction followed by hydrolysis.

24. Give the structure of amylose and amylopectin, specify the glycosidic bonds. Their relation to hydrolysis.

25. Starch and cellulose. Give the reactions of their complete hydrolysis. Name the products you received.

26. Cellulose and its esters: diethylaminoethylcellulose, nitrates, acetates-preparation, relation to hydrolysis.

27. By what sequence of reactions can carboxymethyl - and trinitrocellulose be obtained from cellulose? Their relation to hydrolysis. Give all the corresponding reaction equations.

LESSON №17

Theme: Saponified lipids. Properties of fats.

The purpose of the lesson: To form knowledge about the reactivity of saponified lipids in relation to their structure.

Objectives: by the end of the lesson, the student should know:

1. classification of fats;
2. fat nomenclature;
3. structural formulas of fats;
4. reactions that demonstrate the chemical properties of fats.

Basic training questions.

1. Classification, nomenclature of fats.
2. Zigzag conformation-cis-and all-cis-forms.

3. The relationship of the consistency of triacylglycerols with the structure of acids.

4. Chemical properties of fats: hydrolysis (alkaline, acidic, enzymatic), hydrogenation, oxidation.

5. Analytical characteristics of fats (iodine number, saponification number).

Laboratory work. Properties of fats.

Self-study (performed in preparation for the lesson).

Saponified lipids.

LABORATORY WORK

Experience 1. Fat emulsification

Reagents: vegetable oil, 10% sodium hydroxide solution, 10% sodium carbonate solution, soap solution

Equipment and chemical utensils: test tubes, pipette, tripod

Getting the job done:

1. Add 1-2 drops of vegetable oil to four test tubes.

2. In the first tube, add 1 ml of water, in the second-1 ml of a 10% solution of sodium hydroxide, in the third-1 ml of a 10% solution of sodium carbonate, in the fourth-1 ml of a soap solution.

3. The contents of each test tube are shaken violently.

4. In all test tubes, an emulsion is formed – a turbid liquid in which small droplets of fat are suspended in water.

5. Test tubes with the obtained emulsions are placed in a tripod and after a few minutes mark which substances form stable emulsions.

The least stable emulsion is oil in water. It quickly breaks down, as the oil droplets stick together in larger drops and finally form a layer of fat on the surface of the water.

Experience 2. Determination of unsaturated fat

Reagents: vegetable oil, bromine solution in chloroform, chloroform

Equipment and chemical utensils: test tubes, pipette

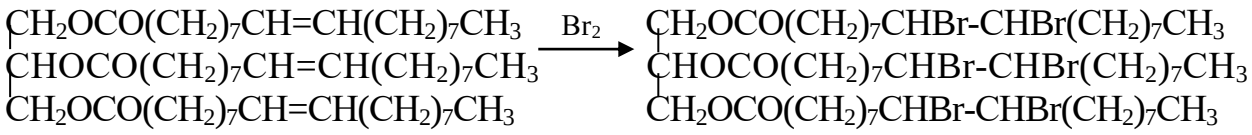
Getting the job done:

1. Add 1 drop of vegetable oil to the test tube.

2. Pour in drops of chloroform until dissolved.

3. To the solution of fat in chloroform, add a solution of bromine in chloroform drop by drop until a non-fading yellow color appears.

4. Vegetable oil, due to a higher degree of unsaturated content, requires a larger amount of bromine solution.



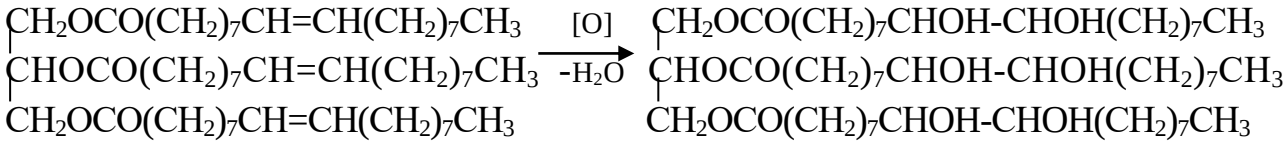
Experiment 3. Oxidation of vegetable oils with potassium permanganate

Reagents: vegetable oil, 0,5% solution of potassium permanganate, 10% solution of sodium acetate

Equipment and chemical utensils: test tubes, pipette

Getting the job done:

1. Add 0,5 ml of vegetable oil to the test tube.
2. Add a 10% solution of sodium acetate.
3. Pour a 0,5% solution of potassium permanganate.
4. Shake the contents of the test tube thoroughly.
5. The characteristic crimson-purple color of the potassium permanganate solution disappears, as a result of the oxidation of unsaturated acid glycerides entering the vegetable oil.



Experience 4. Saponification of fats

Reagents: vegetable oil, 10% sodium hydroxide solution, saturated sodium chloride solution

Equipment and chemical utensils: porcelain cup, glass stick, gas burner

Getting the job done:

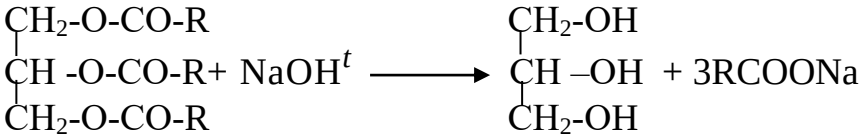
1.Place 2-3 ml of liquid fat (vegetable oil) in a small cup.

2. Pour in a solution of alkali and boil, adding water until a drop of liquid taken with a glass stick is completely dissolved in distilled water.

3. The solution is cooled and 20 ml of saturated sodium chloride solution is added.

4. When stirring, the soap floats to the surface and hardens.

5. The surfaced layer is removed on cheesecloth, squeezed out and stored for the next experiments.



Experience 5. Soap Properties

Reagents: soap (from previous experience), 10% solution of sulfuric acid, 5% solution of calcium chloride

Equipment and chemical utensils: test tubes, measuring cylinder, gas burner

Getting the job done:

1. A piece of the resulting soap (from previous experience) is dissolved in 2-3 ml of water.

2. Heat the test tube and make sure that when heated, the soap dissolves much faster.

3. When the contents of the test tube are shaken, there is a heavy foaming.

$$RCOONa + HOH \longrightarrow RCOOH + NaOH$$

4.5 ml of the resulting soap solution is placed in two test tubes.

5. In one test tube, add 1 drop of 10% sulfuric acid solution, in the other – add a 5% solution of calcium chloride drop by drop when shaken.

6. In the first test tube, a flaky white oily precipitate of free fatty acids that do not dissolve in water falls out, in the second – a white precipitate of a calcium salt of fatty acids that is difficult to dissolve in water falls out.

$$C_{17}H_{33}COONa + HOSO_3OH \longrightarrow C_{17}H_{33}COOH + NaHSO_4$$

$$C_{17}H_{35}COONa + CaCl_2 \longrightarrow NaCl + (C_{17}H_{35}COO)_2Ca$$

Control questions

1. What organic compounds are called lipids?
2. How are lipids classified according to the ability of their molecules to hydrolytic cleavage?
3. Classification of lipids by chemical structure, by function.
4. Define saponified lipids.
5. What are saponified lipids by chemical nature?
6. What types of saponified lipids are classified into?
7. What compounds belong to the class of saponified lipids?
8. The role of lipids in the body.
9. What are fats?
10. What carboxylic acids are included in the composition of fats?
11. Explain the effect of the structure of fatty acids on the consistency of fats.
12. What are neutral fats?
13. Explain the chemical structure and properties of animal and vegetable fat.
14. What reactions can be used to prove the unsaturated nature of fats?
15. What do fats form during hydrolysis?

LESSON №18

Theme: Unsaponifiable lipids.

The purpose of the lesson: To form knowledge about the reactivity of unsaponifiable lipids in relation to their structure.

Objectives: by the end of the lesson, the student should know:

1. Classification of unsaponifiable lipids;
2. structural formulas of terpers, their classification;
3. reactions for the production of limonene, validol, menthol, camphor.

Basic training questions.

1. Classification of unsaponifiable lipids.
2. Prostaglandins and isoprenoids (terpenes, carotenoids, steroids).
3. Terpenes. Isoprene rule (L. Ruzichka).
4. Classification of terpenes: by the number of isoprene fragments, by the presence and absence of a cycle, depending on the number of cycles.
5. Acyclic terpenes: myrcene, geraniol, nerol, citral A and citral B.
6. Monocyclic terpenes (limonene, terpin, menthol). Stereoisomers. Hydration of limonene. Preparation of menthol by reduction of mentone and alkylation of m-cresol followed by hydrogenation.
7. Bicyclic terpenes: α - pinene, borneol, camphor. Conformations of camphor stereoisomers. Obtaining camphor from α - pinene. Obtaining bromocamphora.
8. Carotenoids (plant pigments). α -Carotene.
9. Low-molecular-weight bioregulators of lipid nature. Retinol. Vitamin A. Oxidation.

Laboratory work. Properties of unsaponifiable lipids.

Self-study (performed in preparation for the lesson).

Steroids.

LABORATORY WORK

Experience 1. Proof of unsaturated properties of α-pinene

Reagents: bromine water, turpentine, 1% solution of potassium permanganate

Equipment and chemical utensils: test tubes, pipette

Getting the job done:

Experiments are carried out in the fume hood!

1.5 drops of bromine water are placed in one tube, and 1 drop of potassium permanganate solution and 3 ml of water are placed in the second tube.

2.Add 5-10 drops of turpentine to both test tubes.

3. Shake the test tubes.

4. Discoloration of solutions is observed.

The reaction confirms the unsaturated properties of α-pinene, the main substance of turpentine.

Experience 2. Camphor sublimation

Reagents: camphor crystals

Equipment and chemical utensils: Petri dish, spatula

Getting the job done:

1. Pour a little water into a petri dish.
2. Add 1-2 camphor crystals.
3. At the same time, the static movement of camphor crystals is observed.

Control questions

1. What organic compounds are called unsaponifiable lipids?
2. What are the unsaponifiable lipids chemical structure of a molecule?
3. What sochineniya belong to the unsaponifiable lipids?
4. What are the isoprenoids?
5. What is equal to the number of carbon atoms in the molecular structure of monoterpenes?
6. How many atoms of carbon in the composition of the molecules of diterpenes?
7. What is the Mentana?
8. What compounds react menthol as a secondary alcohol?
9. What is a Turpin?

The lesson is the final lesson, which summarizes the results of the semester. If there is a score within 55-100%, the student is allowed to pass the final control in organic chemistry, if the semester score is less than 55% – the student is considered an academic debtor and is not allowed to pass the final control.