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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

PRODUCTION OF AMINO ALCOHOLS BY INDUCTIVE OXIDATION OF UNSATURATED C_6-C_7 MONO- AND BİCYCLIC HYDROCARBONS TO HYDROXYGALOGENIDES

Speciality: 2314.01- Petrochemistry

3303.01– Chemical technology and engineering

Field of science: Chemistry

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Baku-2024

The work was performed at the laboratory of «Chemistry of alicyclic compounds» of the Institute of Petrochemical Processes named by acad. Y.H.Mammadaliyev of of the Ministry of Science and Education of the Republic of Azerbaijan.

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GENERAL CHARACTERISTICS OF WORK

Relevance of the work and degree of development. Amino alcohols are organic compounds with a wide range of applications, containing -NH_2 and -OH groups on different carbon atoms in the molecule. These amino alcohols are used as solvents, intermediates in the production of surfactants, corrosion inhibitors, metalworking cutting fluids. The fact that they have potential biologically active properties has led to the creation of drugs used in the treatment of pathological changes occurring in the cardiovascular system, malignant tumors, and widespread diseases such as Alzheimer's disease in pharmacology. Amino alcohol derivatives containing a norbornene, adamantane, morpholine, and piperidine ring are included in currently used synthetic drugs.[1, 2, 3]

In the industry, amino alcohols are obtained through the aminolysis process of ethylene and propylene oxides with ammonia and amines. Ethylbenzene and cumene hydroperoxides are used in the production of epoxides. However, the indicated processes are carried out with multi-stage technologies at high temperature and pressure. It is difficult to obtain epoxide from unsaturated compounds of any structure.

Considering all that points, the development of a convenient method of obtaining amino alcohols with mono- and bicyclic structures, the determination of the dependence between the biological activity properties of the obtained compounds and the structures of the reagents, as well as their application areas remains up-to-date and is one of the problems awaiting solution.

For this reason, the synthesis of new compounds containing hydroxyl, amine, and oxirane groups in the molecule, determining

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[1] Caifeng, L. Norbornene in organic synthesis / L.Caifeng, L-Liu, X.Fu, J.Huang // Synthesis, - 2018, -Vol.50, -N.15, -p. 2799-2823.

[2] Пальчиков В.А. Морфолины. Синтез и биологическая активность // ЖОрХ, - 2013, -Т 49, -№ 6, -с .807-831.

[3] Машковский, М.Д. Лекарственные средства: В 2т-Изд. 14-е, М.: Новая волна, -2002, -т.1, 540 с; т. 2, 608 с.

optimal reaction conditions for their preparation, and studying areas of practical application are of great importance.

Object and subject of work. Cyclohexene and bicyclo-[2.2.1]hept-2-ene, their methyl-, acyl, vinyl derivatives were used as the object of the research. The subject of the research is the synthesis of bromo(chloro)hydroxides, epoxides of these cyclic olefins and aminoalcohols from their reaction with amines.

The purpose and objectives of the dissertation work. It is the study of the reaction of obtaining hydroxyhalides in the presence of various oxidants under the conditions of connected reactions from mono- and bicyclic olefins and based on hydroxyhalides, the reaction of obtaining amino alcohols is studied.

The following issues were resolved in the dissertation work:

- Study of the reaction of chlorine(bromo)hydroxides of cyclohexene, bicyclo[2.2.1]hept-2-ene, their methyl-, vinyl-, acyl derivatives in the presence of hydrohalide acids and hydrogen peroxide, КУ-2х8, КУ-23х8 sulphocations;

- Study of synthesis reactions of appropriate amino alcohols based on mono-aliphatic, dicyclic amines and hydroxyhalides of C_6-C_7 mono-, bicyclic olefins and study of the effect of various factors on yield of target products and selectivity of the process;

- Study of the kinetics, kinetic model and probable mechanism of the in situ production of halogen hydroxides of C_6-C_7 mono- and bicyclic olefins under the conditions of coupled reactions;

- Synthesis of epoxides of C_6-C_7 mono-, bicyclic olefins and corresponding amino alcohols based on them by reciprocal synthesis and comparison of their structures;

-Study of the biocidal properties of amino alcohols in the composition of lubricating oils, coolant-lubricants at the different concentrations.

Research methods The implementation of the processes of obtaining electrophilic metastable HOX (X=Cl, Br) complexes (MSC) (in the olefin + HOX (RCO_2H) + oxidizing system in situ mode) and peroxoacids of C_6-C_7 mono- and bicyclic olefins and alkyl

derivatives with correspondingly formed halohydrins and epoxides which react with amines to form amino alcohols.

The main provisions put forward for defense.

-Cyclohexene, bicyclo[2.2.1]hept-2-ene, their methyl-, vinyl-, acyl derivatives were obtained under the conditions of conjugate reactions of hydrohalic acids and hydrogen peroxide, its adduct with urea, sodium hypochloride, tertbutyl-, cumyl hydroperoxide. The kinetic model of the reaction for the production of chloro(bromo)hydrins derivatives in the presence of sulfonic cation exchange catalysts КУ-2х8, КУ-2х8, its probable mechanism and optimal conditions for the process have been determined;

- The optimal conditions for the process of epoxidation of C_6-C_7 mono- and bicyclic olefins with hydrogen peroxide and its adduct with urea in the presence of catalysts containing phosphorus heteropolymolybdate, phosphorus heteropolytungstate modified with transition metals (Nd,Ce,Co,Gd) were found;

- Corresponding aminoalcohols were obtained from the aminolysis of chloro(bromo)hydroxides of C_6-C_7 mono-, bicycloolefins and alkyl derivatives with aliphatic and cyclic amines in basic condition;

-To clarify the structures of amino alcohols, epoxides were synthesized by the mutual synthesis reaction of C_6-C_7 cycloolefins and the comparison of the aminoalcohols obtained from the aminolysis of these amines with the analogs obtained from the aminolysis of halogenhydrins shows that their structures are practically the same and do not change depending on the method of preparation;

-The biocidal and bactericidal properties of C_6-C_7 mono- and bicyclic amino alcohols in the composition of lubricating oils, coolant-lubricants at the different concentrations have been studied.

Scientific novelty of the dissertation. For the first time, under the conditions of coupled reactions in situ, electrophilic metastable reagents (HOX, X=Cl, Br, RCO_3H, R=H,CH_3) of C_6-C_7 alicyclic olefins, their alkyl derivatives in inductive systems [H_2O_2, $H_2O_2 \cdot CO(NH_2)_2$] adduct + HCl (HBr, RCO_2H) acids], halogenhydrins, epoxides and aminoalcohols from their reaction with mono- and

diamines were synthesized, the kinetic model and mechanism of the reaction were given.

Theoretical and practical value of the work. The proposed mechanism of the reaction can be used to study the mechanisms of theoretically similar types of reactions. Obtaining C_6-C_7 amino alcohols opens the way to ecologically clean production according to the requirements of "green chemistry".

Reliability of research results. In the dissertation work, known methods of petrochemical synthesis were used, physico-chemical parameters of the prepared catalytic complexes, new compounds were determined, their composition and structures were confirmed by X-ray, IR, ^{1}H and ^{13}C NMR spectroscopy, analytical (permanganatometric, iodometric) methods, which is scientific confirms the integrity of the results.

Personal participation of the author. Determining the goals and tasks of the research work, choosing research methods, preparing catalysts, checking their activity, synthesizing primary substances, conducting experiments, collecting literature data, and compiling the review were performed independently by the applicant. Processing of received data, their analysis and preparation and presentation of reports in the form of scientific articles were carried out directly by the claimant.

Publications.Based on the materials of the dissertation, 19 scientific works were published, including 9 articles (3 without co-authorship, 6 with impact factor), 1 Azerbaijani patent, and the abstract of 9 reports.

Approbation of work. The main results of the dissertation were presented at a number of international symposiums and conferences: International scientific and technical conference “Chemical reagents, reagents and processes of small-scale chemistry”, dedicated to the memory of the academician of the Academy of Sciences of the Republic of Bashkortostan Dilyus Lutfullich Rakhmankulov, (Ufa, November 14-16, 2016), IV International Scientific Conference of Young Scientists, Caucasus University, (April 29-30, 2016, Baku, Azerbaijan), International Scientific and Technical Conference

"Petrochemical Synthesis and Catalysis in complex condensed systems", dedicated to the 100th anniversary of academician B.K. Zeynalov, (June 29-30, 2017, Baku), International scientific and practical conference "Innovative prospects in oil refining and petrochemistry", dedicated to the 110th anniversary of academician V.S. Aliyev, (October 9-10, 2018, Baku), "Current problems of modern natural sciences", International scientific conference, (Ganja, Azerbaijan, May 4-5, 2018), International scientific conference "Petrochemical processes", dedicated to 90-year anniversary of the Institute of Petrochemical Processes (Baku, Azerbaijan, October 4-5, 2019).

Place of the dissertation work The work was carried out in the laboratory "Alicyclic Compounds" of the Institute of Petrochemical Processes named after Academician Yu.H Mammadaliyev Ministry of Science and Education of Azerbaijan.

The total volume of the dissertation indicating the volume of structural sections. The dissertation consists of an introduction, 6 chapters, 8 conclusions and a bibliography of 165 sources. The total volume of work is 165 pages. The work consists of 34 tables, 10 figures, diagrams and applications. Without taking into account figures, tables, and literary sources, it contains 171449 characters (introduction - 9569, chapter I - 40762, chapter II - 9279, chapter III - 45640, chapter IV - 35773, chapter V - 15552, chapter VI – 11287, conclusion - 3587).

The introduction discusses the relevance of the chosen topic, indicating the purpose, novelty and practical significance of the work.

The first chapter is devoted to modern problems of obtaining amino alcohols and areas of their application, as well as a review of literature materials on the main areas of their use.

The second chapter describes the experimental part of the work: starting compounds, their preparation, physicochemical parameters, degree of purity, description of instruments and experimental techniques.

In the third chapter, the results of research conducted in the direction of the synthesis of chloro-, bromohydroxyhalide derivatives

of mono- and bicycloolefins in the induced system in situ mode are given. Also, the results and discussion of the optimal values of the parameters affecting of metastable complexes and cycloolefins to the yield of halohydrins and amino alcohols, the kinetic model, and the mechanism are shown.

The fourth chapter is devoted to the production of amino alcohols from the reaction of chloro- and bromohydroxides of cycloolefins with single and double amines. The physico-chemical indicators, purity of the obtained substances were determined by GC-LC, their structures were confirmed by IR-, ^{1}H and ^{13}C NMR spectral, elemental analysis, mutual synthesis methods.

In the fifth chapter, the results of investigation of conformational and stereochemical properties of hydroxyhalides of alkylcyclohexenes and bicyclo[2.2.1]hept-2-enes, as well as amino alcohols, respectively, are presented.

In the sixth chapter, the additive properties of the synthesized amino alcohols, the study of their functional properties and the field of application are determined. The principle technology and material balances of the process of purchasing products are given.

At the end of the dissertation, the main conclusions of the research and a list of references are given.

MAIN CONTENT OF THE WORK

1. Regularities of synthesis of chloro(bromo)hydroxides of alkyl derivatives of cyclohexene and bicyclohept-2-ene

The participation of cycloolefins and alkyl derivatives of mono-, bicyclic structure in the HX (X=Cl,Br) + oxidative system is of interest from both a scientific and practical point of view.

In this regard, the use of H_2O_2 solutions for the oxidative functionalization of cycloolefins of various structures can be considered an environmentally friendly method. On the other hand, given that cycloolefins are not soluble in water, requires them to be carried out in a heterophase system at the water-organic interface or their separation boundary. For this reason, the choice of oxidants,

catalysts and optimal conditions to increase the selectivity of processes comes to the fore.

For this purpose, studies were carried out using cyclohexene as a model reaction. The results obtained are shown in Table 1. As can be seen from the results, more effective oxidizing agents are a 26-30% aqueous solution of H_2O_2 and solutions of sodium hypochloride (with an active chlorine content of 110-118 g-ion/l). They can generate active electrophilic MSCs in situ in induced systems and transport them along the double bonds of substrates in the system. When converting cyclohexene with the adduct of hydrogen peroxide with urea (with an active oxygen content of 30-35%), the yield of hydroxyhalide and epoxide is less than with H_2O_2 It can be assumed that the reason for this is that after using H_2O_2 for oxidation, free urea enters into a transformation reaction with the resulting target products.

As shown in Table 1, the oxidation of HCl to HOCl does not occur under mild conditions when using environmentally friendly molecular oxygen. However, HBr is oxidized to molecular Br_2 and HOBr (as determined by iodometric analysis).

Table 1.

Results of the influence of various oxidizing agents (Ox) on the yield of hydroxychloro(bromo) derivatives of CH. (T=50°C, τ=4.5-5 h, molar ratio CH:Ok:HX (X=Cl, Br)=1:1.2:1.5, cat. КУ-2x8, CH - 5 mas.%), Ec=4.5g-equ/g)

Oxidizing agents and concentration	Conversion of CH** (HCl / HBr), %	Yield, %	
		Hydroxychloride	Hydroxybromide
H_2O_2 (30%-water solution)	86.3 / 81.2	78.4	73.5
NaOCl (110-118 g-ion/l active chlorine)	82.6 / 78.6	76.2	71.8
H_2O_2•$[CO(NH_2)_2]$ (30-35% active oxidizer	76.5 / 72.6	67.6	64.7
$(CH_3)_3COOH$	42.3 / 52.6	35.4	41.3
$C_6H_5C(CH_3)_2OOH$	45.2 / 58.5	38.6	46.4
*Air oxygen	- / 8.2	-	6.0

* under these conditions, HCl is not oxidized; HBr is mainly oxidized to molecular bromine Br_2 and partially to HOBr, ** the numerator of the fraction is HCl and the denominator is HBr.

For this reason, the yield of hydroxybromide is very low. As can be seen, H_2O_2 and NaOCl can be considered effective oxidizing agents for these processes, since they provide high conversion of cycloolefin and the yield of hydroxyhalide.

2. The influence of various factors on the course of the reaction and the yield of target products

The yield of hydroxyhalide cycloolefin derivatives is highly dependent on the type of catalysts used and their acidic properties. The results obtained in this direction are summarized in tables 2 and 3. As can be seen from the results, water-soluble catalysts of the homogeneous type demonstrate stable efficiency, providing cycloolefin conversion and high yield of target products. However, their removal from products after the reaction and reuse leads to a technological problem.

It has been established that low-concentrated solutions of acids HCl and HBr in the presence of H_2O_2 or NaOCl form active electrophilic MSC, HOX (X=Cl, Br) by a reversible reaction

$$HX + H_2O_2\ (NaOCl) \rightleftharpoons HOX + H_2O\ (NaCl) \quad (1)$$

H-form sulfonic cation exchangers КУ-2х8 and КУ-23х8 provide both high conversion of cycloolefins and the yield of target products. This is probably due to the maintenance of stable acidity (pH value) of the reaction medium in the oxidation reaction of HX with H_2O_2 or NaOCl, shifting the balance to the right - towards the production of MSC and facilitating attack and combination. the resulting active electrophilic MSC to the double bonds of the substrates.

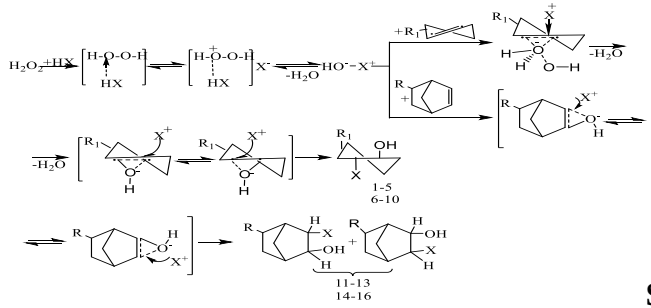
On the other hand, these catalysts can be easily separated from the catalyst by filtration and reused after regeneration. For this reason, in subsequent studies we used solutions of H_2O_2 and NaOCl as oxidants, and КУ-2х8 and КУ-23х8 as catalysts.

Table 2.
Influence of the nature of the catalyst on the yield of hydroxychloro(bromo)ides CH (T=50°C, τ=4,0 h, molar ratio CH:H_2O_2:HX (X=Cl, Br)=1:1.2:1.5, cat. КУ-2х8, CH- 5 mas.%,Ec=4.5 g-equ/g

Catalysts	Conversion of CH (HCl / HBr), %	Yield, %	
		Hydroxychloride	Hydroxybromide
MoO_3	59 / 54	48.0	45.0
V_2O_5	75 / 64	55,0	51,0
$Na_2WO_4•2H_2O$	68 / 58	53.0	49.0
$(NH_4)_2MoO_4$	79 / 75	65.0	60.0
$(NH_4)_2WO_4$	82 / 80	75.0	73.0
NH_4VO_3	79 / 69,5	64	56
KU-2x8	89 / 85	83.0	79.4
KU-23x8	86 / 84	81.0	80.6

* the numerator corresponds to the conversion of CH during the production of hydroxychloride; and the denominator corresponds to the conversion of hydroxybromide upon receipt.

It has been established that CH, BCH-2-ene, alkyl derivatives under mild conditions in the H_2O_2 (or NaOCl) - HX system (8-15% solution) in situ through metastable HOX electrophilic complexes according to the above equation are added via the double bond with the formation of the corresponding chloro(bromo)hydroxyhalides according to scheme 1:



Scheme 1

where: X=Cl (1-5 and 11-13), Br (6-10 and 14-16); R_1=H (1,6), 1-CH_3 (2,7), 3(4)-CH_3 (3,8), 4-CH=CH_2 (4,9), 1-$COCH_3$ (5,10); R=H (11,14), 5-CH_3 (12,15), 5-CH=CH_2 (13,16)

The yields of chloro(bromo)bicyclo[2.2.1]heptanols and hexanols are given in Table 4. An increase in temperature from 30°C to 50°C led to a corresponding increase in the yield of hydroxyhalides [73.4–79.5% (1–5), 70.3–63.4% (11–13) for chlorohydrins and 75 .4–77.6% (6–10), 64.5–67.5% (14–16) for bromohydrins]. With some exceptions, the yield of bromine hydroxy halides is only 3-5%. This may be due to the fact that HOBr is less reactive than HOCl and the electrophilicity of bromine is relatively low. In contrast, cycloolefins have different reactivity due to their different structures.

Table 3.

Effect of temperature on the yield of hydroxychloro(bromo)ides of cycloolefins (molar ratio CH:HX:OK*=1:1,2:1,5, τ=6-8 h, without the presence of a catalyst)

№	Compound	Yield, %			
		Temperature, °C			
		30	40	50	60
1	2-chlorocyclohexane-1-ol	77.2	78.4	79.5	76.6
3	2-chloro-4-methylcyclohexane-1-ol	69.3	73.3	74.8	72.5
4	2-chloro-5-vinylcyclohexane -1-ol	61.5	67.3	68.5	65.7
12	3-chloro-5-methylbicyclo[2.2.1]heptane-2-ol	61.4	68.0	70.3	65.8
13	3-chloro-5-ethenylbicyclo[2.2.1]heptanes-2-ol	58.7	62.6	63.4	59.7
6	2-bromocyclohexane-1-ol	69.6	73.5	75.4	70.2
7	2-bromo-1(2)-methylcyclohexane-1-ol	66.8	70.6	73.4	68.5
9	3-bromo-5-ethenylbicyclo[2.2.1]hexane-2-ol	61.5	64.7	65.6	60.0
10	1-[2-bromo-1-hydroxycyclohexyl]ethane-1-one	72.0	76.0	77.6	71.5
16	3-bromo-6-ethenylbicyclo[2.2.1]heptanes-2-ol	61.2	65.0	67.5	60.4

*- oxidizer

Since the first stage of the reaction we studied occurs in a heterophase system, at the initial stage of our research, cyclohexene was chosen as a model reaction and kinetic region where the formation of electrophilic MSCs (HOX) and hydroxyhalide derivatives occurs.

As can be seen from the results shown in Fig. 1a,b, changing the rate of stirring of the reaction mass significantly affects the formation of electrophilic MSCs, the yield of hydroxyhalide derivatives of cycloolefin and the rate of these reactions.

When carrying out the process under stationary conditions, without stirring the reaction mass, according to the results of GLC analysis (curve 1), the yield of the target product does not exceed 8-10%.

The stirring speed is 300-450 cycles/min. and increases the yield of the target product by 75-82%. Increasing the stirring speed to another 500 cycles/min does not significantly affect the product yield and reaction rate.

A comparison of the values of the initial rates calculated on the basis of the curves shown in Figure 1a shows that the initial reaction rate in the absence of stirring (Table 4) is $0.667.10^{-3}$ mol/l.min, and stirring at a speed of 400 cycles/min. leads to a rate of $6.33.10^{-3}$ mol/l.min. A further increase in this parameter does not have a significant effect on the speed of the process (Fig. 1b).

Under the conditions of coupled reactions, the first stage of the process is the consumption of H_2O_2; the formation of electrophilic MSCs (in the absence of cycloolefin) occurs at a high rate, which in turn leads to unproductive consumption (decomposition) of H_2O_2. and HOX. This factor can be eliminated by regulating the rate of supply of H_2O_2 to the reaction zone.

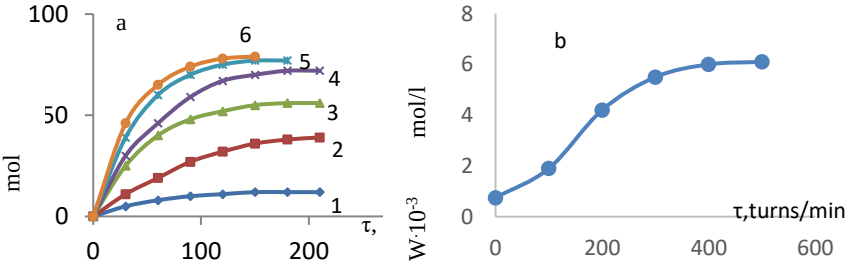


Fig 1. Dependence of the yield of CH hydroxychloride (a) and the initial speed (b) on the intensity of stirring the reaction mass (T, 30°C; molar ratio of CH:HCl: H_2O_2=1:2:1, H_2O_2 (time of feeding into the system) =120 min.; stirring speed – turns/min: 1-0.2-100, 3-200, 4-300, 5-400, 6-500)

It is necessary to select optimal conditions that regulate both the formation of electrophilic MSCs and their attack on the double bonds of the substrate and its attachment.

From the results given in Table 4, it is clear that the rate decreases from $7.17 \cdot 10^{-3}$ mol/l•min to $2.25 \cdot 10^{-3}$ mol/l•min with the introduction of peroxide for 150 minutes. Apparently, the presence of cycloolefin in the reaction mixture and the gradual introduction of H_2O_2 into the reaction zone lead to an increase in the yield of the target product and the reaction proceeds with relatively high selectivity.

Table 4.

The effect of changing the acid concentration and the time of supply of H_2O_2 to the system on the yield of hydroxychlor(brom)ide and the reaction rate (T, 40°C, CH:HX:H_2O_2=1:1.5:1.5)

submission time H_2O_2 , min.	Reaction rate $W \cdot 10^{-3}$ mol/l min	HCl mas.%	Yield of hydroxychloride of CH, mas..%	Reaction rate $W \cdot 10^{-3}$ mol/l min	HCl mas.%	Yield of hydroxychloride of CH, mas..%	Reaction rate $W \cdot 10^{-3}$ mol/l min
Once	7.17	36	10	0.1575	15	19.5	0.9583
30	4.75	26	20.5	0.6875	8	76.3	6.875
90	3.65	16	12.6	1.542	5	72.0	3.583
150	2.25	12	80	3.042	3	41.5	2.233
		6.0	43	6.917			

On the other hand, as can be seen from the results given in tables 4 and 5, the yield of target products, the reaction rate and the selectivity of the process directly depend on the concentration of the hydrohalic acids used. Reducing the concentration of hydrochloric acid from 36.0 to 12 wt.% increased the yield of cyclohexene hydroxychloride from 10 to 80 wt.% and the reaction rate from $0.1575.10^{-3}$ mol/l.min to $3.042.10^{-3}$ mol/l min. Despite the increase in speed to . $6.17.10^{-3}$ mol/l.min., the yield of the target product does not exceed ~43%. A similar situation is observed when the concentration of HBr acid is reduced from 15 wt.% to 5 wt.%.

Table 5.

Effect of acid activity on the yield of hydroxyhalides (HOX). (*in the absence of CH, temperature 20°C, HX: H_2O_2=1:1.5) (X=Cl, Br)

Concentration of HCl		*Yield,%	Concentration of HBr		*Yield, %
mas, %	mol/l	HOCl	mas, %	mol/l	HOBr
3	0.82	8.2/ 2.3	3	0.37	3.75/ 3.33
5	1.4	13.7/ 4.6	5	0.62	6.23/ 5.2
10	2.7	23.6/ 6.86	8	0.98	10.4/ 9.8
12	3.3	27.42/ 10.1	10	1.23	-
15	4.1	31.0/ 6.8			-

* the numerator corresponds to the theoretical output, the denominator to the practical output.

Taking this into account, we carried out further studies by adding the required amount of water to the reaction zone.

From the above, we can conclude that when using low-concentrated solutions of hydrohalic acids and H_2O_2 (NaOCl), the balance of the oxidation reaction can be completely aimed at obtaining MSC and can be considered a practically important system for obtaining functional derivatives of unsaturated compounds *in situ*.

The speed of the process and the yield of products largely depend on the amount of catalyst and temperature changes. The results obtained in this direction are shown in Tables 8-9, respectively. From the results of table 8 shows that when the amount of catalyst (KU-23x8) increases from 5 to 20%, the rate of the hydroxychlorination reaction increases from $1.97.10^{-2}$ mol/l.min to $13.4.10^{-2}$ mol/l.min, and for the hydroxybromination reaction it increases from $2.42•10^{-2}$ mol/l.min to $16.13•10^{-2}$ mol/l.min. This is due to the fact that as the amount of cation exchange resin increases, the reaction medium (pH value) remains stable and more suitable conditions for the oxidation of acids H_2O_2 (NaOCl). The easier oxidation of HBr compared to the acid HCl is likely due to their bond energies and electronegativity values (Cl has greater electronegativity than Br).

Taking this into account, we carried out further studies by adding the required amount of water to the reaction zone.

From the above, we can conclude that when using low-concentrated

solutions of hydrohalic acids and H_2O_2 (NaOCl), the balance of the oxidation reaction can be completely aimed at obtaining MSC and can be considered a practically important system for obtaining functional derivatives of unsaturated compounds *in situ*.

Under conditions of coupled reactions, the rate of MSC formation and its productive consumption directly depend on changes in the temperature regime of the process. From the results given in table. 9, it is clear that the reaction rate in both cases varies from $2.77 \cdot 10^{-2}$ to $19.1 \cdot 10^{-2}$ mol/l.min for the hydroxychlorination reaction and from $1.76 \cdot 10^{-2}$ to $15.33.10^{-2}$ mol/l.min for the hydroxybromination reaction.

Table 6.

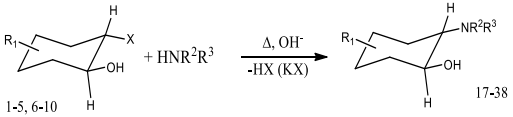
Change in the rate of HX oxidation during the production of CH hydroxychloro(bromo)ides (cat. KU-2x8, 10 wt.%, CH:HH:H_2O_2=1:1.5:1.5) on temperature

Temperature, °C	Concentration of HCl (12 wt..%)	Concentration of HBr (8 wt.%)
	$W \cdot 10^{-2}$ mol/l•min	$W \cdot 10^{-2}$ mol/l•min
20	2.77	1.767
30	3.15	3.723
40	4.57	5.467
50	19.1	15.33
40*	1.67*	0.911*

*- in the absence of cyclohexene in the system

3. Synthesis of N-substituted cyclohexanols based on bromo(chloro)hydroxides of alkyl derivatives of cyclohexene and bicyclohept-2-ene

Chloro(bromo)hydroxy halides of cycloolefins react with primary or secondary amines in a basic medium at 40-50°C for 3-5 hours to form the corresponding N-substituted cyclohexanols, scheme 2:



Scheme 2

where (1-5, 6-10)- see scheme 1; R^1=H (17-20,33), 1-CH_3, 1-C(O)CH_3 (25-28), 3(4)-CH_3 (34,35), 4-CH=CH_2 (29-32), R^2=R^3=C_2H_5 (17,25,29), CH_2CH_2OH (18,22,26,30), R^2+R^3=(-CH_2-)$_5$ (19,23,27,31), (-CH_2CH_2-)$_2$O (20,24,28,32); R^2=H, R^3=C_4H_9 (27,34,37), C_3H_7 (36), i-C_4H_9 (35,38).

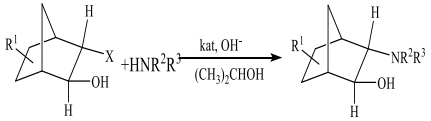
The structure of the obtained hydroxyhalides and amino alcohols was determined by IR, ^{1}H, ^{1}3C NMR spectral analysis. In the IR spectrum, absorption bands are observed at δ=3480-3492, 3350 (OH), 550-619 (CBr), 780, 760 (CCl), 1666, 1658 (CN), cm^{-1}. In the ^{1}H NMR spectrum, depending on the structure of the substituents, signals are 1.33-1.76 ppm. correspond to the protons of the cyclohexane ring and 1.32-multiplets, 2.0-2.3 and 3.61 ppm. broad singlets are observed for the protons of the N-H and OH functional groups, respectively. The protons of the methyl group are in a doublet or triplet at δ = 0.92-1.13 ppm, and the protons of the vinyl group are at 4.89-4.98 ppm are found in the form of double doublets (spin-spin coupling constants J = 10.3, 2.3Hs and 16.8,2.1Hs). The results of the obtained amino alcohols and their physicochemical characteristics are given in Table 7. From the results given in the table, it is clear that the yields of amino alcohols vary depending on the structure of the substituent and the amine.

Table 7.
Yields and characteristics of N-substituted bicyclo[2.2.1]heptanols

№	Compounds	Yield %	T.melt °C
17	2-(Diethylamin)cyclohexane-1-ol	82,0	$T_{boil.}$115-170°C (2.5mm.Hg)
19	2-(Piperidine-1-yl)cyclohexane-1-ol	73.0	49-52
20	2-(Morfoline-4-il)cyclohexane-1-ol	68,0	66-68
21	2-(Dietihylamin)-2-methylcyclohexane-1-ol	56.7	$T_{boil.}$127-128.5 (2mm.Hg)
22	2-[Bis-(2-hydroxyiethyl)-amin]-2-cyclohexane-1-ol	48.4	178-180
23	2-Methyl-2-(piperidine-1-yl)-cyclohexane-1-ol	71.1	84-86
24	2-Methyl-2-(morfoline-4-yl)-cyclohexane-1-ol	45.2	98-101
31	5-Vinyl-2-(piperidine-1-yl)-cyclohexane-1-ol	57.4	67-69
32	5-Vinyl-2-(morfoline-4-yl)-cyclohexane-1-ol	54.5	82-84

3.1. Preparation of aminoalcohols based on chloro(bromo)hydroxides of BCGH2-ene and alkyl derivatives

The preparation of the corresponding amino alcohols was carried out according to the following scheme:



11-16 39-52

Scheme 3

where, R=H, $R^2=R^3=C_2H_5$ (39,43,46); CH_2CH_2OH (40,47); $R^2+R^3=(-CH_2-)_5$ (41,44,48); $(CH_2CH_2)_2O$ (42,45,49); $R^2=H$, $R^3=C_3H_7$ (50), C_4H_9 (51), i-C_4H_9 (52).

The yields and indices of the some amino alcohols are given in Table.

In the IR spectrum of N-substituted bicyclo[2.2.1] heptanols, the following absorption bands are observed, characteris-tic of stretching and bending vibrations of various bonds of groups located in the structural fragment of the molecule: 724, 774, 1345, 1360, 1460-1470 cm^{-1} bond C-H groups (CH_2 and CH_3) and 1224-1250 cm^{-1} (C-O-C), 1296, 1521 cm^{-1} (CN, ν), 1045, 1112, 3280-3564 cm^{-1} (OH). In the ^1H NMR spectrum, depending on the structure of the substituents, the multiplets are in the region of 1.32-2.18 ppm. for protons of the norbornene fragment, 2.3, 4.1 and 3.58 ppm. broad singlets are observed for the protons of the N-H and OH groups, respectively. Protons of the methyl group are detected as a doublet or triplet at δ=0.92-1.13 ppm, protons of the vinyl group are detected as a doublet at 4.89-4.98 ppm. (J=10.3,2.3 Hs and 16.8, 2.1 Hs).

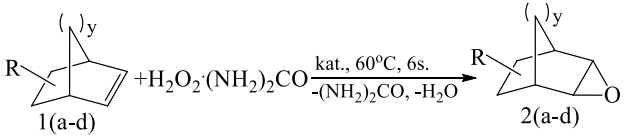
Table 8.
Yields and characteristics of N-substituted bicyclo[2.2.1]heptanols

№	Compounds	Yield %	T.melt °C
39	3-(Diethylamin)bicyclo[2.2.1]heptane-2-ol	81.8	57-59
41	3-(Piperidine-1-yl)bicyclo[2.2.1]heptane-2-ol	70.1	83-85
42	3-(Morfoline-4-il)bicyclo[2.2.1]heptane-2-ol	67.3	96-98
43	3-(Diethylamin)-5-methylbicyclo[2.2.1]-heptane-2-ol	78.6	81-83
44	5-Methyl-3-(piperidine-1-yl)bicyclo[2.2.1]heptane-2-ol	71.8	85-87
45	5-Methyl-3-(morfoline-4-yl)bicyclo[2.2.1]-heptane-2-ol	74.2	103-105
46	3-(Propylamin)-5-methylbicyclo[2.2.1]-heptane-2-ol	78.1	70-72
51	5-Viniy-3-(piperidine-1-yl)bicyclo[2.2.1]heptane-2-ol	67.9	98-101
52	5-Vinyl-3-(morfoline-4-yl)bicyclo[2.2.1]heptane-2-ol	74.8	114-116.5

3.2. Counter synthesis of alkylcyclohexene and bicyclo[2.2.1]hept-2-ene aminoalcohols

In order to elucidate the structure of amino alcohols obtained by the reaction of halohydrin derivatives of cycloolefins with secondary amines, epoxy derivatives 4-methyl-, 4-vinyl-CH and 5-methyl-, 5-vinyl-BCH were used. The synthesis of epoxy derivatives of CH and BCH and subsequent aminolysis of the oxirane ring of the latter with morpholine and piperidine to the corresponding amino alcohols was carried out.

The reaction of epoxidation of reactants on a binary catalyst $[(NH_4)_{10}W_{12}O_{11}+CoBr_2]$ (2.5-3.5 g/l, W^{6+}-15-20 wt. %) was carried out with the participation of the reactant system: olefin : $H_2O_2.(NH_2)_2CO$: CH_3COOH = 1:2:0.2 molar ratio on microstructured carbon according to scheme 4:



Scheme 4

where, y=0, R=1-CH_3-(a), 4-CH_2=CH-(b); y=1, R=5-CH_3-(c), 5-CH_2=CH-(d)

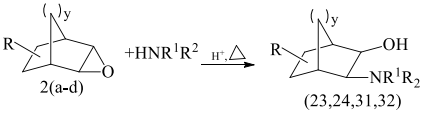
Table 9

Indices of epoxides of methyl and vinyl derivatives of alkylcyclohexene and bicyclo[2.2.1]hept-2-ene (olefin:CH_3COOH:H_2O_2·$(NH_2)_2CO$=1:0.2:2, cat.-[$(NH_4)_{10}W_{12}O_{41}$+$CoBr_2$=2g (W^{6+}, 15% wt.; T=60^{0}C, τ=6 h)]

Epoxides	Yield, %	T.boil °C	d_4^{20}
(a) 4(3)-Methyl-7-oxabicyclo[4.1.0] heptane	76.5	143-145	0.9412
(b) 4-Vinyl-7-oxabicyclo[4.1.0] heptane	70.4	142-143	0.9508
(c) 6-Methyl-3-oxatricyclo [3.2.0$^{2.4}$]octane	68.0	140-141	0.9795
(d) 6-Vinyl-3-oxatricyclo [3.2.0$^{2.4}$]octane	63.6	155-156	0.9863

As can be seen from table. 14, the yield of epoxides is 70.4%, 76.5%, for alkyloxybicyclo[4.1.0]heptanes 2(a,b), and for alkyloxytricyclo[3.2.0$^{2.4}$]octanes (2c,d), 63.6%, 68%). respectively.

Reaction of the oxirane ring of epoxides 2(a-d) with piperidine and morpholine in a weakly acidic medium (in the presence of КУ-2х8 or КУ-23х8) containing CH (23,24,31,32) and BCH (44, 45, 51, 52) the corresponding aminoalcohols were synthesized, Scheme 5:



Scheme 5

The physicochemical properties of the obtained amino alcohols correspond to analogues obtained by aminolysis of chloro(bromo)hydroxides of bicyclo[2.2.1]hept-2-ene with piperidine and morpholine. This shows that, regardless of the method of obtaining amino alcohols, the structural fragments of the substrate do not change during the reaction.

4. Conformational properties of hydroxyhalogen- and N-substituted hydroxy derivatives of CH.

2,3-disubstituted cyclohexenes, containing oxygen-containing functional groups (OH, OCH_3, $OCOCH_3$, etc.) and bromine (chlorine) atoms in their molecules, are predominantly in a pseudoaxial orientation, which indicates their dependence on the spatial structure and the effect of hyperconjugation.

However, information about the oxidative hydroxyhalogenation of 1-, 4-alkyl-, 1-acyl- and 4-vinylcyclohexenes and the conformational properties of N-substituted alcohols is practically rare in the literature.

Substituents that are located in the plane of the double bond of the molecule or on a carbon atom close to it are 1-methyl, 1-acyl- and 4-methyl-, 4-vinylcyclohexenes, as well as 5-methyl, 5-vinyl-substituted norbornenes in the process of addition. HOBr and HOCl in situ and the conversion of bromo(chloro)hydrins with amines to amino alcohols also depend on the orientation, conformation, and stereochemical properties of alkyl substituents and can be expect the formation of the following possible conformers *in situ* (1-8):

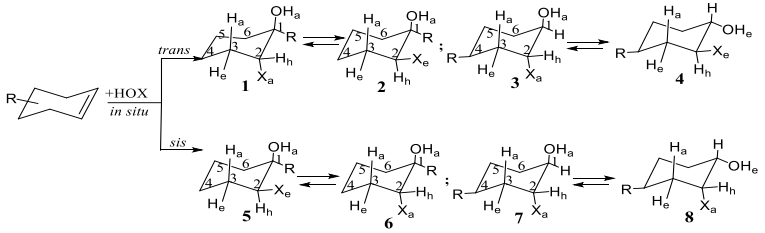


Fig. 2. Conformers of alkylcyclohexene hydroxyhalides in situ (R=1-CH_3 and 1-C(O)CH_3 (1,2,5,6); 4-CH_3- and 4-vinyl (3,4,7,8) ; X=Cl-, Br-

Depending on the nature of the attack of MSC elements (electrophilic Cl (Br) and nucleophilic OH group) on the double bonds of substrates, conformational isomers change differently. For example, the trans coupling of HOX (X=Cl, Br) produces 1-CH_3(e) and 1-acyl(e)-2-*trans*-Cl(Br)(a)-OH(e)- (conf. 1) and 1-CH_3(a) and 1-acyl(a)-2-*cis*-Cl(Br)(e)-OH(a)-cyclohexane (conf. 2), as well as in the case of *cis*-coupling one can expect the formation of 1-CH_3(e) and 1-acyl(e)-2-*cis*-Cl(Br)(e)-OH(a)- (conf. 5) and 1-CH_3(a) and 1-acyl(e)-2-*trans*-Cl(Br)(a)-OH(a)-cyclohexane (conf. 6).

In 4-CH_3- and 4-vinylcyclohexenes, since the substituent groups are located relatively outside the double bond, the trans-coupling of MSCs produces 4-CH_3(e) and 4-vinyl-*trans*-1-OH(a)-2-Cl(Br)(a))-(conf. 3) and *cis*-2-Cl(Br)(e)-1-OH(e)- (conf. 4), and with a *cis* combination one can expect the formation of *trans*-2-Cl (Br)(a)-1-OH(a)- (conf. 7) and 4-CH_3(a) and 4-vinyl-*trans*-2-Cl(Br)(a)-1-OH(e)- cyclohexane (conf. 8) (Fig. 2).

In the equilibrium system of conformers, halogen, hydroxyl groups mainly consist of a diaxial, diequatorial spatial structure, methyl, vinyl,

acyl and NR_1R_2 groups are located in an equatorial spatial position (Fig. 2).

4.1. Stereochemical properties of alkylbicyclo[2.2.1]hept-2-enhalohydroxides and derivatives of N-substituted alcohols.

BCH and its alkyl derivatives, amino alcohols obtained as a result of the conversion reaction with halohydrins and amines (according to GLC) are obtained predominantly in the form of a mixture of two isomers, and the ratio of isomers depends on the orientation properties of the CH_3 and CH_2=CH- groups and on the position they take in space relative to the bicycloheptene fragment depends on the temperature and polarity of the solvents.

Based on the spectral parameters of the reaction products we obtained: halohydrins and amino alcohols, their conformation and stereochemical structure were determined from well-known considerations[4]:

1) an electrophilic particle attacks the double bond of BCH-2 from the *exo* side; 2) As a result of the Wagner-Meerwein rearrangement, electrophilic and nucleophilic species can occupy the C_7 carbon atom in the upper part of the framework; In Scheme 6, the rearranged transition complex (A) is attacked from the endo side of the nucleophile; occurs by producing Wagner-Meerwein type rearrangement products with hydride displacement and proton abstraction

According to other authors [5], in hydrocarbons of the bicyclo[2.2.1]hept-2-ene series, since the bicycloheptene ring is more strained (according to Bayer), electrophilic coupling reactions with its double bond occur.

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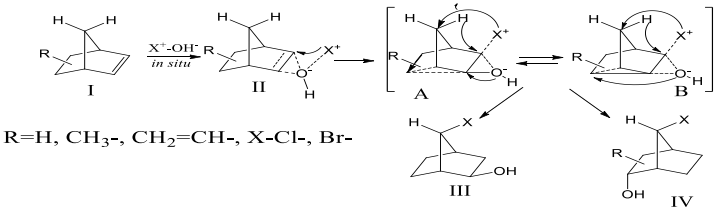
[4] Зык Н.В. Регио и стереохимические аспекты бромхлорирования норборнена / Н.В. Зык, Е.К. Вепоглазкина, В.С. Тюрин, Ю.К. Гришин // Изв. АН.Сер.Хим., -1996, –№.10, -с.2522-2525

[5] Zefirov, N.S. New method for increasing of electrophilicity of weak electrophiles in addition-reactions - wagner-meerwein rearrangement in a reaction of 2,4-dinitrobenzenesulfenyl chloride with norbornene / N.S. Zefirov , N.K. Sadovaja, A.M. Magerramov et.al. // Tetrahedron, -1975, -Vol.31, -N.23, -p. 2948-2952.

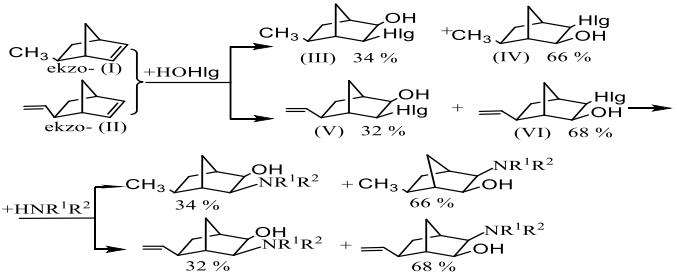
Using GLC, IR, ^{1}H and ^{13}C NMR spectroscopy, the main isomers in the reaction products are 5-alkyl-*exo,endo*-2(3)-halobicyclo[2.2.1]heptan-3(2)-ols (87-92%) , as well as up to 6%, the products of rearrangement of functional groups are obtained: 5-vinyl-*endo(exo)*-2-bromo(chloro)-bicyclo[2.2.1]heptan-7-*syn(anti)*-ol and 5-vinyl-*endo(exo)*-*syn(anti)*-7-(bromo(chloro)bicyclo-[2.2.1]heptan-7-*endo*-ol.

Under our conditions, the generation of rearrangement products in situ can occur according to the scheme of sequential passage of the stage of formation of an oxirane fragment and a transition complex A and B with a three-membered cyclen structure. in equilibrium according to the Fuerst-Platter rule (isomers III and IV), scheme 7:



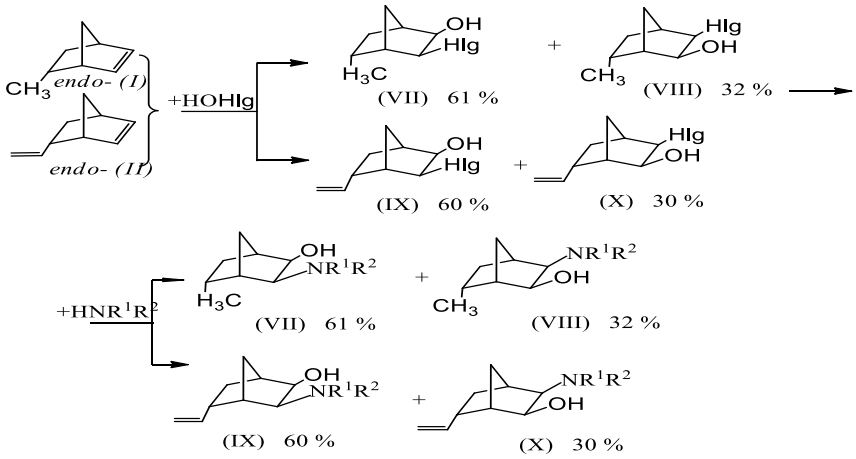
Scheme 6

According to the results of GLC analysis, the oxidative hydroxyhalogenation of *exo*-5-methyl-(I) and *exo*-5-vinyl-(II) bicycloheptanols produces a mixture of 5- and 6-methyl(vinyl)-3-chloro(bromo)-BCH-2-ols. In the case of *exo*-(I) and *exo*-(II), the reaction products seem to be dominated by the 6-methyl(vinyl)BCH-2-ol isomer (IV, VI), Scheme 7:



Scheme 7

In the case of *endo*-isomers of these hydrocarbons (I, II), a mixture of isomers is obtained from a combination of electrophilic intermediates, and at this time isomers (VII and IX) predominate in the mixture, Scheme 8:



Scheme 8

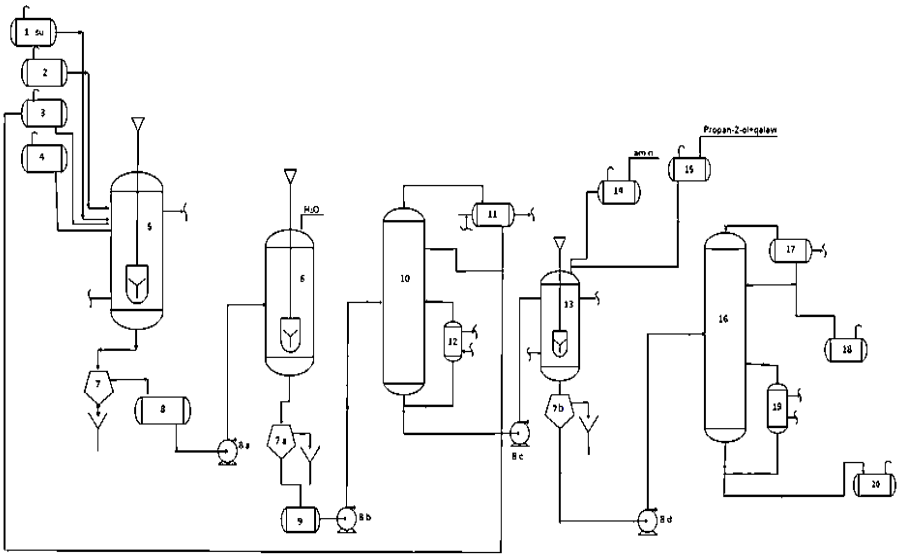
5. Principal technological scheme and material balance of the process for producing hydroxyhalides of mono- and bicyclic unsaturated hydrocarbons and aminoalcohols based on them

Based on the experimental results obtained, a technological scheme for the production of chloro(bromo)hydroxides of cycloolefins and amino alcohols based on primary aliphatic and secondary bicyclic amines has been proposed.

According to the proposed technology, the processes are carried out step by step in the following order. Initially, processes are carried out for the production of chloro(bromo)hydroxides of cycloolefins, their purification and separation, and at the second stage - processes for the production of N-aminoalcohols by reacting them with primary or secondary amines.

The calculated amount of water per container 1 and the estimated amount of cycloolefin per container 2 and hydroxychloro(bromo)hydrohydric acid in container 3 are poured into

reactor 4, then the reaction mass is stirred at intense (500-700 rpm) speed, and from container 4, an aqueous solution of an oxidizing agent (H_2O_2 or sodium hypochlorite) is added at a selected speed. The progress of the reaction is monitored by determining the amount of chloro(bromo)hydroxy derivatives of cycloolefins formed in the organic part (using the GLC method) and determining the consumption of oxidizing agents (H_2O_2-permanganometric, NaOCl-iodometric analysis methods). After completion of the process, the reaction mixture is transferred to fluorescent tank No. 7 to separate the water and the organic layer. The lower organic part is supplied by a transfer pump (No. 6) to container 8 and from there to the neutralizer. There, the organic part is neutralized by washing with a weakly alkaline solution to remove excess hydrogen chloride (hydrogen bromide). Then the neutralized part is fed into apparatus No. 7a for layering. The lower organic part is supplied by a transfer pump (8a) to container No. 9 and from there to the distillation column. Excess cycloolefin from the top of the flask is removed and returned to the cycle. Chloro(bromo)hydroxides obtained from the lower part of the olefin are fed into reactor No. 13 by pump No. 8v, the calculated amount of amine (14) and an alkaline (NaOH or KOH) solution dissolved in propan-2-ol. -ol is added to it from container No. 15. After the reaction is completed, it is supplied to the fluorine tank No. 7v, and from there to the rectification tank No. 16 by transmission pump No. 8d. Propan-2-ol is separated from the top of the flask, collected in container No. 17, and the amine is collected in container No. 18 and returned to the system. The amino alcohol formed in the lower part of the tank is collected in container No. 20. The temperature regime in the rectification coils is regulated using heaters No. 12 and 19.



1-H_2O; 2-cycloolefin; 3-HBr(HCl); 4-oxidizer; 14-amine; 15- containers for propanol-alkali solution, 5-reactor, 6-neutralizator, 7,7a,7b-fluoret, 8- intermediate capacity, 8a,8b,8c,8d-pumps, 9 - capacity for hydroxyhalides, 10,16- rectification column, 17, 18- capacity 12,19 - heater 13- main reactor, 20- capacity for product

The material balance for obtaining 2-chlorocyclohexan-1-ol and 2-(piperidin-1-yl)cyclohexan-1-ol is shown in tables 10 and 11.

Table 10. Material balance for the production of 2-chlorocyclohexane-1-ol (CH:HCl:H_2O_2=1:1:1)

№	Taken compounds	Products	
		Gram	Wt. %
1	Cyclohexene (1)	82	15.3
2	HCl (33 wt. % solution)	110.6	20.6
3	Water	221.4	41.2
4	Hydrogen peroxide H_2O_2 (30 wt.% water solutionp)	113.3	21.1
5	Catalyst	9.8	1.8
	Tottal	537.1	100

Continuation of table10

	Received 2-chlorocyclohexane-1-ol Unreacted cyclohexene Aqueous part (from H_2O_2 consumption, water in acid and H_2O_2 solutions 18+72.1+79.31) Catalyst (used) Loss	125* 393.8 9.8 8.5	23.3 73.4 1.9 1.6
	Total:	537.1	100

* Yield is determined by the amount of the substance that entered the reaction

Table 11. Material balance of the preparation of 2-(piperidin-1-yl)cyclohexane-1-ol (I:II:III=1:1)

№	Taken compounds	Products	
		Gram	Gram
1 2 3 4	2-chlorocyclohexanol (I) Piperidine (II) Propane-2-ol[$(CH_3)_2CHOH$] KOH	135 85 140 56	32.5 20.6 33.6 13.5
	Total	416	100
	Received 2-(Piperidin-1-yl)cyclohexane-1-ол Excess 2-chlorocyclohexan-1-ol Excess of piperidine Propane-2-ol Excess of KOH KBr Loss	 150.5* 2.9 7.6 140 18.0 91.5 5.5	 36 0.7 1.9 33.6 4.4 22.0 1.4
	Total:	416	100

* Yield is determined by the amount of the substance that entered the reaction

CONCLUSION

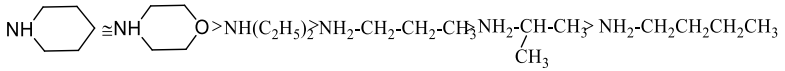
1. The production of hydroxychloro(brom)ides of C_6-C_7 mono-, bicycloolefinic hydrocarbons, their alkyl derivatives, active electrophilic MSC HOX (Cl, Br) in situ mode in the system containing oxidants and HCl, HBr acids under the conditions

of connected reactions in the liquid phase, a new method of obtaining amino alcohols from the reaction of amines with various composition and structure was created [1-3, 12,13,14, 18].

2. It is established that cyclohexene, bicyclo[2.2.1]hept-2-ene and their methyl-, acyl-, ethenyl-derivatives in situ occurs in two stages:
   a) – at the first stage, in mild conditions (20-50°C) with the interaction of 6-15% solutions of HX (X= Cl-, Br-) acids and oxidizers [(H_2O_2, $(NH_2)_2CO.H_2O_2$ (adduct)] the formation of electrophilic MSC (HOX) is observed, which are formed in situ and bind to the substrates by double bonds. Among the applied oxidants (26-30%), H_2O_2 and NaOCl solutions with an active chlorine of 110 g-ion/l are more effective, and in their presence, respectively, 72.6-78.4% yield of chlorine-, 70.6-76.0% yield of bromocyclohexanols, and 62.6-66.0% yield of chlorine - 61.0-65.0% brombicyclo[2.2.1]-heptanols are obtained;
   b) - at the second stage, N-substituted cyclohexanols with a yield of 45.8-82% and bicyclo[2.2.1]heptanols with a yield of 61.2-74.3% were obtained, respectively, by the reaction of chloro(bromo)hydroxides of alkylcycloolefins with C_5-C_6-cyclic and C_3-C_4 aliphatic amines in the basic environment [4-6, 11, 12].
3. It was determined that during the synthesis of chloro(bromo)hydroxides of bicyclo[2.2.1]hept-2-ene and alkyl derivatives (at a temperature above 60°C) as a result of migration of halogen and hydroxyl groups to the 7th carbon atom by Wagner-Meerwein rearrangement and endo- or exo attack of the electrophile MSC to the 2nd carbon atom, the main isomers with a yield of 87-92% - 5-vinyl-exo-, 5-vinyl-endo-2(3)-bromo(chloro) 3-6% 5-vinyl-endo-, endo-2(3)-bromo(chloro)bicyclo[2.2.1]heptan-3(2) along with bicyclo[2.2.1]heptan-3(2)-ol and 5-vinyl(exo)endo-2-bromo(chloro)bicyclo[2.2.1]heptane-7-syn(anti)-ol, as well as

5-vinyl-endo(exo)-syn(anti). It is also observed that 7-bromo(chloro)bicyclo[2.2.1]heptan-2-endo(exo)-ol is obtained [7, 8, 13, 16, 18].

4. The isomeric composition of amino alcohols varies depending on the isomeric composition of chloro(bromo)hydroxides of cycloolefins. Their yield depends on the molar ratio of amines, when changing the ratio of chloro(bromo)hydroxides to cycloolefins by 1.5-2.5 mol, the yield of aminocyclohexanols is 45.8-82%, and in the case of aminobicyclo[2.2.1]heptanols, the yield is 61 ,2-74.3%. In each case, the yield of amino alcohols from bromohydroxides of cycloolefins is 3-6% higher than from their chlorine analogues, and this is due to the fact that the C-Br bond is more mobile than the C-Cl bond [9, 15, 17].
5. According to the proposed mechanism of the process, halohydrins are formed by oxirane ring according to Platter's rule, and Wagner-Meerwein rearrangement products are formed by sequentially passing through the stages of formation of oxirane and three-membered nortricyclene fragments [10-12].
6. Epoxides of methyl, vinyl derivatives of cyclohexene and bicyclo[2.2.1] hept-2-ene in the presence of $H_2O_2(NH_2)_2CO$ adduct and polyoxoperoxotungstate catalyst with 70-83% yield and the corresponding amino alcohols were obtained from the aminolysis of the latter with piperidine and morpholine. It was determined that the physico-chemical and spectral indicators of these amino alcohols correspond to their analogues obtained from chlorine (bromine) hydroxides [1, 11-14, 17, 19].
7. The addition of aminoalcohols in the amount of 1.0-2.0 wt.% to M-8, M-10, coolant-lubricants increases fungicidal and bactericidal properties and it was established that this is due to the change in the nucleophilic properties of the N-substituted fragments of the amino alcohol molecule and changes in the following order.



8. For the first time, the process of obtaining chloro/bromohydrins of mono- and bicyclic olefins and corresponding amino alcohols based on them with a yield of 60-85% was developed, the principle technological scheme was drawn up and the material balance was calculated.

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The defense will be held on 19 April 2024 at 14.00 at the meeting of the One-time Dissertation Council with registration number BFD 1.16/1 in the Dissertation Council ED 1.16 Supreme Attestation Commision under the President of the Rebublic of Azerbaijan operating at the Institute of Petrochemical Processes named after acad. Y.H.Mammadaliyev of the Ministry of Science and Education of the Rebublic of Azerbaijan

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Dissertation is accessible at the Institute of Petrochemical Processes named after acad. Y.H.Mammadaliyev, Ministry of Science and Education of the Republic of Azerbaijan Library

Electronic versions of dissertation and its abstract are available on the official website of the www.nkpi.az

Abstract was sent to the required addresses on 18 March 2024.

Signed for print: 13.03.2024

Paper format: A5 60x90 1/16

Volume: 39532

Number of hard copies: 20