ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 1, pp. 63–71. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © Kh.M. Alimardanov, N.I. Garibov, M.Ya. Abdullaeva, O.A. Sadygov, A.D. Kuliev, E.G. Ismailov, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 1, pp. 70–79.

Oxidative Dihydroxylation of Alicyclic Unsaturated Hydrocarbons with Vinyl- and Norbornene Fragments in Pseudohomogenic System

Kh. M. Alimardanov, N. I. Garibov, M. Ya. Abdullaeva,
O. A. Sadygov, A. D. Kuliev, and E. G. Ismailov

Mamedaliev Institute of Pertochemical Processes, National Academy of Sciences of Azerbaijan,
Khojaly avenue 30, Baku, 1025 Azerbaijan
e-mail: omar.sadiqov@gmail.com

Received November 22, 2011

Abstract—Oxidation of alicyclic unsaturated hydrocarbons (4-vinylcyclohexene, 5-vinylnorbornene, 5-cyclohexenylnorbornene, and 5-vinylbicyclooctene) with 30% hydrogen peroxide solutions and percarbamide is studied. Reaction was carried out at 40–70°C in the presence of heterogenized peroxocomplex compounds of molybdenum and tungsten formed "in situ" in the reaction of metal oxohalides with H_3PO_4, nano-dimensional particles of carbon material, and hydrogen peroxide. Main oxidation products of alicyclic diene hydro-carbons are the corresponding unsaturated epoxides and diols. Depending on the reaction condition their ratio varies in a wide range.

DOI: 10.1134/S1070363213010118

As known, many biologically active compounds of natural and synthetic origin having oxirane or hydroxyl fragments are formed by introduction of the corresponding oxygen-containing function in the unsaturated compound [1, 2]. The synthesis and transformations of epoxides of different structures is sufficiently well described in a series of reviews [3–6].

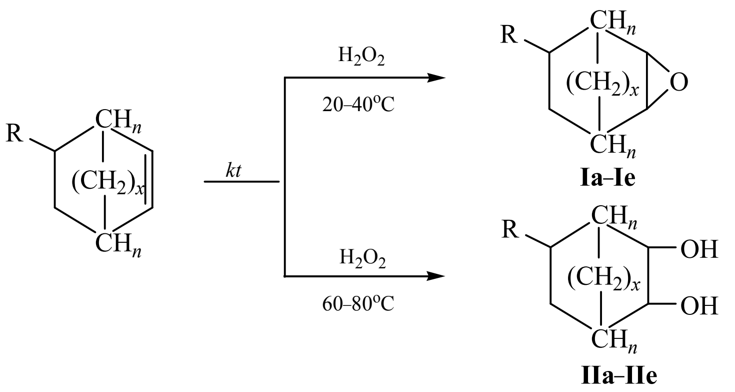
One of the practically important directions of transformation of these compounds is the synthesis of alcohols with sterically hindered structure among which a special place is occupied by mono- and polyhydroxy derivatives of di- and tricyclic hydrocarbons.

No data was found on the liquid phase oxidation of alicyclic dienes into saturated and unsaturated alcohols with the participation of heterogenized compounds of polyvalent metals and hydrogen peroxide.

Recently we have studied one-stage dihydroxylation of cyclohexene and its alkyl and vinyl derivatives in the presence of soluble molybdenum oxohalides and carboxylates [7–9]. In this paper there have been presented results of the one-pot liquid phase oxidation of cycloolefines with the vinyl and norbornene substituents in the presence of finely dispersed carbon material modified with the compounds of the VIb group metals in the presence of aqueous or dioxane solution of hydrogen peroxide or its adduct with carbamide. Among the problems under study was the investigation of some rules of oxidation of isolated structural fragments of diene hydrocarbons with no more than one double bond in a single ring.

Main products of oxidation of the above-mentioned hydrocarbons in the presence of pseudohomogenic catalytic system under mild conditions were the corresponding epoxides and diols formed according to the scheme below.

Catalytic epoxidation and dihydroxylation of unsaturated hydrocarbons with hydroperoxides is the electrophilic addition reaction. The rate of oxidation depends on the structure of the substrate molecule as well as on the electron density of the double bond. In particular, *cis*-isomers of alkenes are usually oxidized faster than their trans-analogs [10, 11]. This rule is observed also in the reaction of 4-vinylcyclohexene and 5-vinylnorbornene with organic peroxides [11, 12]. The epoxidation of the substrate at the ratio 4-vinylcyclohexane (vinylnorbornene) : ROOH equal to 1:2 proceeds strictly by the double bond of the ring having higher



$n = 2$, $x = 0$, R = $CH=CH_2$ (**a**); $n = x = 1$, R = $CH=CH_2$ (**b**); $n = x = 1$, R = cyclo-C_6H_9 (**c**); $n = 1$, $x = 2$, R = $CH=CH_2$ (**d**); $n = 1$, $x = 2$, R = cyclo-C_6H_9 (**e**).

electron density than the side vinyl group. Under the analogous conditions the epoxidation of cyclopentadiene dimer leads to the mixture of isomers of monoepoxide in the ratio close to equimolar [13].

Use of the hydrogen peroxide instead of organic hydroperoxides does not affect significantly the direction of the oxidation. As known, the oxidation of alicyclic unsaturated hydrocarbons C_6–C_{12} with peroxocomplex compounds of molybdenum and tungsten at 65°C gives 1,2-epoxycyclanes in 70–90% yield. But vinylcyclohexane is not oxidized under these conditions [14]. It is interesting to note that 4-vinylcyclohexane in the presence of Mo(V) oxobromide and acetic acid is oxidized at a high rate mainly with the formation of 1,2-dihydroxy-4-vinylcyclohexane [7].

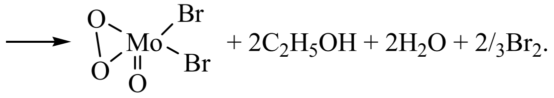
Preliminary experiments carried out with the participation of alicyclic dienes having different location of double bonds showed that while using 30% hydrogen peroxide or percarbamide in pseudohomogenic catalytic systems the oxidation of substrates proceeded strictly at the more strained double bond with the formation of the corresponding epoxides and vicinal diols.

For the investigation of state of catalysts highly dispersed on the carbon carrier we used Fourier-IR, EPR, and UV spectral methods. IR spectra of heterogenized catalysts were compared with the spectra of ethanol solution of molybdenum blue, of the solid residue obtained after evaporation of solvent, and also of the batches treated with hydrogen peroxide and 85% phosphoric acid.

In the IR spectrum of ethanol solution and of the solid residue of molybdenum blue (Fig. 1) strong bands are observed at 985 and 940 cm^{-1} characteristic of molybdenyl groups MoO^{3+} and MoO^{4+} respectively. While treated with 30% H_2O_2, the blue color of the starting sample changes to golden yellow, and the intensity of the band at 985 cm^{-1} strongly decreases. Simultaneously intense bands at 920 and 952 cm^{-1} corresponding to MoO^{4+} fragment appear, and also intense bands at 889, 680, 592, 562, 531, and 515 cm^{-1} related to the vibrations of peroxide bond –O–O–, to the symmetric and asymmetric vibrations of MoO_2 fragment [15]. In the IR spectrum of peroxophosphate complex of molybdenum the absorption bands of the PO_4^{2-} group vibration at 1090 and 1024 cm^{-1} were observed. The results obtained by us permit a suggestion that in the reaction of ethanol solution of molybdenum blue with H_2O_2 and H_3PO_4 peroxophosphate complexes of the dimeric or oligomeric forms of molybdenyl groups are formed according to the following scheme.

$$MoOBr_3{\cdot}2HBr + 2C_2H_5OH \rightleftarrows MoOBr_3{\cdot}2C_2H_5Br + 2H_2O,$$

$$MoOBr_3\ 2C_2H_5Br + 3H_2O$$



$$\longrightarrow MoO(O_2)Br_2 + 2C_2H_5OH + 2H_2O + 2/3Br_2.$$

IR spectra of heterogenized samples contain all the above-mentioned bands. But some of these bands, in particular, those characteristic of PO_4^{2-} group, are shifted to the long-wave range which is caused by their interaction with some fragments of the carbon material.

Electron absorption spectra of ethanol solution of $MoOBr_3{\cdot}2HBr$ have characteristic maxima at 14200 cm^{-1} (20), 21100 cm^{-1} (400), 24100 cm^{-1}

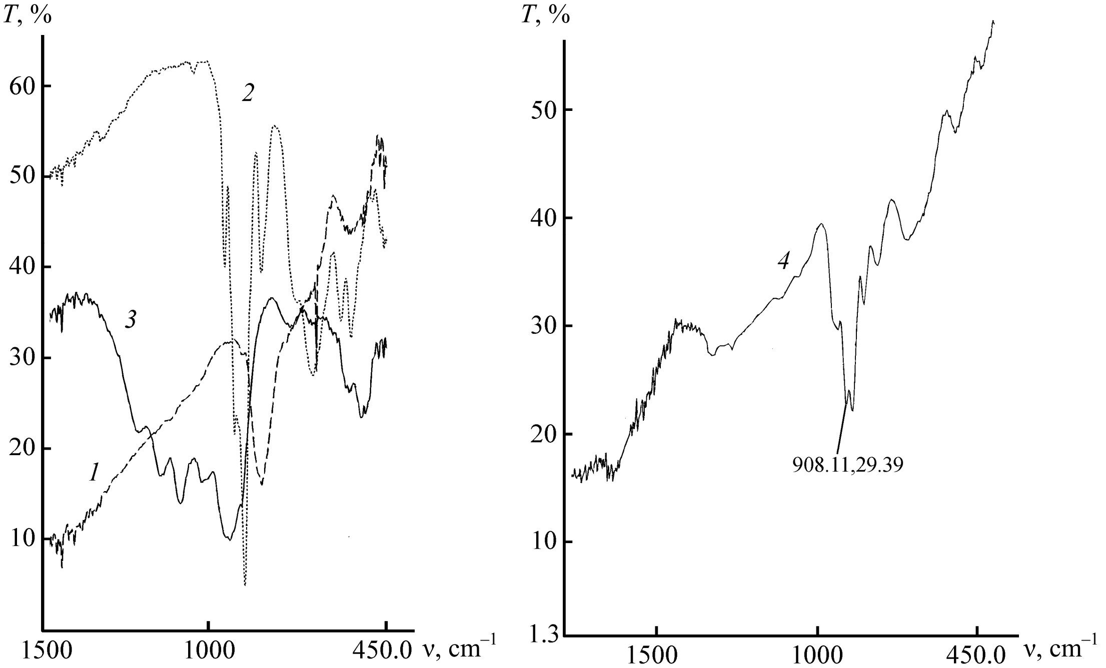


Fig. 1. Fourier IR spectra (*1*) of solid $MoOBr_3 \cdot 2HBr$ isolated from ethanol solution, (*2*) after treating with 30% H_2O_2, (*3*) a mixture of H_3PO_4 and H_2O_2, and (*4*) after four times application.

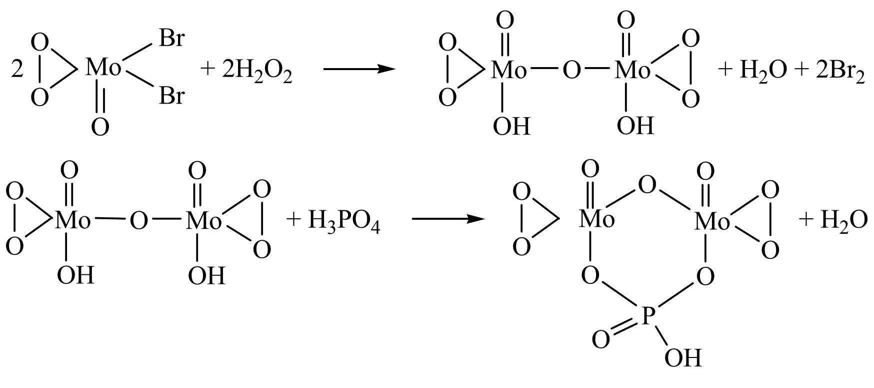
(2400), 26500 cm^{-1} (2000) which indicate the presence of MoO^{3+} ion in the complex (Fig. 2).

ESR spectra of $MoOBr_3 \cdot 2HBr$ contain the signals with g_{11} 2.094, g_1 1.943, A_{11}(Mo) 82 Gs, A_1(Mo) 31 Gs. The dependence of the intensity of ESR signal on the concentration of $MoOBr_3 \cdot 2HBr$ in acetone and ethanol solutions (Fig. 3) show that the main part of MoO^{3+} ion is in the dimeric state.

ESR spectra of acetone solution of $MoOBr_3 \cdot 2HBr$ show that it contains at least two complexes of MoO^{3+} with close values of magnet resonance parameters. At the increase in concentration of $MoOBr_3 \cdot 2HBr$ in the solution the intensity of signals of paramagnetic complexes of the second type increases as compared to that of the first type. In the ethanol solution bromide ligands of $MoOBr_3 \cdot 2HBr$ are gradually substituted with ethoxy and ethyl bromide ligands. Under these conditions Mo(V)=O group is retained.

In the course of the reaction of the above-mentioned solutions with H_3PO_4 these ligands are partially substituted with the phosphate ones, but the valence state of MoO^{3+} practically does not change. The addition of H_2O_2 to this solution leads to formation of a mixture of at least two peroxocomplexes with the participation of MoO^{4+} which is also confirmed by their IR spectra (absorption bands at 985, 952, 920, 889, 680, 592, 561, 531, 515 cm^{-1}). The obtained peroxocomplexes exhibit high activity in oxidation of unsaturated compounds.

The selection of the effective catalyst and oxidant was carried out by an example of oxidation of 4-vinylcyclohexene and 5-vinylnorbornene chosen as model



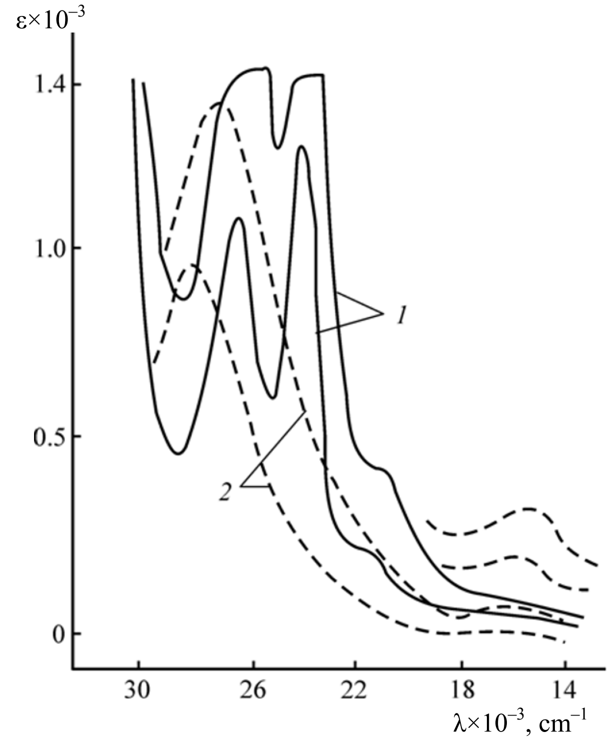


Fig. 2. Electron absorption spectra of ethanol solutions of $MoOBr_3 \cdot 2HBr$ (Mo = 6×10^{-3} g-at/l) (*1*) before and (*2*) after the oxidation of 4-vinylcyclohexane (*T* = 70°C, *t* = 2 h).

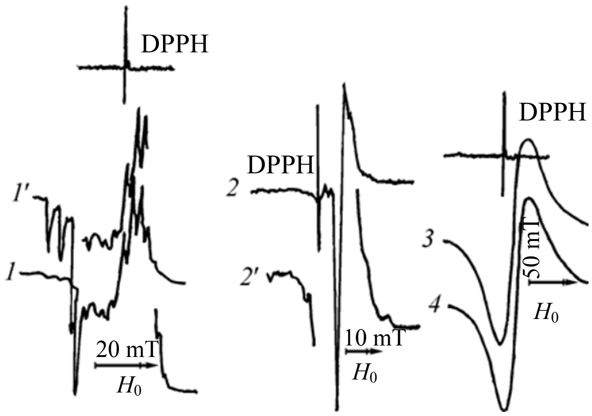


Fig. 3. ESR spectra at 77 K of frozen solutions of $MoOBr_3 \cdot 2HBr$ (1%) (*1, 1'*) in acetone and (*2, 2'*)ethanol; ESR spectra at 300 K of $MoOBr_3 \cdot 2HBr$ on carbon carrier treated with H_3PO_4 and H_2O_2 (*3*) before and (*4*) after the

substances. For comparison of the results ethanol solutions of molybdenum and tungsten blue and specially prepared diolate complex of molybdenum were used. The activity of catalysts and the effectiveness of oxidant were evaluated from the conversion of cycloolefin and the selectivity of the reaction by the overall amount of the formed epoxide and isomers of dihydric alcohol (see Tables 1–3).

Data of Tables 1–3 show that the conversion of starting hydrocarbons and the composition of the reaction products depend significantly on the nature of the catalyst and the oxidant used. In the presence of molybdenum and tungsten blue and also of the diolate complex **VIIk** in acetic acid the oxidation proceeds non-specifically. At the conversion of hydrocarbons 26.4–91.5% the product contains mainly mono-epoxides (9.3–27.4 wt %) and a mixture of isomers of glycols (47.3–72.7 wt %). Using the molybdenum and tungsten blue and especially complexes **VIIk** without the addition of carboxylic acids (formic, acetic, and oxalic) blue green color of solution conserves for 30–40 min. Under these conditions non-productive transformation of H_2O_2 prevails over the oxidation of substrates. The induction period of accumulation of oxidation products in the presence of complex **VIIk** reaches 50–60 min. The oxidation is accelerated only after the formation in the system of peroxocomplexes of Mo(VI) and W(VI), and it is accompanied by the change of the solution color to the golden yellow. But after the complete consumption of H_2O_2 the color again becomes blue green. In this case the use of acetic or oxalic acid (pH 1.8–3.7) favors the transformation of low active diolate complex to the active peroxide form. The catalysts **I** and **II** exhibit high activity in oxidation of substrates, and the reactions proceed practically without the inductive period. In contrast to the oxidation in the presence of homogenic catalysts, the peroxophosphate complexes of Mo and W heterogenized on the carbon material (catalysts **IIIk–VIk**) in the process 6 h long at 70°C provide mainly trans-glycols (ratio of *cis*- and *trans*-isomers from 5–25 to 75–85 at the conversion of the starting substances 72–78%. Some decrease in the activity of complexes **IIIk–VIk** as compared to homogenic catalysts **Ik** and **IIk** may be connected with the complications by diffusion. It is confirmed indirectly by the relatively high activity of the samples **Vk** and **VIk** prepared on the basis of highly dispersed nanocarbon material as compared to the samples **IIIk** and **IVk** prepared on the basis of the AG-3 carbon. Catalysts **Vk** and **VIk** after four times use retain their high activity.

According to the reported data [14, 15] the acidic groups in the peroxocomplexes MoO^{4+} and WO^{4+} (in this case PO_4^{3-} ions) under the conditions of epoxidation and dihydroxylation of unsaturated compound successfully compete with the oxidation products, in particular with diols, for the occupation of

Table 1. Activity and selectivity with respect to diol (*S*, %) of Mo- and W-containing catalysts in the oxidative dihydroxylation of 4-vinylcyclohexene with 30% aqueous H_2O_2 ($T = 70^oC$, $t = 6$ h, vinylcyclohexene : H_2O_2 : CH_3COOH = 1:2:0.2)

Catalyst	Conversion, %	Composition of product, wt %				*S*, %
		epoxide	diol+ monoacetate	α-oxyketone	unknown compounds	
Molybdenum blue	81.7	14.8	68.6	6.2	10.4	66.3
Tungsten blue	82.4	4.8	72.7	6.5	16.0	62.6
Ik	89.5	8.1	75.4	4.5	12.0	73.1
IIk	88.1	6.2	81.3	4.0	8.5	79.0
IIIk	69.2	6.0	58.0	10.4	25.6	55.5
IVk	65.7	4.0	61.6	11.8	22.6	58.0
Vk	77.0	8.2	76.5	4.6	10.7	74.4
VIk	72.3	5.0	72.0	8.4	14.6	69.0
VIIk	31.0	17.3	57.0	11.4	14.3	54.1
Vk[a]	51.7	3.8	74.5	7.0	14.7	72.7
VIk[a]	46.3	3.0	69.4	9.2	18.4	67.1

[a] Results obtained after 4-time use of catalyst.

Table 2. Activity and selectivity with respect to diol (*S*, %)of Mo- and W-containing catalysts in the reaction of oxidative dihydroxylation of 5-vinylnorbornene with 30% aqueous H_2O_2 ($T = 70°C$, $t = 6$ h, vinylnorbornene : H_2O_2 : CH_3COOH = 1:2:0.2)

Catalyst	Conversion, %	Composition of product, wt %				*S*, %
		epoxide	diol+ monoacetate	α-oxyketone	unknown compounds	
Molybdenum blue	87.0	9.3	73.5	3.8	13.4	71.4
Tungsten blue	91.5	5.0	74.8	4.7	15.5	72.1
Ik	92.7	6.2	80.1	5.0	8.7	78.3
IIk	93.0	4.8	80.5	6.0	8.7	78.6
IIIk	73.4	5.9	64.0	8.3	21.8	60.8
IVk	70.0	4.2	62.2	10.7	22.9	58.8
Vk	76.2	7.8	73.0	4.8	14.4	70.2
VIk	78.0	4.5	74.6	6.7	14.2	71.7
VIIk	26.4	27.4	47.3	3.2	22.1	44.7
Vk[a]	54.7	5.1	70.9	8.0	16.0	69.2
VIk[a]	58.1	3.6	66.5	9.6	20.3	64.3

[a] Results obtained after 4-time use of catalyst.

coordination centers on the MeO^{4+} ion. It prevents washing out of peroxocomplexes and the products of its transformation from the surface of carbon material.

From the data of table 4 it is seen that in going from aqueous H_2O_2 solution to dioxane and then to percarbamide both the rate of oxidation of 5-vinylnorbornene and the composition of reaction products considerably change. Whereas at the use of 30% aqueous hydrogen peroxide the main reaction products are isomers of 5-vinylbicyclo[2.2.1]norbornandiol, in the case of percarbamide under the same conditions monoepoxide becomes the main component of the product. Probably at the use of percarbamide this compound forms a complex with acetic acid and with the liberated water preventing the hydrolysis of epoxide, the primary reaction product.

The epoxidation proceeds exclusively at the double bond of the ring. The formation of bis-epoxide was observed only at a high ratio of H_2O_2 to 5-vinylnorbornene (4–6 : 1). But the epoxide yield does not exceed 8–12% because the reaction is accompanied by the opening of the oxirane fragments of the ring and the formation of carboxylic acids in the system [16–18].

The direction of transformation of active oxygen and the selectivity of the reaction significantly depend on the temperature of the experiment (see Fig. 4).

In the temperature range 30–50°C the oxidation of 4-vinylcyclohexene in the presence of complex **Vk** proceeds with the expressed induction period, and at low conversion of cycloolefin (8–15%) the main reaction product is 1,2-epoxy-4-vinylcyclohexane.

Table 3. Conversion and selectivity of oxidation of cycloolefins with 30% water solution of H_2O_2 in the presence of the catalyst **Vk** at different temperatures (molar ratio cycloolefin : H_2O_2 : CH_3COOH 1 : 2 : 0.2, *t* = 4 h)

Unsaturated hydrocarbon	Temperature, °C									
	30°C		40°C		50°C		60°C		70°C	
	I:**II**	conversion, %	**I**:**II**	conversion, %	**I**:**II**	conversion, %	**I**:**II**	conversion, %	**I**:**II**	conversion, %
4-Vinylcyclohexene	57.3:11.5	8.0	68.4:14.2	10.3	65.8:17.6	12.8	53.7:32.0	21.7	47.0:50.5	30.5
5-Vinylbicyclo[2.2.1]-hept-2-ene	72.4:12.6	11.7	75.0:14.2	14.0	60.6:27.4	19.5	42.1:45.4	32.3	19.4:68.3	45.6
5-Vinylbicyclo[2.2.1]-oct-2-ene	64.4:8.4	9.4	65.0:13.5	11.0	59.7:23.2	13.1	44.2:42.5	20.4	30.7:52.5	32.2
5-(Cyclohexen-3-yl)-bicyclo[2.2.1]pent-2-ene	70.7:13.0	12.3	74.2:18.3	14.5	57.0:31.4	18.0	40.8:49.2	28.8	24.2:62.6	47.0
5-(Cyclohexen-3-yl)-bicyclo[2.2.2]oct-2-ene	64.0:10.5	11.0	68.7:14.0	13.0	53.3:29.8	17.0	49.0:34.5	28.0	32.0:53.2	37.4

Table 4. Dependence of the conversion of 5-vinylnorbornene and the selectivity of the reaction on the nature of oxidant used (catalyst complex **Vk**, *T* = 70°C, *t* = 6 h, [CH_3COOH] 0.2 M)

Oxidant	Starting rate of consumption of active oxygen, (mol l^{-1} s^{-1})$\times10^{-3}$				Conversion[a], %	Selectivity[a], %	
	5-vinylnorbornene:H_2O_2 ratio					by epoxide	by diol
	1:0.5	1:1	1:1.5	1:2			
H_2O_2 (30% water solution)	0.71	1.13	1.84	2.53	76.2	6.6	70.2
H_2O_2 (30% dioxane solution)	1.22	1.89	2.42	2.82	92.6	52.3	37.5
Percarbamide [adduct H_2O_2 and $CO(NH_2)_2$]	2.34	3.51	4.43	5.54	90.0	73.7	14.7

[a] Amount of oxidant is 2 mol.

After 7 h of the process the summary yield of epoxyvinylcyclohexane is only 25.7–32.0% though the degree of transformation of active oxygen reaches 75.0–82.5%. Probably the formation of intermediate with the participation of oxoperoxocomplex compound MoO^{4+} and the transfer of active oxygen to substrate under these conditions is connected with energy hindrances, therefore its oxidation is accompanied by non-productive transformation of H_2O_2. At the increase in temperature from 50 to 70°C the rate of oxidation and the degree of dihydroxylation of 4-vinylcyclohexene sharply increase, and the yield of glycol reaches 67.5–73.0%. Further increase in temperature to the range 70–90°C causes the decrease in selectivity of the reaction with respect to diol, though conversion of 4-vinylcyclohexene reaches 95–97%. Under these conditions dihydroxylation of 4-vinylcyclohexene is accompanied by intensifying of oxidation of glycol to the isomers of α-oxyketones and further to carboxylic acids.

Note that in the presence of complexes **Vk** and **VIk** dihydroxylation of 4-vinylcyclohexane in the temperature range 40–60°C proceeds with the forma-tion of a mixture of *trans*-(75–85%) and *cis*-isomers (15–25%). At the increase in temperature the content of *trans*-isomer in product increases and above 70°C *cis*-1,2-dioxy-4-vinylcyclohexane practically does not form.

The investigation of dynamics of accumulation of the oxidation products of 4-vinylcyclohexene by means of GLC and IR spectroscopy shows that in the temperature range 30–50°C mainly the epoxidation of cycloolefine takes place, and the accumulation of epoxide passes through the maximum. In this case the oxirane ring forms only in the cyclohexene fragment, and the vinyl group remains untouched. The formation

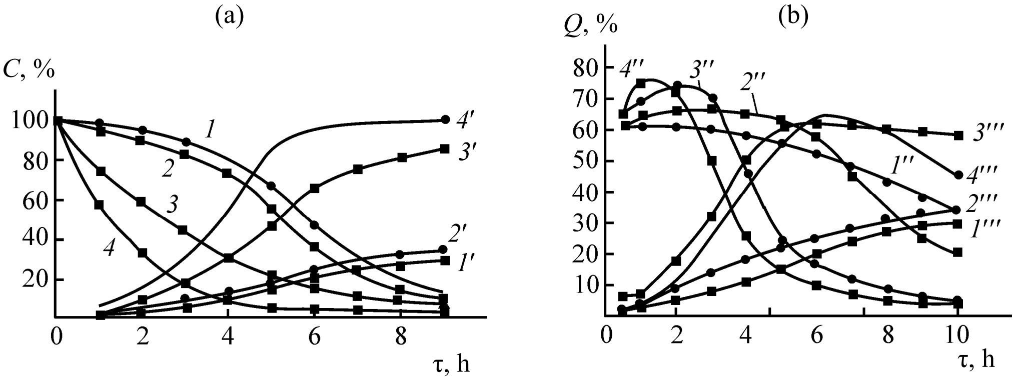


Fig. 4. Dynamics of transformation of (a) starting substances and (b) accumulation of main reaction products of dihydroxylation of 4-vinylcyclohexene at various temperatures. Catalyst: $H_3\{PO_4[MoO(O_2)_2]_4\}/C$ (catalyst A), 4-vinylcyclohexene : H_2O_2 :CH_3COOH = 1:2:0.1. Temperature: (*1, 1′, 1″, 1‴*) 30°C; (*2, 2′, 2″, 2‴*) 50°C; (*3, 3′, 3″, 3‴*) 70°C; (*4, 4′, 4″, 4‴*) 90°C; (*1–4*) is the degree of transformation of hydrogen peroxide; (*1′–4′*) is the conversion of vinylcyclohexene; (*1″–4″*) is the yield of 4-vinyl-1,2-epoxycyclohexane; (*1‴–4‴*) is the yield of 4-vinylcyclohexane-1,2-diol.

of some amount of diepoxide, the product of oxidation of 4-vinylcyclohexene at both double bonds is observed in more rigid reaction conditions (temperature range 70–90°C, 4-vinylcyclohexene-H_2O_2 molar ratio 1 : 4–6). Its content in the product according to GLC data does not exceed 5–8% from the amount of 4-vinyl-1,2-epoxycyclohexane. Under such conditions the epoxidation of vinyl group competes with the hydrolysis of oxirane cycle and further with the oxidation of glycol.

The substitution of vinyl group with cyclohexenyl one in the molecule of 5-vinylnorbornene practically does not affect the direction of the attack of the active oxygen from the peroxocomplexes (Table 3). The epoxidation and dihydroxylation of substrate proceeds mainly at the norbornene fragment. The reactivity of 5-cyclohexenylbicyclo[2.2.1]-octen-2 to some extent differs. The part of its epoxidation by cyclohexene fragment reaches 20–25 wt %.

The composition and structure of synthesized monoepoxides **Ia-e** and diols **IIa-e** were established by the IR and ^{1}H and ^{13}C NMR spectroscopy.

In the IR spectra of monoepoxides synthesized **Ia–Id** the absorption bands characteristic of the multiple bond of cyclohexene (680 and 1649 cm^{-1}, **Ia**), bicycloheptene, and bicyclooctene (720 and 1670 cm^{-1}, **Ib–Id**) fragments are absent. Strong absorption bands at 910, 990, and 3040 cm^{-1} belong to vinyl group (in the compounds **Ia, Ib**), and in the range 800, 858, and 1260 cm^{-1}, to the oxirane ring [22]. Characteristic signals of carbon atoms at the double bond of cyclohexene (for compounds **Ia** and **IIa** in the range 126 ppm), of bicyclo[2.2.1]heptene and bicyclo[2.2.2]-octane fragments (for compounds **Ib–Id**, **IIb–IId** at 131 ppm) in the ^{13}C NMR spectra of epoxides **Ia–Id** and diols **IIa–IId** were also absent. Signals at 57-60 ppm (for **Ia**) and at 63–68 ppm (for compounds **Ib–Ie**) are attributed to the carbon atoms of oxirane fragment. For diols **IIa-e** these signals appear at 72–82 ppm respectively. The obtained data are also confirmed by the ^{1}H NMR spectra [20,21]. Besides, in the IR, ^{1}H, and ^{13}C NMR spectra of starting substances and the products **Ia–Ie, IIa–IIe** the absorption bands and signals characteristic of the vinyl and cyclohexenyl residues practically do not change.

Hence, it was established that heterogenized peroxocomplexes prepared on the basis of molybdenum and tungsten oxohalides with the participation of orthophosphoric (or oxalic and acetic) acid and nanoparticles of carbon exhibit high efficiency in the oxidation of cyclic diene hydrocarbons to the corresponding unsaturated epoxides and diols which may be used as starting substances for preparing organic compounds for different applications.

EXPERIMENTAL

Fourier IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum BX spectrometer in KBr pellets in the range 450-4400 cm^{-1}. ESR spectra were measured on a JEOL JES-PL 3x radiospectrometer (9300 MHz) at 77 and 300 K. Diphenylpicrylhydrazyl was used as a standard while measuring g factor values (g = 2.0036). Electron absorption spectra were measured on a Specord M 40 UV/Vis spectrophotometer. IR spectra were obtained on an UR-20 spectrometer. ^{1}H NMR spectra were taken on a Varian T-60 (60 MHz) and Jeol FX 90Q (90 MHz) spectrometers in CCl_4 and acetone-d_6. ^{13}C NMR spectra were recorded on a Varian T-60 (20 MHz) and Bruker AM-300 (75.432 MHz) spectrometers.

The composition and purity of starting hydrocarbons and products of their oxidation were evaluated by GLC on a Tsvet-500 chromatograph with flame ionization detector, 2000×2 mm column filled with polyethyleneglycol succinate on Chromosorb (5 wt %), and helium carrier gas. Column temperature 160°C, evaporator temperature 280°C.

The composition of obtained catalysts was confirmed by IR, ESR, and UV spectroscopy.

4-Vinylcyclohexene, 5-vinylnorbornene, and the adducts of 4-vinylcyclohexene to cyclopentadiene and 1,3-cyclohexadiene were used as starting substances. The latter were prepared by (4+2) addition of hydrocarbons in a pressure reactor in the presence of 5.0 wt % of synthetic mordenite or natural clinoptilolyte transformed to H-form. The reaction was carried out under nitrogen at 200–220°C and molar ratio vinylcyclohexene–cyclopentadiene (or cyclohexadiene) 1:1.5 in the course of 2–4 h. After the reaction was complete, the reactor was quickly cooled, and the reaction mixture was distilled in a vacuum. Physicochemical properties of the dienes synthesized coincide with the reported data [22, 23].

The catalysts heterogenized on carbon material were synthesized according to the following procedure.

(a) A powder of metallic molybdenum or tungsten was heated to 80–100°C in a porcelain cup and treated with an excess of bromine under moist air atmosphere. After that reaction mixture was dissolved in anhydrous ethanol or acetone and filtered. The filtrate obtained was evaporated to dryness. Yield of the molybdenum or tungsten blue was 45-48%. The solid obtained was treated in succession with the required amount (Mo^{n+} : PO_4^{3-} = 4:1) of 85% H_3PO_4 and 30% hydrogen peroxide (catalysts **Ik** and **IIk**). Heterogenized catalysts (**IIIk** and **IVk**) were prepared by impregnation of the powder-like AG-3 carbon with the ethanol solutions of the molybdenum or tungsten blue. The obtained mass was treated with water solutions of phosphoric acid and hydrogen peroxide and heated for 2 h at 50–60°C and 2 h at 120–150°C. The content of molybdenum in the catalyst **IIIk** or tungsten in the catalyst **IVk** was 15 wt %.

(b) A powder of metallic molybdenum and tungsten was reacted with carbon tetrachloride or bromoform at 75–78°C in the presence of the metallic aluminum activator. Subsequent treating of obtained batches according to the above-reported procedure gave highly dispersed molybdenum- and tungsten-containing catalysts **Vk** and **VIk** on nanocarbon material.

For comparison of the activity of catalyst the diolate complex of molybdenum **VIIk** was used. It was prepared by heating of a mixture of isomers of norbornandiol and molybdenum blue at 50–60°C for 1.5–2 h. The oxidation of unsaturated hydrocarbons was carried out in glass 100 cm^3 microreactor equipped with temperature-controlled jacket, dropping funnel, and condenser under the intense stirring by means of magnetic stirrer. The reactor was loaded with the given amount of unsaturated hydrocarbon, of the catalyst, and of acetic acid and heated to the temperature 40–70°C. After that 30% water or dioxane solution of hydrogen peroxide was added dropwise. For comparison of the results a solution of percarbamide in acetic acid was used.

Hydrogen peroxide concentration was evaluated by permanganatometric method.

6-Vinyl-*exo*-3-oxatricyclo[3.2.1.0^{2,4}]octane (Ib)was prepared from 12.0 g of 5-vinylnorbornene, yield 9.0 g (66%), bp 83–86°C (3.5 mm Hg), d_4^{20} 1.0235, n_D^{20} 1.4876. IR spectrum, ν, cm^{-1}: 3060, 3040, 1620, 890, 930–900 (–CH=CH$_2$); 1250, 866, 858 (–C–O–C–) [21]. ^{1}H NMR spectrum, δ, ppm: 3.47 (2H, H^2, H^4), 2.13 t (1H, H^5), 5.79 q (H^9), 4.89–4.96 m (2H^{10,} $J_{9,10''}$16.4 Hz, $J_{9,10}$ 9.0 Hz, $J_{10',10''}$ 2.0 Hz), 1.25–1.75 m (6H, cycle, $J_{7a,7s}$ 11.4 Hz, $J_{6,7exo}$ 3.9 Hz, $J_{6,7endo}$ 9.2 Hz) [20, 21].

***exo*-6-(Cyclohex-3-enyl)-*exo*-3-oxatricyclo-[3.2.1.0$^{2.4}$]-octane (Ic)** was prepared from 17.4 g of 5-vinylnorbornene, yield 9.8 g (51.6 %), bp 108–110°C (2 mm Hg), mp 46–48°C. IR spectrum, ν, cm^{-1}: 3068, 1640–1650 (–CH=CH–), 840, 920, 1250–1260 (–C–O–C–). ^{1}H NMR spectrum, δ, ppm: 5.59 m (2H, H$^{3'}$, H$^{4'}$, $J_{3',4'}$ 11.2 Hz), 1.48–2.03 m (6H, 3CH$_2$ of cyclohexene, $J_{5',6'}$ 4.4 Hz), 2.89 q (2H, H^2, H^4), 1.25–1.76 m (7H of tricyclooctane, $J_{6endo,7endo}$ 9.2 Hz, $J_{6endo,5}$ 4.5 Hz, $J_{6endo,1'}$ 4.5 Hz).

***exo*-6-(Cyclohex-3-enyl)-*exo*-3-oxatricyclo-[3.2.2.0$^{2.4}$]nonane (Id)** was prepared from 18.8 g of 5-cyclohexenylbicyclo[2.2.2]octane. Yield 8.6 g (42.3%), mp 58–60°C. IR spectrum, ν, cm^{-1}: 3060, 1620–1640 (–CH=CH–), 835, 842, 860, 910, 1260 (epoxy group).

^{1}H NMR spectrum, δ, ppm: 5.58 d (2H, $H^{3'}$, $H^{4'}$, $J_{3',4'}$ 11.4 Hz) 1.49–2.04 m (6H, 3H^2 of cyclohexene, $J_{5',6'}$ 4.4 Hz), 2.86 q (2H, H^2, H^4), 1.27–1.78 m (9H, tricycloninane, $J_{6endo,7endo}$ 9.2 Hz, $J_{6endo,5}$ 4.3 Hz), 1.26 t (2H, H^{8a}, H^{9a}, $J_{8a,9a}$ 2.6 Hz), 1.51 t (2H, $H^{8b,}$ H^{9b}, $J_{8b,9b}$ 3.5 Hz).

5-Vinylbicyclo[2.2.1]heptan-*exo,endo*-2,3-diol (IIb) was prepared from 12.0 g of 5-vinylnorbornene, yield 8.2 g (53.5%), mp 57–59°C. IR spectrum, ν, cm^{-1}: 3050, 1650 (–CH=CH$_2$), 3600–3200, 1150, 1120, 1100, 1080, 1050 (OH). ^{1}H NMR spectrum, δ, ppm: 3.25 d (2H, H^1, H^4), 3.12 d.d (1H, H^5), 2.91 d.d (1H, H^6, $J_{5endo,6endo}$ 9.1 Hz, $J_{1,6}$ 5.2 Hz), 3.87–4.93 m (2H, H^{9a}, $H^{9b,}$ $J_{9a,9b}$ 2.8 Hz, $J_{8,9a}$ 12.4 Hz), 4.95 d (1H, OH$_{endo}$), 4.89 d (1H, OH$_{exo}$).

***exo*-5-(Cycloxex-3-enyl)-bicyclo[2.2.1]heptan-*exo,endo*-2,3-diol (IIc)** was prepared from 17.4 g of 5-vinylnorbornene. Yield 10.3 g (48.7%), mp 112–114°C. IR spectrum, ν, cm^{-1}: 3020–3050, 1620–1650 (–CH=CH–), 3600–3200, 1150, 1100, 1180 (OH). ^{1}H NMR spectrum, δ, ppm: 5.61 t (2H, $H^{3'}$,$H^{4'}$, $J_{3',4'}$ 12.4 Hz), 1.51–1.99 m (6H, 2CH$_2$ of cyclohexene), 3.25 d (2H, H^2, H^3, $J_{1',2}$ 6.8 Hz), 3.08 d.d (1H, H^5, $J_{4,5}$ 5.2 Hz, $J_{5,6}$ 10.2 Hz) 1.25–1.56 m (6H, bicycloheptane, $J_{5endo,6endo}$ 9.2 Hz, $J_{6,6}$ 12.1 Hz), 4.93 d (1H, OH$_{endo}$),4.93 d (1H, OH$_{exo}$).

***exo*-5-(Cyclohex-3-enyl)bicyclo[2.2.2]octan-*exo,endo*-2,3-diol (IId)** was prepared from 18.8 g of *exo*-5-(cyclohex-3-enyl)bicyclo[2.2.2]oct-2-ene. Yield 10.75 g (48.4%), mp 120–122°C. IR spectrum, ν, cm^{-1}: 3020–3050, 1650 (–CH=CH–), 3200–3600, 1150, 1120, 1180, 1050 (OH). ^{1}H NMR spectrum, δ, ppm: 3.24 d (H^2, H^3), 5.61 t ($H^{3'}$, $H^{4'}$ of cyclohexene), 4.81 br.s (2OH).

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