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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

**INDUCTIVE OXIDATION OF C₁₀-C₁₂-POLYCYCLIC
UNSATURATED HYDROCARBONS IN THE LIQUID PHASE
WITH HYDROGEN PEROXIDE**

Specialty: 2314.01-Petroleum chemistry

Field of science: Chemistry

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Baku - 2023

The work was performed at the laboratory of "Alicyclic compounds" of the Institute of Petrochemical Processes named by academician Y.H. Mammadaliyev of Ministry of Science and Education of the Republic of Azerbaijan.

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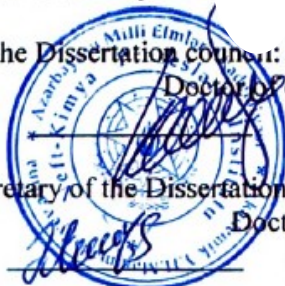
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GENERAL CHARACTERISTICS OF THE WORK

Relevance and development of the topic. In the field of modern petrochemical and organic synthesis, the main attention is given to the development of energy and material-saving processes for the formation of small amounts of additives and obtaining the desired products with high yield.

Currently, one of the main directions is the development of processes for obtaining polyfunctional compounds that store oxygen through oxidation carried out in the liquid phase in accordance with the requirements of "green chemistry". These reactions are carried out at lower temperatures and with the formation of fewer side compounds.

Oxidative catalytic functionalization of saturated and unsaturated hydrocarbons remains a priority direction in modern times. Although the catalytic systems used are not completely perfect compared to enzymes, carrying out oxidation processes with their participation is technologically more efficient.

Since it is practical to use H_2O_2 , it is preferred in modern research for the oxidation of hydrocarbons. This is due to the fact that, firstly, reactions involving H_2O_2 are carried out selectively in the liquid phase, according to the requirements¹ of "green chemistry". Secondly, the processes are carried out with the participation of complex systems made from the immobilization of aluminosilicates, carbon or nanostructured materials, and other heterogeneous catalysts.

Numerous studies have been devoted to the research on the oxidation of aliphatic, alicyclic, alkenylaromatic unsaturated hydrocarbons and their derivatives from the carbon-carbon double

¹ Hamamoto, N.A. Recyclable catalytic system for green oxidation using. Temperature responsive catalysis/N.A.Hamamoto, S.İkagami//J.Synt.Org.Chem. - 2008, V.6, №3, pp.205-214

bond^{2,3}. Oxidative functionalization of unsaturated compounds on an industrial scale is carried out with the participation of compounds of molybdenum, tungsten and other transition metals.

One of the main problems in the process of oxidation of hydrocarbons in the liquid phase with the presence of homogeneous catalysts is their separation and reuse from the reaction mixture. The current problem can be solved by heterogenization of these compounds. In this direction, it is considered appropriate to introduce transition metals or their compounds, cations, into the vacant places in the structure of micro- and mesoporous materials.

The examination of literature sources shows that in modern times, the main research works are carried out in the direction of oxidation of C₅-C₈ monocyclic unsaturated hydrocarbons with the participation of the above-mentioned catalysts. Oxidation of di-, tri- and polycyclic unsaturated hydrocarbons, including bridged compounds, was studied only in the presence of peroxyacids. In the literature, information in this direction is found in episodic cases.

Currently, one of the urgent issues is the development of methods of oxidation of polycyclic unsaturated hydrocarbons with the participation of environmentally friendly oxidants (molecular oxygen, hydrogen peroxide) and the development of effective catalytic systems for the implementation of this process. The study of the epoxidation process of tri- and tetracyclic bridged unsaturated hydrocarbons with the presence of these catalysts is of both scientific and practical interest.

The presented dissertation work is aimed at solving a topical issue of catalytic functionalization of bi-, tri- and tetracyclic unsaturated hydrocarbons of various structures by means of

² Matienko, L.I. Selective catalytic oxidation of hydrocarbons/L.I. Matienko, L.A. Moslova, G.E. Zaikov//Успехи химии, - 2009, Т.78, No.3, - p. 227-247

³ Alimardanov, Kh.M. Oxidative dihydroxylation of alicyclic unsaturated hydrocarbons with vinyl and norbornene fragments in a pseudo-homogeneous system//Kh.M.Alimardanov, N.I.Garibov, M.Ya.Abdullaeva [et al.] Russian Journal of General Chemistry, - 2013, Т.83, No.1, - p.70-79

hydrogen peroxide and summarizing the obtained results.

Object and subject of research. The presented thesis dedicated catalytic oxidation synthesized bridged tri- and tetracyclic unsaturated hydrocarbons and some of their alkyl derivatives based on cyclopentadiene, cyclohexa-1,3-diene, 4-vinylcyclohexene and bicyclo [2.2.1] hept-2-en with hydrogen peroxide or hydroperite (a clathrate adduct of urea with hydrogen peroxide) for preparation of corresponding epoxides and diatomic alcohols.

Research goals and objectives. The issues to be resolved in the dissertation include the following:

- Synthesis of tri- and tetracyclic bridged diene hydrocarbons based on cyclopentadiene, cyclohexa-1,3-diene, 4-vinylcyclohexene and norbornene and their catalytic hydrogenation to monoolefins, research of the reaction and finding of optimal conditions;
- Preparation of phosphorheteropolymolybdate catalytic systems modified with Co^{3+} and Ce^{3+} cations and HBr for selective oxidation of C_{10} - C_{12} tri- and tetracyclic olefins with hydrogen peroxide;
- Investigation of the factors influencing the reaction of catalytic oxidation of C_{10} - C_{12} tri- and tetracyclic bridged unsaturated hydrocarbons to epoxides and diatomic alcohols through H_2O_2 with the participation of the developed catalytic system and determination of their optimal conditions;
- Study of the comparative dependence of structure and oxidation capacity of C_{10} - C_{12} tri- and tetracyclic unsaturated hydrocarbons;
- Production of vicinal aminoalcohols with polycyclic fragments based on C_{10} - C_{13} macrocyclic bridged epoxide and diols and investigation of the field of application.

Research methods. To determine the composition and structure of the catalytic complexes prepared in the research process, obtained tri- and tetracyclic bridged unsaturated hydrocarbons and their oxygenated compounds were used gas-liquid chromatographic, chromato-mass-spectroscopic, as well as IQS, NMR, DSK, SEM, RFA and other physical-chemical methods.

Main clauses defended

- The results of research conducted in the direction of synthesis of C₁₀-C₁₂ tri- and tetracyclic bridged diene hydrocarbons based on cyclopentadiene, cyclohexa-1,3-diene, bicyclo [2.2.1] hept-2-ene and 4-vinylcyclohexene and their hydrogenation to monoolefins;
- Results obtained in the direction of preparation of cobalt-molybdenum bromide and cerium-molybdenum-bromide catalytic systems for oxidation of synthesized hydrocarbons through hydrogen-peroxide and its complex with urea (hydroperite) and research by physico-chemical methods;
- The results of research conducted in the direction of epoxidation and hydroxylation of C₁₀-C₁₂ tri- and tetracyclic bridged diene and monoolefin hydrocarbons;
- Results from a comparative study of the relationship between the structure and oxidizability of tri- and tetracyclic bridged unsaturated hydrocarbons and their alkyl derivatives.

Scientific novelty of the research. For the first time, macrocyclic epoxides and diatomic alcohols were obtained by inductive catalytic oxidation of C₁₀-C₁₂ polycyclic, bridged unsaturated hydrocarbons with hydrogen peroxide (or H₂O₂·CO(NH₂)₂ adduct).

Catalysts with high activity for selective oxidation (epoxidation and dihydroxylation) of polycyclic (tri- and tetracyclic) unsaturated hydrocarbons were prepared and optimal conditions of reactions were determined with their participation.

It was determined that the epoxidation of C₁₀-C₁₂ polycyclic dienes synthesized on the basis of cyclopentadiene, cyclohexadiene, norbornene, and vinylcyclohexene mainly proceeds from cyclopentene or cyclohexene fragments in the molecule. The comparative nature of the epoxidation and hydroxylation ability of the indicated hydrocarbons is shown.

Theoretical and practical significance of the research. The development of the theoretical and experimental bases of the epoxidation reaction of C₁₀-C₁₃ tri- and tetracyclic bridged unsaturated hydrocarbons allows the introduction of fundamentally

new epoxidation processes based on petrochemical raw materials using new catalytic systems on an industrial scale.

Oxyoligomerization of C₁₀-C₁₂ tricyclic diene hydrocarbons can be used to obtain high-quality thermoset coating material.

These compounds are recommended to be widely used as plasticizers in polymer materials and synthons in the production of biologically active substances.

Synthesized new C₁₀-C₁₃ bridged polycyclic amine alcohols have antimicrobial properties and are recommended for use as antimicrobial additives in motor oils.

Personal involvement of the author. Determination of goals and tasks, selection of research methods, preparation of catalysts, verification of their activity, synthesis of primary substances, conducting experiments were performed independently by the applicant. Processing of received data, their analysis and interpretation in the form of reports, preparation for publication and presentation in the form of scientific articles were carried out directly by the claimant.

Published works. 21 scientific works on the topic of the dissertation were published, including 9 articles, 4 conference materials, 7 theses were published, and 1 Azerbaijani patent was obtained. The articles were published in "Russian Petroleum of Chemistry", "Russian Journal of General Chemistry", "Processes of petrochemistry and oil refining", "Chemical problems", "Молодой ученый", "Azerbaijan chemical magazine".

Approval and application. The materials of the dissertation work were heard and discussed at the following conferences: "Republic scientific and practical conference dedicated to the 100th anniversary of Academician S.C. Mehdiyev" (Baku 2014), Materials digest of the XI International scientific and practical conference "Trends of modern science" (Sheffield, 2014), materials of the scientific-practical conference dedicated to the 92nd anniversary of the birth of national leader Heydar Aliyev (Ganja, 2015), "Actual problems of modern chemistry and biology. International scientific conference" (Ganja, 2016), "Chemical reagents, reagents and processes of milling chemistry" Reaktiv-2016. XXX International

scientific and technical conference, dedicated to the memory of Academician of the Academy of Sciences of the Russian Federation Dilyus Rakhmankulov (Ufa, 2016), international scientific conference "Petrochemical synthesis and catalysis in complex condensed systems", post. 100th anniversary of Acad. B.K. Zeynalova, (Baku-2017), International scientific and technical conference "Innovative prospects for the development of oil refining and petroleum chemistry", devoted to the 110th anniversary of academician V.S. Aliyev (2018, Baku), Materials of the XXXII International scientific and technical conference "Chemical reagents, reagents and processes of low-tonnage chemistry", dedicated to the 80th anniversary of the Academy of Sciences of the Republic of Bashkortostan Dilyus Lutfulich Rakhmankulova, (Ufa, 2019), "Conference dedicated to the 90th anniversary of Academician Museyib oglu Aliyev" (Baku 2023).

Name of the organization where the dissertation work was performed.

The work was carried out at the Y.H. Mammadaliyev Institute of Petrochemical Processes of the Ministry of Science and Education of the Republic of Azerbaijan.

The total volume of the dissertation with a sign indicating the volume of the structural sections of the dissertation separately.

The dissertation consists of an introduction, 4 chapters, a list of 220 used literature sources, 32 images and 38 tables and is printed on 171 pages. It includes introduction (11575 marks), chapter I (50876 marks), chapter II (21377 marks), chapter III (44969 marks), chapter IV (43872 marks), conclusions (3993 marks). The total volume of the dissertation is 176 662 characters (excluding figures, tables, graphs, appendices, and the bibliography).

The introduction provides information on the relevance of the work, the goals of the dissertation, the main propositions defended, the scientific novelty and practical importance of the obtained results, and the total number of published scientific works.

In **the first chapter**, an overview and critical analysis of modern literature data on oxidation of unsaturated hydrocarbons in

the liquid phase with the presence of metal complex catalysts, epoxidation of bi-, tricyclic bridged, condensed and macrocyclic unsaturated hydrocarbons is provided.

The second chapter provides information on the synthesis of primary substances used in the research process, their physico-chemical properties, preparation of catalysts, conducting research and basic analysis methods, and the physical apparatus used.

In **the third chapter**, the results of the study of the epoxidation of C₁₀-C₁₃ tri- and tetracyclic monoolefins and dienes synthesized on the basis of cyclopentadiene, norbornene, 4-vinylcyclohexene and styrene, the effect of various factors on the course of reactions, and the physical and chemical characteristics of the obtained products were interpreted. The structure of the obtained compounds was studied and confirmed by IR, -NMR ¹H and ¹³C spectroscopy methods.

In **the fourth chapter**, epoxidation and dihydroxylation of tricyclic, as well as some tetracyclic unsaturated hydrocarbons synthesized on the basis of cyclohexadiene, the results of aminolysis reactions of synthesized oxiranes and diols with some amino compounds, and studies of the antimicrobial properties of the obtained compounds in oils are devoted.

The thesis is completed with the main results and the list of used literature sources.

THE MAIN CONTENT OF THE DISSERTATION

1. Catalysts and research methods.

Phosphoropolyoxomolybdate catalysts modified with CoBr_2 and Ce_2O_3 were used for epoxidation and oxidative hydroxylation of C_{10} - C_{13} polycyclic bridged unsaturated hydrocarbons.

The effectiveness of the catalysts was checked in the reaction of tricyclo [5.2.1.0^{2,6}] epoxidation of tricyclo [5.2.1.0^{2,6}] with an aqueous solution of hydrogen peroxide and hydroperite (a clathrate complex of hydrogen peroxide with urea) under standard conditions.

Surface morphology of initial and H_2O_2 treated samples of phosphorus polyoxomolybdate modified with CoCO_3 and HBr as well as Ce_2O_3 was determined using SEM (scanning electron microscope). IR spectra were obtained on Alpha (Bruker) and Vertex (Bruker) spectrometers in the range of 400-4000 cm^{-1} and 100-700 cm^{-1} , respectively.

Based on the X-ray phase analysis in the Miniflex (Rigaku) diffractometer, the phase composition of the catalyst was studied and it was determined that the modifiers are in the outer sphere of the complex.

Control of the conversion of H_2O_2 in the oxidation process was carried out by the permanganometry method.

The purity of the primary hydrocarbons and the composition of the obtained oxide were determined by QMX and IR-spectroscopic methods. QMX analysis was performed on "Svet-500" chromatograph. Chromato-mass spectra were performed on GC 7890 A-MSD 5975 C Agilent Technologies (column HP5-MS, temperature regime from 40 to 280°C, carrier gas-helium), and NMR ^1H and ^{13}C -spectra were performed on a Bruker spectrometer. It was recorded at a frequency of 300.18 MHz.

2. Oxidation of C_{10} - C_{13} tri- and tetracyclic mono- and diolefins based on cyclopentadiene, cyclohexa-1,3-diene, norbornene and 4-vinylcyclohexene

Preliminary studies for the epoxidation of polycyclic bridged C_{10} - C_{13} unsaturated hydrocarbons were carried out in two directions

in the presence of formic acid.

1) Tricyclodecene (TTDE) and tricyclodecadiene (TTDD) in the presence of 30-41% H_2O_2 aqueous solution and 85% HCOOH ;

2) By oxidation of these hydrocarbons in hydroperitin HCOOH solution.

In both cases, the epoxidation reaction takes place in the presence of peroxomethane acid, which is formed "in situ". Its formation is highly dependent on the molar ratio of $\text{H}_2\text{O}_2:\text{HCOOH}$. When this ratio is 1:4-5, it is observed that the epoxidation proceeds quite quickly.

Since the indicated peroxocomplex is formed in the aqueous phase, the main factor affecting the oxidation of TTDE and TTDD is the reaction temperature and the mixing speed of the reagents.

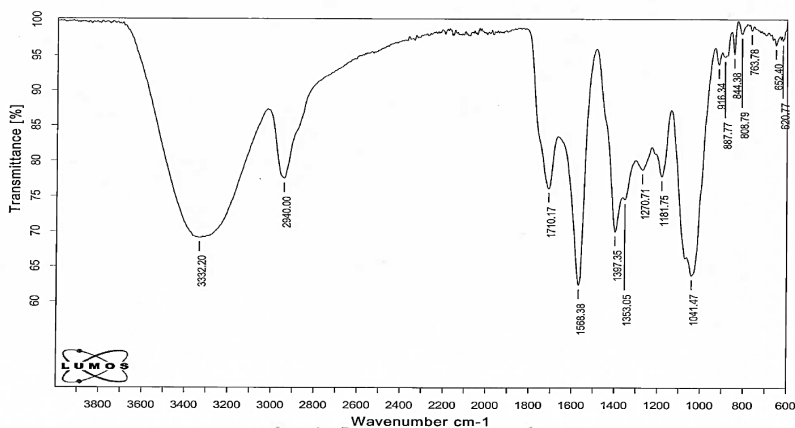


Fig. 1. IR spectrum of the oligomeric fraction obtained from the oxidation of TTDD with hydrogen peroxide.

A high yield is obtained at a temperature of 70-80°C and a stirring speed of 600-700 rpm. In the temperature range of 30-40°C, the induction period of the reaction is very large, and the conversion of hydrocarbons in 24 hours is 2-3%. The degree of conversion of TTDE at 70-80°C is 23.7-24.0%, the selectivity to monoepoxide is 71.8-78.7% when using a 35% aqueous solution of H_2O_2 , and 83.0 in the case of hydroperite -83.7%. Unlike TTDE, epoxidation of TTDD

is accompanied by its oxyoligomerization.

In addition to epoxytricyclodecane, the assumed isomers of diepoxide, diol, tetraol, and their condensation products were determined in the reaction mixture. The obtained oligomer fraction was tested as a thermosetting coating material.

The epoxidation of TTDE and TTDD is more selective in the presence of a modified phosphorus polyoxomolybdate catalyst.

3. Catalytic epoxidation tricyclo [5.2.1.0^{2,6}]-decene with hydrogen peroxide

Phosphorpolyoxomolybdate and phosphorpolyoxo-volframate catalysts modified with CoCO_3+HBr or $\text{Ce}(\text{NO}_3)_3+\text{HBr}$ were used in the epoxidation of tricyclodecene with H_2O_2 . The activity of the catalysts was determined by the conversion of the substrate and the selectivity according to the main oxidation products - epoxide and diol. Preliminary results are presented in table 1.

Table 1
Results of catalytic oxidation of tricyclodecene with 35% H_2O_2 solution [T=70 °C, $\tau=6$ hours, $\text{CMe}=4 \cdot 10^{-2}$ g-ion/l, TTDE: $\text{H}_2\text{O}_2:\text{CH}_3\text{COOH}+1:2.0:0.1$, TTDE-50 mmol] (Me=Mo,W)

№	Catalyst	Conv. of TTDE, %	Composition of oxydat, %			Yield, %	
			Epoxyd	Diol	Oligomer	Epoxyd	Diol
1	$\text{P}_{0,17}\text{Mo}_{2,14}\text{CoBr}_{0,27}\text{O}_{6,8}$	88.4	79.2	13.2	7.6	70.0	11.7
2	$\text{P}_{0,22}\text{Mo}_{2,67}\text{CoBr}_{0,26}\text{O}_{6,8}$	87.3	83.0	11.0	6.0	72.5	9.6
3	$\text{P}_{0,25}\text{Mo}_{3,0}\text{CoBr}_{0,25}\text{O}_{10}$	90.2	85.0	6.6	8.4	76.7	6.0
4	$\text{P}_{0,28}\text{Mo}_{3,45}\text{CoBr}_{0,2}\text{O}_{11,2}$	86.4	82.3	10.4	7.3	71.1	9.0
5	$\text{P}_{0,28}\text{Mo}_4\text{CoBr}_{0,2}\text{O}_{11,2}$	87.0	83.0	8.1	8.9	72.2	7.0
6	$\text{P}_{0,17}\text{W}_{2,14}\text{CeBr}_{0,27}\text{O}_{6,8}$	81.2	81.0	9.8	9.2	65.8	8.0
7	$\text{P}_{0,22}\text{W}_{2,67}\text{CeBr}_{0,26}\text{O}_{6,8}$	76.4	78.3	11.7	10.0	59.8	8.9
8	$\text{P}_{0,25}\text{W}_{3,0}\text{CeBr}_{0,25}\text{O}_{10}$	78.3	81.0	10.6	8.4	63.4	8.3
9	$\text{P}_{0,28}\text{W}_{3,45}\text{CeBr}_{0,23}\text{O}_{11,2}$	85.4	82.4	5.9	11.7	70.4	5.0
10	$\text{P}_{0,28}\text{W}_4\text{CeBr}_{0,2}\text{O}_{11,2}$	86.0	82.0	5.4	12.6	70.5	4.6

The epoxidation of tricyclodecene with the presence of the specified catalysts requires a certain induction period (30-40 min). However, if you lower the pH of the system ($\text{pH} \leq 3-4$), it is possible to drastically reduce the induction time. $\text{C}_1\text{-C}_2$ carboxylic acids are used for this purpose. The data given in table 1 show that the used

catalytic systems have high activity. However, a common drawback of homogeneous catalysts is the difficulty of their separation and regeneration from the reaction products.

The data given in Table 1 show that the used catalytic systems have high activity. However, a common drawback of homogeneous catalysts is the difficulty of their separation and regeneration from the reaction products.

Considering this, the sample showing higher activity was heterogenized by impregnation on different carriers and their activity was checked in the oxidation reaction (table 2).

Table 2.
Results of oxidation of tricyclododecene with 35% H₂O₂ in heterogenized P_{0,25}Mo_{3,0}CoBr_{0,25}O₁₀ catalytic system [T=70°C, τ=6 hours, cat-2g (Moⁿ⁺- 15%), TTDE: H₂O₂: CH₃COOH=1:2:0.1, TTDE-50 mmol]

Provider	Conv. TTDE, %	Composition of oxydat, %			Yield, %	
		Epoxyd	Diol	Olygomer	Epoxyd	Diol
HNaMor	67,2	58,3	36,9	4,8	39,2	24,8
HNa-YMS	42,3	65,7	31,3	3,0	27,8	13,2
TiO ₂	58,4	68,0	28,2	3,8	39,7	16,5
Microstructured carbon material (MCM)	68,6	70,4	24,4	5,2	48,3	16,7

Comparing Tables 1 and 2, it is noticeable that heterogeneous catalyst samples are active in this reaction.

However, although catalysts prepared on the basis of HNaMor, HNa-YMS zeolites and TiO₂ show high activity, their activity decreases sharply after the first experiment. The active mass impregnated with zeolites and titanium (IV) oxide is washed with reaction products and they go into solution.

Since the activity of catalyst samples prepared on microstructured carbon material remained stable for a long time, they were used in subsequent studies. Higher results were obtained in samples containing 7.5-10.0 mass % Mon+ (or Wn+) (figure 2).

A number of factors affecting the epoxidation reaction of TTDE with the presence of these catalysts: the effect of the nature and concentration of the oxidant, temperature, duration of the

reaction, and pH of the solution were studied.

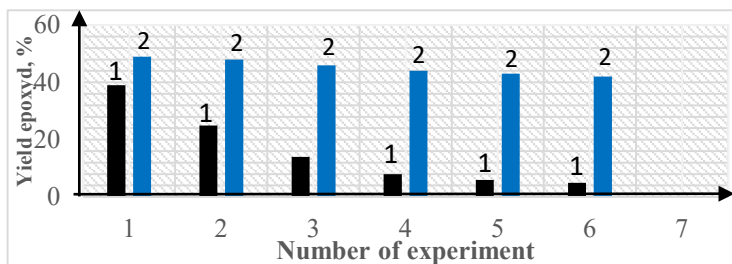


Fig. 2. Changes in stability of $P_{0,25}Mo_{3,0}CoBr_{0,25}O_{10} /HNaMor$ (1) and $P_{0,25}Mo_{3,0}CoBr_{0,25}O_{10} /MKM$ (2) systems during oxidation of TTDE with 35% H_2O_2 solution ($T=70^\circ C$, each experiment duration $\tau=6$ hours) does not change.

3.1. Epoxidation of C_{10} - C_{12} tri- and tetracyclic unsaturated hydrocarbons in the presence of phosphorus polyoxomolybdate modified with cobalt and cerium cations

Catalytic epoxidation of TTDE with hydrogen peroxide has an induction time of up to 50-60 minutes. However, pre-treatment of the catalyst with H_2O_2 allows to drastically reduce the induction time. (figure 3)

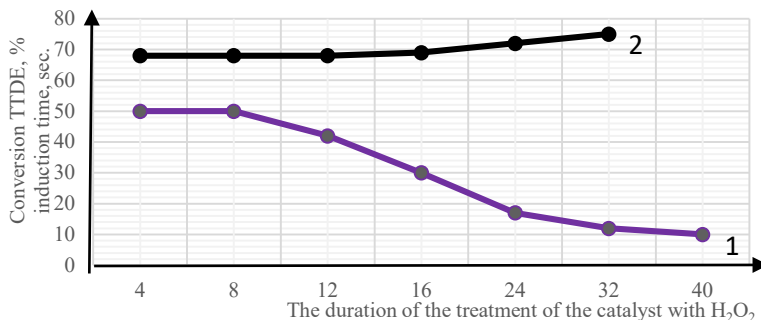


Fig. 3. Effect of treatment of $P_{0,25}Mo_{3,0}CoBr_{0,25}O_{10} /MKM$ catalyst with 35% H_2O_2 ($Mo^{n+}:H_2O_2=1:100$) on induction time (1) and catalyst activity (2)

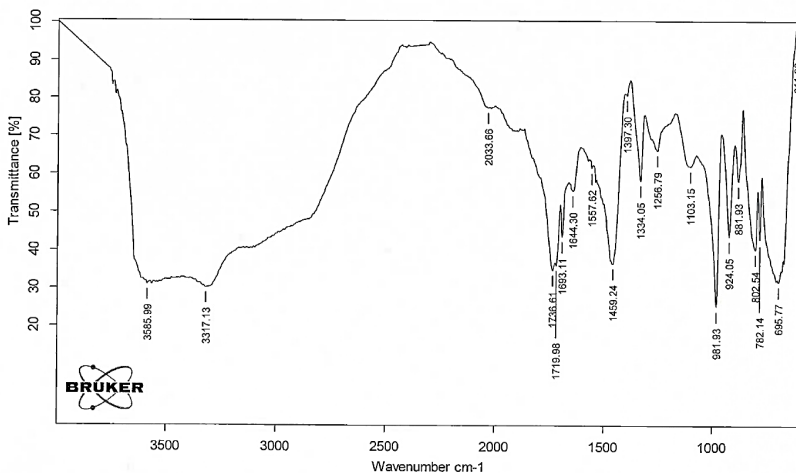

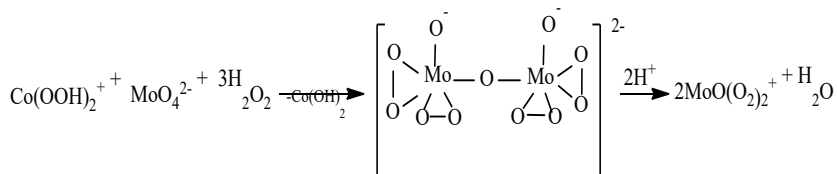
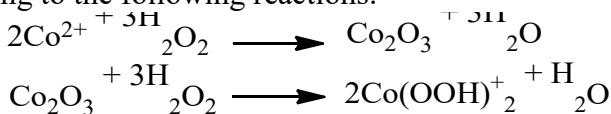


Fig. 4. IR spectrum of P_{0.25}Mo_{3.0}CoBr_{0.25}O₁₀ sample treated with hydrogen peroxide.

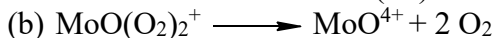
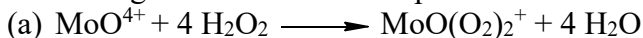
The induction time is reduced from 50 min to 10-15 min by processing the catalyst in the ratio of Moⁿ⁺: H₂O₂=1:100 mol for 24-48 hours. In the presence of this catalyst, the conversion of TTDE reaches 75.4%.

In the IR-spectrum of the received catalyst, it was determined that Mo-O-OH (3587.7 and 3306.1 cm⁻¹) and  its bond (869, 781, 706 cm⁻¹) have symmetric and asymmetric oscillation bands.

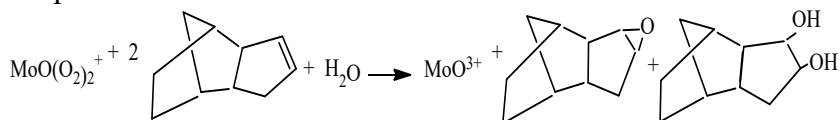
It is assumed that the inductive formation of oxoperoxocomplex in the presence of hydrogen peroxide proceeds according to the following reactions:



When the obtained golden-yellow molybdenum-peroxocomplex is heated, it turns into a greenish-blue mass. At this time, the following oxidation-reduction process is assumed to occur:



Since step (b) in the oxidation process of TTDE takes place in the presence of the substrate



the unproductive decomposition of the peroxide is replaced by the formation of the corresponding epoxide and diol. The conversion of TTDE and the composition of the oxidizer depend on the substrate:oxidant mole ratio (Table 3) and temperature. Thus, when the TTDE:H₂O₂ molar ratio changes in the range of 1:1-3, the main oxidation product is epoxytricyclodecane, when this ratio changes in the range of 1:4-6, the oxidate contains isomers of the corresponding glycol and other oxidation products (α -oxyketone, dicarbonic acid, oxyoligomers). is dominated by. When 35.0% H₂O₂ is used as an oxidizer, the yield of epoxide is 48.3%, and when hydroperite is taken, it is 74.5%.

Table 3

Effect of mole ratio of TTDE and hydrogen peroxide on yield and composition of oxide (T=70°C, τ =8h, catalyst- $\text{P}_{0,25}\text{Mo}_{3,0}\text{CoBr}_{0,25}\text{O}_{10}/\text{MKM}=2 \text{ gr}$ (Mo^{n+} -15%) CTTDE= 50mmol, H_2O_2 -35 % aqueous solution, TTDE:CH₃COOH=1:0.1)

Proportion TTDE: H ₂ O ₂	Conversion TTDE, %	Comp. oxydat, %			
		Epoksyd	Diol and its monoefyr	Other oxidation products	Oksioligomers
1:1	33,4	78,3	18,6	-	3,1
1:2	68,6	70,4	24,4	-	5,2
1:3	75,0	61,5	27,0	4,5	7,0
1:4	81,8	42,0	38,0	8,0	12,0
1:5	87,3	30,4	44,3	10,4	14,9
1:6	92,6	22,3	47,6	10,9	19,2

In the latter case, the content of the oxide depends on the concentration of the acetic acid used. In the presence of 40-60% acid,

the conversion of TTDE is 9.7-67.6%, the amount of epoxide and diol in the oxide is practically equal.

The decrease in the conversion of the substrate is explained by the decrease in the peroxocomplex in the system and, conversely, the increase in the inactive molybdenum or tungsten aquacomplex. When 90-95% acid is used, the conversion rate of TTDE reaches 82.8-83.5%, and the yield of epoxide reaches 85.4-89.2%.

To further study the effect of the nature of the oxidant, tert-butylhydroperoxide (TBHP) and cumyl-hydroperoxide (KHP) were also used in the oxidation of TTDE. (Figure 5)

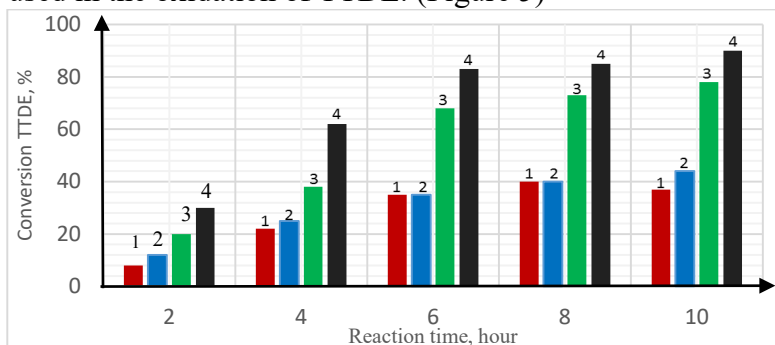


Fig. 5. Results of catalytic oxidation of TTDE in the presence of different oxidants. 1. Tert-butyl hydroperoxide; 2. Cumyl-hydroperoxide; 3. 35% solution of H₂O₂ in water; 4. Hydroperite [H₂O₂·CO(NH₂)₂]

A mixture of toluene and isopropyl alcohol (1:1) was taken as a solvent in both cases.

3.2. Effect of various factors on epoxidation and dihydroxylation of TTDE

One of the main factors affecting the catalytic oxidation of TTDE is the change of catalyst amount and temperature. Oxidation practically does not proceed without a catalyst. When increasing the amount of catalyst in the solution to 15.0 g/l, the reaction rate increases linearly. In the range of 15.0-17.0 g/l, the speed increase decreases. In this interval, the composition of the reaction according to the catalyst varies between zero and unity. Above 17.0 g/l, the composition of the reaction according to the catalyst is close to zero.

The effect of temperature on the direction of the reaction was considered in the range of 40-80 °C. (figure 6)

In the range of 40-60 °C, the oxidation of TTDE proceeds with a long induction time (2 hours).

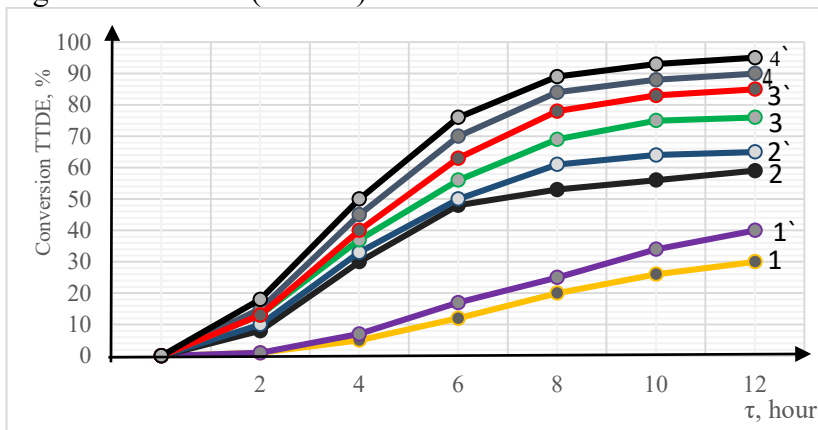


Fig. 6. Dynamics of oxidation of TTDE with 35% aqueous solution of H₂O₂ and hydroperite at different temperatures. Temperature, °C: 1.1'-40; 2.2'-60; 3.3'-70; 4.4'-80; 1,2,3,4-oxidizing- 35% solution of H₂O₂, 1',2',3',4'-hydroperite (H₂O₂ +urea adduct)

Within 7 hours, the degree of conversion is 12.0-15.5%, the yield of the main product of the reaction - endo-4-oxa-exotetracyclo [6.2.1.0^{3.5}.0^{2.7}] undecane is 9.3-10.5%.

Under these conditions, the conversion of H₂O₂ was 72.0-83.5%. This can be explained by the energetic difficulty of the molybdenum oxoperoxocomplex formed as a result of the reaction to form a ternary complex with the substrate. The conversion rate of TTDE increases dramatically when the temperature is raised from 60°C to 80°C. The composition of the oxidizer depends greatly on the nature of the oxidizer used (table 4).

When the epoxidation reaction is carried out in the presence of a weak polar solvent, the main product of the reaction is endo-4-oxa-exo-tetracyclo [6.2.1.0^{3.5}.0^{2.7}] undecane. As the polarity of the solvent increases, the yield of epoxide decreases, while the yield of its hydrolysis (acetolysis) products, diol and its monoacetate,

increases. As a result of the conducted studies, the following conditions were taken as optimal for the epoxidation of TTDE: temperature 80 °C, reaction time 7-8 hours, TTDE:H₂O₂:CH₃COOH=1:2:0.1-0.3; floor P_{0,25}Mo_{3,0}CoBr_{0,25}O₁₀/MKM. Under these conditions, when using an aqueous solution of 35% H₂O₂, the conversion of TTDE is 78%, the yield of epoxide is 59.8%, and when using hydroperite is 89.4 and 71.0%, respectively.

Table 4.
Effect of the nature of the oxidant on the oxidation of TTDE in the presence of P_{0,25}Mo_{3,0}CoBr_{0,25}O₁₀/MKM (TTDE:[0]:CH₃COOH=1:2:0.1, τ=8 hours, CTTDE=50mmol)

T, °C	Conv. TTDE	Compounds oxydat, %				Yield, %	
		Epoxyd	Diol and its monoefyr	Other oxidation products	Oligomer	Epoxyd	Diol
35%-li H₂O₂ aqueous solution							
60	47,8	77,4	22,6	-	-	37,0	10,8
70	68,6	70,4	24,4	-	5,2	48,3	16,7
80	78,0	66,5	27,0	1,3	5,2	51,9	21,0
30%-li H₂O₂ dioksan solution							
60	32,6	81,7	18,3	-	-	26,6	6,1
70	53,4	74,0	16,5	2,8	6,7	39,5	8,8
80	70,6	72,4	14,0	3,9	9,7	51,1	9,9
Hydroperit [H₂O₂+CO(NH₂)₂]+CH₃COOH							
60	61,5	89,4	10,6	-	-	55,0	6,5
70	70,3	68,9	24,4	-	6,7	48,5	17,2
80	89,4	79,4	28,9	4,7	7,0	71,0	8,0
Tertbutylhydroperoxide							
60	16,6	91,6	-	3,1	5,3	15,2	-
70	21,7	84,2	1,3	6,1	8,4	18,3	0,3
80	48,4	82,0	2,0	6,3	9,7	39,7	1,0
90	65,7	71,7	5,2	8,8	14,3	47,1	3,4

3.3. Catalytic oxidation of alkyl-, cyclohexenyl- and phenyl-substituted bi-, tri- and tetracyclic unsaturated hydrocarbons

The hydrocarbons used for the study were obtained by [4+2] condensation of cyclopentadiene with various alkyl derivatives of 4-vinylcyclohexene, styrene and norbornene under conditions of monomerization of cyclopentadiene dimer (160-180°C, HNa-mordenite).

Researches were carried out in the presence of 30% solutions of H₂O₂ in dioxane and hydroperitin in HCOOH, at a temperature of 80°C, in the ratio of substrate:oxidizer:HCOOH =1:(1-2):(0.2-0.4) mol, under the established standard conditions. was carried out using P_{0,25}Mo_{3,0}CoBr_{0,25}O₁₀/MKM as a catalyst. The introduction of methyl groups into the tricyclodecene molecule sharply reduces the oxidation capacity of the substrate, and increases the induction time up to two times. Presumably, the presence of a methyl group on the carbon atom holding the double bond has a shielding effect, making it difficult for the oxoperoxocomplex formed "in-situ" to form a ternary complex with the substrate. The conversion rate of dimethyltricyclodecene relative to tricyclodecene decreases from 68.6% to 36.4% under the same conditions.

QMX analysis shows that the isomer composition of dimethylcyclodecene taken into the reaction and returned from the reaction is significantly different. Since the isomers with the methyl group directly on the double-bonded carbon atom are hardly included in the epoxidation reaction, their amount in the isomer mixture returning from the reaction increases in percentage.

Radicals shown in cyclohexenyl- and phenylnorbornene molecules have practically no effect on the course of the reaction since they are separated from the double bond by the endo-methylene group. The degree of oxidation of tetracyclododecene molecules where the alkyl groups are further away from the double bond is higher (table 5). It should be noted that the selectivity for epoxide and diol increases as the rate of oxyoligomerization decreases among di-, tri-, and tetracyclic unsaturated hydrocarbons.

Table 5.

Results of oxidation of alkyl-, cyclohexenyl- and phenyl-substituted bi-, tri- and tetracyclic unsaturated hydrocarbons with hydroperite (T=70°C, τ=8s, substrate:[O]:HCOOH mole ratio 1:2:0.4, cat.- P_{0,25}Mo_{3,0}CoBr_{0,25}O₁₀/ MKM)

Carbohydrogens	Conv. Degree Carb., %	Yield, %	
		Epoxid	Diol
2-cyclohexenylbicyclo [2.2.1] hept-5-ene	47,8	39,2	7,0
2-phenylbicyclo [2.2.1] hept-5-ene	43,6	32,2	9,4
Dimethyltricyclo [5.2.1.0 ^{2.6}] desen (mixture of isomers)	36,4	29,1	6,6
Tetracyclo [6.2.1.1 ^{3.6} .0 ^{2.7}] dodes-4-ene	87,0	72,5	13,0
9-methyltetracyclo [6.2.1.1 ^{3.6} .0 ^{2.7}] dodes-4-ene	89,0	76,5	12,0
9-ethyltetracyclo [6.2.1.1 ^{3.6} .0 ^{2.7}] dodes-4-ene	86,0	76,0	9,0
9-propyltetracyclo [6.2.1.1 ^{3.6} .0 ^{2.7}] dodes-4-ene	83,0	69,0	7,0
9-phenyltetracyclo [6.2.1.1 ^{3.6} .0 ^{2.7}] dodes-4-ene	78,2	63,5	10,2
9-cyclohexenyltetracyclo [6.2.1.1 ^{3.6} .0 ^{2.7}] dodes-4-ene	79,5	66,3	11,3

4.1. Catalytic epoxidation and dihydroxylation of tricyclo [5.2.2.0^{2.6}] undes-3-ene and tricyclo [6.2.2.0^{2.7}] dodes-3-ene with hydrogen peroxide

Preliminary studies have shown that, unlike tri- and tetracyclic unsaturated hydrocarbons based on cyclopentadiene, the catalytic oxidation of the corresponding unsaturated hydrocarbons based on cyclohexa-1,3-diene with H₂O₂ proceeds selectively in a more acidic environment (pH=2-3). For this reason, CH₃COOH was replaced by stronger HCOOH in the reactions. It is assumed that HCOOH is closely involved in the formation of the active catalytic complex by easily forming "in-situ" peroxomethane acid in addition to creating a strong acidic environment. (Figure 6).

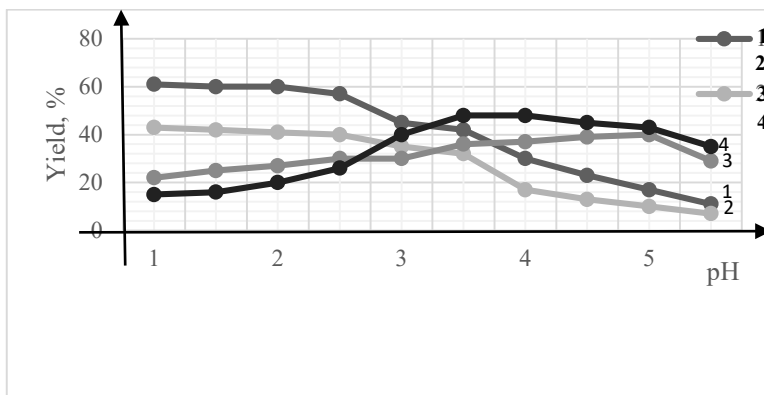


Fig. 6. Solution pH of catalytic oxidation of tricyclo [5.2.2.0^{2.6}] undec-3-ene (1,4) and tricyclo [6.2.2.0^{2.7}] dodec-3-ene (2,3) with 35% H₂O₂ dependence on Catalyst P_{0,25}Mo_{3,0}CoBr_{0,25}O₁₀ T=70°C, τ=6 hours, 3,4-diol and its monoformate, 1,2-epoxide.

Apparently, one of the main factors affecting the direction of the reaction when using a 35% H₂O₂ solution as an oxidant is the pH value of the environment. When the pH value varies in the range of 1-3, the main oxidation product of both hydrocarbons is glycol or its monoester (yield 38.2-48.3%). The extreme presence of the curves characterizing the yield of epoxide indicates that glycols are formed according to the parallel-series scheme. At a pH value of 3.5-6.0, the output of glycol is 3.5-5.0% during the first 1.5-2 hours. In this case, it is assumed that mainly the cis-isomer is formed.

In order to determine the regioselective progress of dihydroxylation, the ratio of the 1050-1080 (trans-isomer) and 1110-1125 cm⁻¹ (cis-isomer) bands characterizing the O-H bond in the IR-spectrum of the received glycol was taken.

As a result of IR and QMX analyses, it was determined that the ratio of cis- and trans- isomers is 8-12:88-92. The yield of reaction products and their composition in the oxidation process depends on temperature, reaction time, substrate:H₂O₂ mole ratio, as well as the nature of the hydrocarbon taken (table 6).

So, since the degree of conversion of olefins in the order of tricyclodecene, tricycloundecene and tricyclododecene decreases, the output of epoxide and diol also decreases (tables 2 and 6).

Table 6

Effect of substrate:H₂O₂ mole ratio on the oxidation of tricycloundecene and tricyclododecene with 35% H₂O₂ [cat-P_{0,25}Mo_{3,0}CoBr_{0,25}O₁₀/MKM, T=70°C, τ=6 hours, substrate:HCOOH=1:0,1)

Substrat : H ₂ O ₂ mole ratio	Conv. degree, %	Comp. oxydat, %				
		Epoksid	Diol	Mono formiat efyr	α-oksi keton	Oksi- olygome r
Tricyclo [5.2.2.0^{2,6}] undes-3-en						
1:1	48,3	77,3	11,0	6,8	1,4	3,5
1:1,5	52,4	68,4	17,0	5,1	2,0	7,5
1:2	67,8	53,1	18,1	8,7	6,4	13,7
1:3	70,0	44,7	29,4	8,0	8,3	9,6
1:4	73,	26,0	40,3	4,3	12,4	17,0
1:6	80,6	19,0	36,4	4,6	15,0	25,0
Tricyclo [6.2.2.0^{2,6}] dodes-3-en						
1:1	41,6	79,0	13,7	4,2	-	3,1
1:1,5	44,2	72,6	15,0	4,2	-	8,2
1:2	58,3	58,4	19,2	3,4	1,2	17,8
1:3	64,0	45,0	31,6	4,8	3,7	14,9
1:4	68,3	34,0	46,4	4,7	2,8	12,1
1:6	75,2	21,3	41,7	5,0	4,0	28,0

According to NMR ¹H and ¹³C analysis, epoxidation and dihydroxylation are easier than the cyclopentene fragment. High selectivity to epoxide from tricyclo [5.2.2.0^{2,6}]undes-3-ene (TTUE) is obtained when the TTUE:H₂O₂ molar ratio varies in the range of 1:1-3 (53.1-77.3%). When this mole ratio is changed in the range of 1:4-6, the amount of epoxide decreases, while the yield of diol and its monoester increases (table 6). At the same time, the rate of oxylogomerization of the substrate also increases.

When hydroperite is used as an oxidizer, the concentration of the formic acid taken into the reaction plays a major role. When using 85% HCOOH, the selectivity to epoxy increases to 71.5-87.4% when the molar ratio of H₂O₂·CO(NH₂)₂:HCOOH is 1:1-1.5. When the acid concentration changes in the range of 50-55%, the amount of epoxide in the catalyst decreases (up to 44.8-52.5%), on the contrary,

the selectivity for glycol and its monoformate increases. The cumulative yields of epoxide, diol, and monoether are higher than those obtained with aqueous H_2O_2 .

The optimal conditions for the catalytic oxidation of tricyclo [5.2.2.0^{2,6}]undecene with an aqueous solution of hydrogen peroxide and hydroperite are as follows:

- temperature 70-80°C, reaction time 6-8 hours, TTUE:[O]:HCOOH-1:2:0,1-1, catalyst $P_{0,25}Mo_{3,0}CoBr_{0,25}O_{10}$ /MKM. Under these conditions, a higher yield of epoxide and diol was obtained in the presence of hydroperite (54.4%-75.8%).

After hydrolysis of glycol monoformate ester in the oxide with 40% KOH solution at 70-80 °C for 2 hours, the oxidation products were extracted with ethyl acetate and tricyclo [5.2.2.0^{2,6}] undecane-3,4-diol was precipitated from the hexane solution.

In the IR spectrum of the obtained diol, the bands at 1620-1640 and 3030-3050 cm^{-1} , which are characteristic for double bonds, are lost, on the contrary, the valence oscillation of the O-H bond in the region of 3420-3580 cm^{-1} , as well as three weak bands in the region of 1165-1120 cm^{-1} , 1100- The presence of three strong absorption bands in the area of 1032 cm^{-1} indicates that the obtained diol forms several isomers. Probably the obtained diol exo-; endo-; consists of a mixture of isomers, endo-, endo- and exo-, exo-. NMR 1H and ^{13}C , as well as mass-spectrum confirmed the structure of the obtained compounds.

4.2. Oxidation of tricyclo[5.2.2.0^{2,6}]undecene methyl derivatives by hydrogen peroxide

Oxidation of tricyclic monoolefins is highly dependent on the presence of substituent groups in the molecule in addition to the above factors. For this purpose, it is of theoretical and practical interest to study the reactions of methyl derivatives of tricyclo [5.2.2.0^{2,6}] undecene with aqueous solution of H_2O_2 and hydroperite under optimal conditions, and to compare their reactivity.

Methyltricyclo[5.2.2.0^{2,6}] obtained from the [4+2] condensation of methylcyclohexa-1,3-diene isomers with cyclopentadiene and methylcyclopentadiene with cyclohexa-1,3-

diene isomers as a starting material and obtained from hydrogenation at atmospheric pressure in the flow system. undesen was used. The obtained results are given in table 7. The isomer composition of the substrate was determined based on QMX, NMR ¹H and ¹³C-analyses.

Table 7

Dependence of isomer composition of catalytic oxidation of methyltricycloundecene with 35% H₂O₂ solution and hydroperite. (T=70°C, τ=8 hours, cat. P_{0,25}Mo_{3,0}CoBr_{0,25}O₁₀/MKM, MTTU:[O]:HCOOH=1:2:0,1-1)

The isomer composition of MTTU taken into the reaction, %	Conversion degree of MTTU, %	The isomeric composition of MTTU returned from the reaction, %
With 35 % H ₂ O ₂		
1-methyl-45,1 9-methyl-47,5 10- methyl -7,4	52,4	1- methyl -39,7 9- methyl -51,4 10- methyl -8,9
3- methyl -48,5 4- methyl-50,8 5- methyl -0,7	43,6	3- methyl -46,4 4- methyl -53,4 5- methyl -0,2
With Hydroperit		
1- methyl -45,1 9- methyl -47,5 10- methyl -7,4	55,8	1- methyl -37,3 9- methyl -53,6 10- methyl -9,1
3- methyl -48,5 4- methyl-50,8 5- methyl -0,7	45,7	3- methyl -45,3 4- methyl -54,6 5- methyl -0,1

According to the data given in Table 7, the oxidation of tricycloundecene, which keeps the methyl group in the bicyclooctane fragment, either with an aqueous solution of H₂O₂ or with hydroperite, is practically independent of the position occupied by this group. In other words, since the methyl group is located far from the double bond in the cyclopentene fragment, their shielding ability (E-effect) is practically zero. On the contrary, the reactivity of the isomers that retain the methyl group in the cyclopentene fragment differs significantly from them.

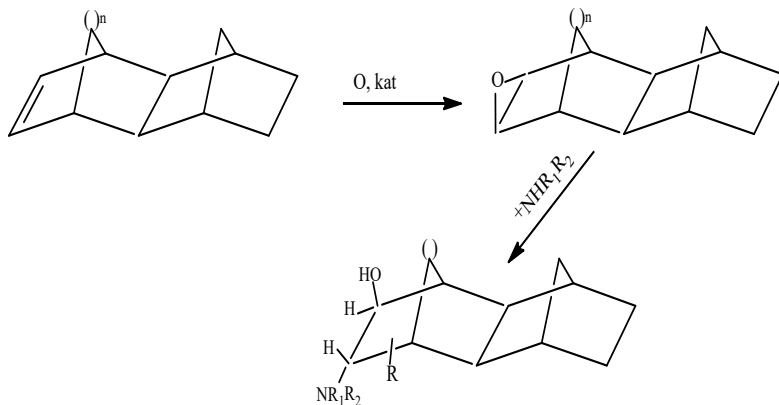
This difference is more pronounced when the methyl group is on the double-bonded carbon atom. Thus, under the same conditions, the conversion of MTTU consisting of isomers containing methyl groups in the 3-, 4-, and 5-positions is lower than the mixture of isomers with a methyl group in the 1-, 9-, and 10-positions (43.6-45.7 and 52, 4-55.8%). Changing the oxidizer has practically no effect on the oxidation process.

The obtained results allow us to evaluate the reactivity and shielding ability of the alkyl group of bridged olefins depending on the position of the double bonds and alkyl groups.

4.3. Preparation and study of aminoalcohols based on C₁₀-C₁₃ macrocyclic bridged epoxide and diols

It is known from the literature that O- and N-derivatives of amino alcohols are widely used as "building blocks" in the preparation of natural and synthetic biologically active compounds. There is practically no information about aminoalcohols with polycyclic bridged hydrocarbon fragments.

This section is devoted to the preparation of vicinal amino alcohols from C₁₀-C₁₃ polycyclic bridged unsaturated hydrocarbons in two steps and to the study of their antimicrobial properties:



Here, $n=1$, $\text{R}_1=\text{R}_2=\text{C}_2\text{H}_5$ (I) $n=2$, $\text{R}_1=\text{R}_2=\text{C}_2\text{H}_5$ (II) $n=1$, $\text{R}_1+\text{R}_2=(\text{CH}_2-\text{CH}_2)_2\text{O}$ (III); $n=2$, $\text{R}_1+\text{R}_2=(\text{CH}_2-\text{CH}_2)_2\text{O}$ (IV); $n=1$, $\text{R}_1+\text{R}_2=(\text{CH}_2)_5$ (V); $n=2$, $\text{R}_1+\text{R}_2=(\text{CH}_2)_5\text{O}$ (VI)

The progress of the aminolysis step depends on the nature of the solvent used and the molar ratio of the reagents. The reaction does not proceed without a solvent or in the presence of a non-polar solvent (benzene, CCl₄). A high yield of the corresponding amino alcohols is obtained in the presence of strong polar solvents (C₁-C₃ alkanols, water+alcohol) (table 8).

Table 8

Effect of solvents on the production of 4 (5)-N₁N diethylamine-(I) and 4 (5)-morpholyltetracyclo [6.2.1^{1.8}.1^{3.6}.0^{2.7}] dodecane-5 (4)-ol (II)

Solvent	ε	Amount of solvent, mol	Yield, %	
			I	II
Carbon-4-chloride	2,3	1,0	-	-
Benzol	2,27	1,0	2,5	1,8
Toluol	2,38	1,0	3,8	4,0
Tertiary-butanol	12,3	2,0	32,4	27,8
Propanol-2	18,3	2,0	49,6	45,4
Ethanol	25,2	2,0	62,3	55,8
Methanol	32,65	2,0	67,8	60,4
Propanol-2+H ₂ O (1:1)	-	3,0	79,3	76,4
Ethanol+H ₂ O (1:1)	-	3,0	80,5	82,3

Note: epoxide:amine=1:2, T=50 °C, τ=8 h, catalyst K₂CO₃

Synthesized amino alcohols are yellowish-white substances with crystalline structure. Their structure was determined by IR-, NMR ¹H and ¹³C-spectroscopic methods. As the oxirane ring is regioselectively opened in the aminolysis process, the obtained compounds consist of a mixture of several isomers. These isomers differ both in the position of the –OH and amino groups in the molecule, and in the exo-endo states of the endomethylene (or endoethylene) group.

RESULTS

1. On the basis of dicyclopentadiene and cyclohexa-1,3-diene, 4-vinylcyclohexene, norbornene and its alkyl derivatives for the first time in the presence of natural mordenite or clinoptilolite HNa-form (degree of decation 75% eq.) by [4+2] catalytic cocondensation A method of selective production of tri- and tetracyclic bridged mono- and diolefins at a temperature of 180-220°C was developed and the structure of these compounds was determined by IR-, NMR ¹H and ¹³C-spectral methods [1, 4, 9].

2. Samples of polyoxometalate (containing P_{0.25}Mo_{3.0}CoBr_{0.25}O₁₀ /MKM və ya P_{0.25}W_{3.0}CoBr_{0.25}O₁₀/ MKM) were prepared for the catalytic epoxidation of synthesized C₁₀-C₁₃ bridged monoolefins, their phase composition was studied and the participation of these catalytic systems was shown. Inductive epoxidation and dihydroxylation reactions of hydrocarbons with 35-41% H₂O₂ aqueous solution and hydroperite [H₂O₂ + CO(NH₂)₂] were studied. 4-oxatetracyclo [6.2.1^{1.8}.0^{3.5}.0^{2.7}] undecane, 4-oxatetracyclo [6.2.2.0^{3.5}.0^{2.7}] dodecane, 5-oxapentacyclo [7.2.1^{1.9}.1^{3.7}.0^{2.8}.0^{4.6}] tridecane, 5-oxapentacyclo [7.2.2^{3.7}.1^{1.9}.0^{2.8}.0^{4.6}] tetradecane optimal conditions for obtaining were determined: substrate: H₂O₂:CH₃COOH molar ratio 1:2-3:0.1-0.2; reaction time 7-8 hours; temperature 70-80°C. Under these conditions, when the oxidizing agent is 35-41% H₂O₂, along with the epoxide, the corresponding diol (total yield 71.0 %), and when hydroperite is obtained, only the epoxide (yield 59.8 %) is obtained [1-3, 5, 6].

3. Epoxidation of C₁₁-C₁₃ bridged tri- and tetracyclic diene hydrocarbons with 35-41% H₂O₂ aqueous solution at 80-90°C in the presence of polyoxotungstate and polyoxomolybdate catalysts modified with CoCO₃, Ce₂O₃ and HBr and impregnated into microstructured carbon material reactions were studied. The epoxidation reaction of these hydrocarbons with an aqueous solution of hydrogen peroxide proceeds along serial-parallel routes. Epoxytricyclododecene and epoxytetracyclotetradecene formed in the first stage are hydrolyzed in the course of the reaction and converted into corresponding unsaturated vicinal diols and diepoxides by epoxidation from the free double bond. Under more

severe conditions, at a temperature of 90°C and a reaction time of 12 hours, the oxidation proceeds in the direction of the formation of polycyclic oxyoligomers [7, 8, 10].

4. A method of selective extraction of appropriate mono- and diepoxides from diene hydrocarbons with C₁₁-C₁₃ bridged double bonds in different fragments was developed. It was determined that in the presence of a system containing H₃[PMo₁₂O₄₀] modified with cerium or gadolinium oxides, when using hydroperite (a clathrate combination of H₂O₂ with urea) as an oxidizing agent, at a temperature of 50-70°C for 2-4 hours, diepoxide is obtained with 78,0-82,0% yield [11-15].

5. Correlative dependence was determined between the epoxidability of tri- and tetracyclic bridged monoolefins obtained from [4+2] condensation of C₁-C₄-alkyl and vinyl derivatives of norbornene and methyl derivatives of cyclopentadiene and cyclohexa-1,3-diene and the position of the substituent groups in the molecule. The presence of alkyl (methyl) groups directly on the double-bonded carbon atom sharply reduces the epoxidation ability of the substrate. As the alkyl group moves away from the double bond, its inductive and shielding effect decreases, and conversely, the epoxidation ability of the substrate increases. When double bonds and alkyl groups are in different fragments of these molecules, the degree of epoxidation of hydrocarbons practically does not differ from unsubstituted analogues [16].

6. The oxyoligomers fraction obtained from the oxidation of tricyclic diene hydrocarbons - tricyclo [5.2.2.0^{2,6}] undecadiene, tricyclo [6.2.2.0^{2,7}] dodecadiene, synthesized on the basis of cyclopentadiene and cyclohexa-1,3-diene, was tested as a coating material. According to preliminary results, these oligomers can be used as thermosetting coating material [17, 20].

7. Corresponding amino alcohols were synthesized from the condensation reaction of the oxide mixture obtained on the basis of tri- and tetracyclic monoolefins with diethylamine, morpholine and piperidine. It was determined that adding 0.25-1.0% of tri- and tetracyclic amino alcohols with morpholyl and piperidinyl fragments to M-10 motor oil increases its fungicidal and bactericidal activity.

These compounds are recommended to be used as bactericidal additives in motor oils [18, 19].

The main content of the dissertation was published in the scientific works:

1. Alimardanov, Kh.M., Sadygov, O.A., Garibov, N.I., Agabeyli, G.B., Dadashova, N.R., Almardanova, M.B. Induced oxidation of tetrahydroindene and 5-vinylnorbornene by atmospheric oxygen in the presence of metal-containing carbon materials // Materials Of the X International scientific and practical conference “Trends of modern science 2014”, -Sheffield: Science and education LTD, - May 30-June 7, - 2014, Vol.23, - p. 20-29.
2. Alimardanov, Kh.M., Garibov, N.I., Dadashova, N.R., Sadygov, O.A., Agabeyli, G.B., Almardanova, M.B. Oxidation of tricyclic olefins with air oxygen with the participation of metal-containing highly dispersed carbon materials // Materials of the Rep. scientific pract. conf. dedicated to the 100th anniversary of acad. S.D. Mekhtiev, - Baku, December 2-3, - 2014, - p. 35-41.
3. Alimardanov, Kh.M., Garibov, N.I., Sadygov, O.A., Almardanova, M.B., Ragimova, F.A., Shafieva, R.N. Epoxidation of polycyclic unsaturated hydrocarbons with hydrogen peroxide in the presence of oxoperoxo complexes of transition metals // Materials of Rep. scientific pract. conf. dedicated to the 100th anniversary of academician S.D. Mekhtiev, - Baku, - December 2-3, - 2014, - p. 27-34.
4. Alimardanov, Kh.M., Sadygov, O.A., Almardanova, M.B., Jalilova, A.A., Mamedov, A.M. Catalytic codimerization of cyclopentadiene, cyclohexadiene-1,3 of their methyl and vinyl derivatives with the participation of H-forms of mordenite and NaU zeolite // Materials of the scientific-practical conference dedicated to the 92nd anniversary of the birth of national leader H. Aliyev, - Ganja, - 2015, - p. 185-188.
5. Alimardanov, Kh.M. Synthesis of C₁₁-C₁₄ cycloolefins of framework structure with participation of H-forms of natural and synthetic mordenite / O.A. Sadygov, A.A. Jalilova, M.B. Almardanova // Azerb.chem.journal, - 2015. No. 3, - p. 67-74.

6. Alimardanov, Kh. Epoxidation of the products of codimerization of cyclopentadiene and cyclohexadiene hydrocarbons catalyzed by lanthanide-molybdenum polyoxometalates / N.I.Garibov, N.R.Dadashova, O.A.Sadygov, A.D.Kuliev, M.B. Almardanova // Russian Journal of General Chemistry, - 2015. Vol.85, №5, - p. 1025-1033.
7. Alimardanov, Kh.M., Musaeva, E.S., Babaev, N.R., Dadashova, N.R., Almardanova, M.B. Epoxidation of tetracyclo-[6.2.1.1^{3.6}.0^{2.7}] dodec-4-ene and its alkyl derivatives by hydrogen peroxide in the presence of polyoxoperoxometalate catalysts // Reaktiv-2016. XXX Inter. Scientific-Technical Conf. «Chemical reagents, reagents and small-tonnage chemical processes. dedicated Memory of Acad. D. L. Rakhmankulova, - Ufa: Reaktiv, - 14-16 november, - 2016, - p. 39-40.
8. Alimardanov, Kh.M., Sadygov, O.A., Almardanova, M.B., Dzhililova, A.A., Mamedov, A.M. Electrophilic oxygenation of indeterminate tetracyclic hydrocarbons by hydrogen peroxide in the presence of P \ominus -containing heteropolyacids // Actual problems of modern chemistry and biology. International scientific conference. - Ganja, - May 12-13, - 2016, T.1, - p. 135-139.
9. Alimardanov, Kh. Epoxidation and oxidative dihydroxylation of C₁₀–C₁₃ unsaturated bridged hydrocarbons involving hydrogen peroxide and modified forms of heteromolybdc compounds / O.A.Sadygov, N.I.Garibov, N.R.Dadashova, M.B. Almardanova [et. al] // Petroleum Chemistry, -2017. 57, №3, - p. 415-423.
10. Alimardanov, Kh. Epoxidation of tetracyclodecene hydrocarbons with the H₂O₂·CO(NH₂)₂ adduct in the presence of heteropoly compounds containing rare-earth metal cations / O.A.Sadygov, N.I.Garibov, E.S.Musaeva, N.R.Dadashova & M.B. Almardanova // Russian Journal of General Chemistry, - 2017. Vol.87, issue 2, №5, - p. 208-214.
11. Alimardanov, Kh. Liquid phase oxidative funktionalization of organic compounds by hydrogen peroxide in a system inducing electrophilic reagents / O.A.Sadygov, N.I.Garibov, N.R.Babayev, M.B. Almardanova // Processes of petrochemistry and oil refining, - 2017. №2, - p. 89-143.

12. Alimardanov, Kh.M., Sadygov, O.A., Garibov, N.I., Babaev, N.R., Almadanova, M.B. Liquid-phase oxidative functionalization of organic compounds with hydrogen peroxide in a system inducing electrophilic reagents // Inter. scientist conf. "Petrochemical synthesis and catalysis in complex codified systems" dedicated to the 100th anniversary of A.B.K. Zeynalov, - Baku, - 29-30 June, - 2017, p. 18-21.
13. Alimardanov, H.M., Alaskarova, M.B. Epoxidation of cyclododecene in the presence of hydrogen-peroxide and polyoxyperoxy-tungstate [Text] // International scientific-practical conference "Innovative perspectives of oil refining and oil chemistry", dedicated to the 110th anniversary of Academician V.S. Aliyev, - October 9-10, - 2018, - pp. 119.
14. Alimardanov, H.M., The method of obtaining epoxide of cycloolefins, Invention I20200028 Original date 18.10.2016; Date of decision 10.05.2018 / Sadygov, O.A., Abbasov, M.F., Garibov, N.I., Musayeva, E.S., Alaskarova, M.B.
15. Alimardanov, Kh.M., Babaev, N.R., Sadygov, O.A., Alaskarova, M.B. Synthesis of bridged polycyclic epoxides and/or polyols with the participation of polyoxo tungstate modified by cerium cations // Reaktiv-2019, Proceedings of the XXXII International Scientific and Technical Conference "Chemical Reagents, Reagents and Processes of Low-Tonnage Chemistry", dedicated to the 80th anniversary of Academician of the Academy of Sciences of the Republic of Bashkortostan Dilyus Lutfullich Rakhmankulov, - 2019, p.12-13.
16. Alaskarova, M.B. Epoxidation of some polycyclic bridged olefins in the presence of a modified polyoxomolybdenum compound // Young scientist, Inter.scientific journal, - Kazan, - 2021. No. 40 (382), - p. 1-4.
17. Alaskarova, M.B. "Preparation of amino alcohols based on oxiranes with C₁₀, C₁₂ polycyclic bridging fragments and their antimicrobial properties" // Young scientist, Inter.scientific journal, - Kazan, - 2021. No. 44 (386), - p. 1-4.
18. Alaskarova, M.B. Preparation of hydroxyamino derivatives of polycyclic bridging hydrocarbons and their antimicrobial properties

// Chemical problems, - 2022. №3 (20), - Pp. 271-276.

19. Aleskerova, M.B. Mono- and diepoxidation of tricyclo [5.2.2.0^{2,6}]undeca-3,8-diene and tricyclo [6.2.2.0^{2,7}]dodeca-3,9-diene with hydrogen peroxide // Processes of Petrochemistry and oil Refining, - 2022. Vol.23, №3, - p. 419-425.

20. Alaskarova, M.B., Musaeva, E.S., Alimardanov, Kh.M. Liquid-phase functionalization of C₁₀-C₁₂ polycyclic unsaturated hydrocarbons with the participation of hydrogen peroxide and amines // Conference dedicated to the 90th anniversary of Academician Sahib Museyib Aliyev, - Baku, - June 23, - 2023, p. 24.

21. Alimardanov H.M., Garibov N.I., Musaeva E.S., Aleskerova M.B. Epoxidation of mono- and polycyclic unsaturated hydrocarbons with organic and inorganic oxidizing agents // Azerbaijan Oil Industry Journal, - August, - 2023, - p. 46-51

The defense will be held on 21 November 2023 at 10⁰⁰ at the meeting of the Dissertation council ED 1.16 of Supreme Attestation Commission under the Institute of Petrochemical Processes named by academician Y.H. Mammadaliyev of Ministry of Science and Education of the Republic of Azerbaijan.

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Dissertation is accessible at the library of the Institute of Petrochemical Processes named by academician Y.H. Mammadaliyev of Ministry of Science and Education of the Republic of Azerbaijan.

Electronic version of the abstract is available on the official website of the www.nkpi.az.

Abstract was sent to the required addresses on 18 October 2023.

Signed for print: 17.10.2023

Paper format: A5

Volume: 38860

Number of hard copies: 20