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Epoxidation of the Products of Codimerization of Cyclopentadiene and Cyclohexadiene Hydrocarbons Catalyzed by Lanthanide–Molybdenum Polyoxometalates

N. I. Garibov, Kh. M. Alimardanov, N. R. Dadashova,
O. A. Sadygov, M. B. Almardanova, and A. D. Kuliev

Mamedaliev Institute of Petrochemical Processes, Azerbaijan National Academy of Sciences,
pr. Khojaly 30, Baku, AZ1025 Azerbaijan
e-mail: omar.sadiqov@gmail.com

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Abstract—[4+2]-Codimerization of cyclohexa-1,3-diene, cyclopentadiene, and their methyl-substituted derivatives in the presence of H-forms of synthetic mordenite and natural clinoptilolite was studied. Application of zeolites as catalyst decreases the rate of di- and trimerization of cyclopentadiene and its methyl-substituted derivatives, increases the reaction selectivity with respect to their codimers with cyclohexa-1,3-diene and its methyl-substituted derivatives as well as 4-vinylcyclohexene. Epoxidation of the synthesized codimers with the adduct of hydrogen peroxide with urea in the presence of gadolinium- and neodymium-containing phosphorus molybdenum complexes as catalysts has been investigated, and optimal conditions for preparation of diepoxides of tricyclic dienes have been found.

Keywords: cyclopentadiene, cyclohexa-1,3-diene, 4-vinylcyclohexene, mordenite, clinoptilolite, acidic form, dimerization, epoxidation, lanthanide-molybdenum polyoxometalate

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The recently emerged interest to cyclopentadiene and cyclohexadiene hydrocarbons is due to the possibility of preparation of polyfunctional bridged compounds, structural analogs of some natural terpene compounds. Due to the increased raw-material precursors of C_5–C_6 cyclic unsaturated hydrocarbons [1] and development of [4+2]-addition reactions, the possibility has appeared to synthesize various adducts [2–4] that can act as monomers and intermediate products for preparation of valuable drugs, perfume-cosmetic goods, biologically active compounds, and special polymers. In particular, condensation of cyclohexa-1,3-diene-5-ol-6-one derivatives with cyclopentadiene into alkyl-substituted tricyclo[5,2,2,$0^{2.6}$]undeca-3,8-diene-10-ol-11-one has been reported [2].

Use of diphenyl- or *tert*-butylcyanoketenes in the reaction with cyclohexa-1,3-diene as dienophile yields ethers with bridged structure, isomerizing into bicyclo [4.2.$0^{3,8}$]oct-4-en-1-one-2.2-diphenyl or bicyclo[4.2.$0^{3,8}$]-oct-4-en-1-one-2-cyano-2-*tert*-butyl [3].

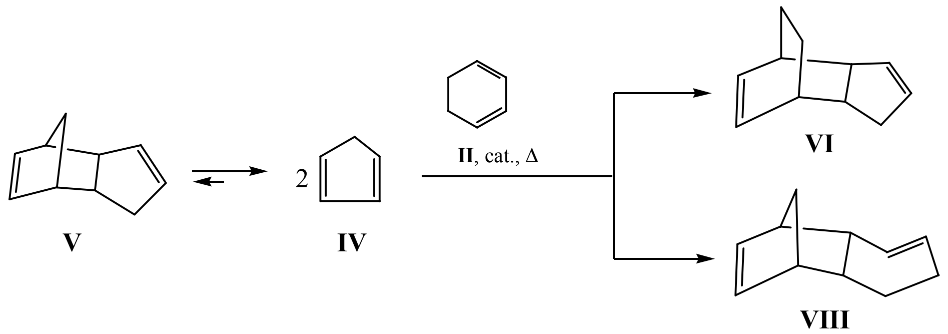
Condensation of pentamethylcyclopentadiene with allene derivatives in the presence of the $[Ar_3N^{\cdot+} + SbF_6^-]$ (Ar = *p*-BrC^6H_4) system yields a mixture of *exo/endo* isomers of methyl- and phenyl-substituted camphenes [4]. Dimerization of cyclohexa-1,3-diene or its codimerization with hexadiene-2,4 in the presence of the same catalytic system in CH_2Cl_2 solution at 0°C leads to tricyclo[6.2.2.$0^{2,7}$]dodeca-3.9-diene and 6-methyl-5-propenylbicyclo[2.2.2]oct-2-ene in ≈70% yield and *endo:exo* diastereoselectivity of 5 : 1 [4].

The Diels-Alder condensation of vinylboronates with cyclopentadiene and cyclohexa-1,3-diene leading to the boron derivatives of norbornene in up to quantitative yield and various ratio of the *endo* and *exo* isomers has been described [5].

Treatment of the adduct of cyclohexa-1,3-diene and maleic anhydride with the solution containing NH_4OH and NaClO yields *endo*-3-aminobicyclo[2.2.2]oct-5-ene-2-*endo*-carboxylic acid [6].

In view of the above and aiming to synthesize a wide range of polycyclic multifunctional compounds, it was of interest to elaborate selective methods of codimerization of cycloalkadiene hydrocarbons of

Scheme 1.



comparable reactivity and to study further functionalization of the condensation products.

Literature analysis has shown that polycyclic unsaturated hydrocarbons oxidation followed by acid-catalyzed transformation of epoxy- or hydroxy-terpenoid structures is among the selective methods to form new oxygen-containing compounds [7–10]. Selectivity of such transformations is determined by the catalytic system efficiency and the reaction conditions [11–14].

This work aimed to investigate condensation of C_5–C_8 cyclic dienes in the presence of H-forms of natural clinoptilolite (Ai-Dag deposit, Azerbaijan) or synthetic mordenite ($SiO_2/Al_2O_3=10$) and epoxidation of the synthesized polycycloalkadiene hydrocarbons with the adduct of hydrogen peroxide and urea involving the *in situ* formed polyoxoperoxogadolinium (neodymium) phosphorus molybdenum complexes.

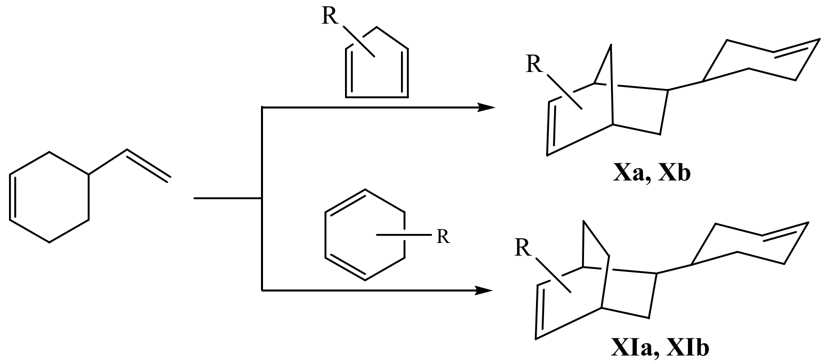
Thermal condensation of methyl-substituted isomers of cyclopentadiene (**I**) with cyclohexa-1,3-diene (**II**) as well as of the isomers of methylcyclohexadiene-1,3 (**III**) with cyclopentadiene **IV** yielded a complex mixture of dimers, codimers, and oligomers of those hydrocarbons, the dimers being the major components [15]. The ratio of dimers and codimers varied in the range of (3–5) : 1. To determine the activity of the H-form of natural clinoptilolite (or synthetic mordenite), codimerization of cyclohexadiene-1,3 with cyclopentadiene was considered as a model reaction.

It was found that dimerization of cyclopentadiene was reversible under the reaction conditions (200–220°C and 5 wt % of catalyst), and the rate of decomposition of the formed dimer, tricyclo[5.2.1.0^{2,6}]deca-3,8-diene (**V**), exceeded the rate of the monomer dimerization. Unlike dimer **V**, codimer of cyclohexa-1,3-diene with cyclopentadiene, *endo*-bicyclo[5.2.2.0^{2,6}]undeca-3,8-diene **VI** was stable under the same conditions and remained the major reaction product. No dimerization of cyclohexa-1,3-diene into tricyclo[6.2.2.0^{2,7}]dodeca-3,9-diene (**VII**) was observed. Thus, the selectivity of co-condensation of cyclopentadiene with cyclohexadiene-1,3 in the presence of H-forms of the above mentioned zeolites reached 90–92% with respect to codimer **VI** (Scheme 1).

Structure of compound **VI** was elucidated using IR, ^{1}H, and ^{13}C NMR spectroscopy as well as chromato-mass spectrometry. Hydrogenation of the above-mentioned mixture consisting mainly of diene **VI** (~98.5%) in the presence of Raney nickel at 100°C and pressure of 10 MPa resulted in *endo*-bicyclo[5.2.2.0^{2,6}]undecane (**IX**) (its physico-chemical constants were consistent with the reference data [15]). According to the GC analysis, content of adduct **VIII** did not exceed 1.0–1.5 wt %. That adduct was formed from cyclopentadiene (a diene) and cyclohexa-1,3-diene (a dienophile). Apparently, adduct **VIII** was unstable under the reaction conditions due to higher strain in the norbornene fragment in comparison with the bicyclooctane fragment in compound **VI** and, similarly to dimer **V**, readily decomposed into monomers. Therefore, under the studied conditions cyclohexadiene-1,3 acted majorly as a diene in the condensation reaction, cyclopentadiene acting as a dienophile.

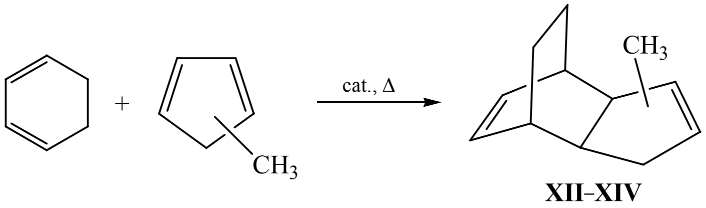
Condensation of 4-vinylcyclohexene with cyclopentadiene, cyclohexa-1,3-diene, and their methyl-substituted derivatives proceeded majorly to form 5-(cyclohexen-3-yl)bicyclo[2.2.1]hept-2-ene (**Xa**), 5-(cyclohexe-3-yl)bicyclo[2.2.2]oct-2-ene (**XIa**), and their methyl-substituted derivatives **Xb** and **XIb**, respectively, under the same conditions. In that case, vinyl group of 4-vinylcyclohexene molecule acted as a dienophile (Scheme 2).

Scheme 2.



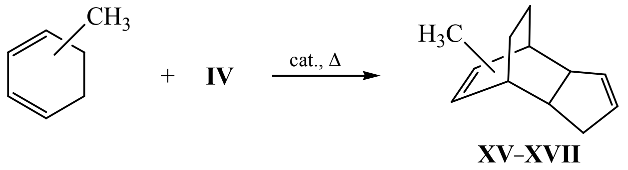
R = H (**a**), CH_3 (**b**).

Scheme 3.



XII, 3-Me; **XIII**, 4-Me; **XIV**, 5-Me.

Scheme 4.



XV, 1-Me; **XVI**, 9-Me; **XVII**, 10-Me.

Reactions of cyclohexa-1,3-diene with the isomers of methylcyclopentadiene or of cyclopentadiene with methyl-substituted isomers of cyclohexa-1,3-diene occurred similarly. In particular, codimerization of a mixture of isomers of methylcyclopentadiene (48.7% of 1-methylcyclopentadiene, 50.6% of 2-methylcyclopentadiene, and 0.7% of 5-methylcyclopentadiene) with cyclohexadiene-1,3 proceeded as shown in Scheme 3, while codimerization of the mixture of isomers of methylcyclohexa-1,3-diene with cyclopentadiene followed Scheme 4.

From the ^1H and ^{13}C NMR as well as GC analysis data, the major products of reaction of methylcyclopentadiene (48.7% 1-methylcyclopenta-1,3-diene, 50.6% 2-methylcyclopenta-1,3-diene, and 0.7% 5-methylcyclopenta-1,3-diene) with cyclohexa-1,3-diene were adducts **XII** and **XIII**. Traces of adduct **XIV** were formed, and 2-methyl-substituted isomers were not detected. According to ^{13}C NMR spectroscopy, methyl groups in adducts **XII** and **XIII** were located in the restricted cisoid position with respect to the bridge.

3-Methylenecyclohex-1ene having rigid transoid configuration did not react with cyclopentadiene [16, 17] (Scheme 4). Other isomers with the methyl group in the cisoid position entered the reaction and the products composition was consistent with the isomeric composition of the original mixture of methylcyclohexa-1,2-dienes. From the GC data, the major products of the reaction were 1- and 9-methyltricyclo[5.2.2.0^{2,6}]undeca-3,8-dienes. The reactivity of isomers of methylcyclohexa-1,2-diene was much lower than that of unsubstituted diene **II** due to the methyl substituent presence at the double bond. Under the same conditions, the yield of codimer of dienes **II** and **IV** was 1.5–1.8 times higher than that of codimers of diene **IV** and the isomers of methylcyclohexa-1,3-diene. A similar trend was observed in the case of codimerization of diene **II** with methylcyclopentadiene compared to codimerization of dienes **II** and **IV**.

We failed to find any physico-chemical, spectral, or chromatographic parameters of isomeric methyltricycloundeca-3,8-dienes **XII–XVII** in the literature. On top of that, ^{1}H NMR spectra of compounds **VI–XXII** contained complex spin systems due to the presence of bi-, tri-, and pentacyclic framework fragments in the structure. Therefore, identification of various C_{10}–C_{12} tricyclic dienes with cyclopentene, norbornene and bicyclo-octene fragments was performed by comparing their GC, IR, ^{1}H, and ^{13}C NMR data with the reference data of their partly or fully hydrogenated analogs. Partial hydrogenation of codimers was carried out in a flow system over nickel catalyst supported on kieselguhr at 80–120°C and volume flow rate of 0.5 h^{-1}. Under those conditions, compounds **XII–XVII** were hydrogenated mainly at the norbornene or bicyclooctene fragments.

According to the data of IR, ^{1}H, and ^{13}C NMR spectroscopy data, compounds **XII–XVII** were of the *endo* configuration. The IR spectra contained absorption bands of the –CR=C– (R = H, CH_3) fragment at 3070–3035, 1578–1553, and 726–700 cm^{-1}. Unusual position of the ν(C=C) band was explained by the strained double bond in the bicycloheptene or bicyclooctene fragment of the molecule [18, 19]. The ν(C–H) absorption appearing as a doublet band at 3065–3050 and 3045–3030 cm^{-1}, different from that both in alkenes with terminal double bond (3080 cm^{-1}) and in cyclohexene (3027 cm^{-1}), was characteristic of the discussed compounds.

^{1}H and ^{13}C NMR spectra of the tricyclic dienes were more informative. In the ^{1}H NMR spectra, the signals of protons at the double bond appeared as a doublet at 5.58–5.62 ppm in the case of the five-membered ring and at 5.64–6.23 ppm in the case of bicycloheptene and bicyclooctene fragments. In the ^{13}C NMR spectra, the signals at 131.4–133.3 ppm were assigned to the olefinic carbons of the five- and six-membered rings, and those at 138.9–142.2 ppm corresponded to the olefinic carbons of bicycloheptene and bicyclooctene groups.

Epoxidation of compounds **X–XVII** was performed via the two methods. In the first case, the reaction was carried out in the presence of HCOOH or CH_3COOH at the substrate : oxidizer : RCOOH molar ratio of 1 : (1–2) : (0.2–0.4), at 60–70°C. Gadolinium(neodymium) phosphorus molybdenum complex $GdPO_4{\cdot}H_2O{\cdot}(MoO_2)P_{0.5}Mo_{12}O_{42}$ was used as catalyst, either without support or supported on microstructured carbon material. IR spectra of the unsupported and the carbon-supported catalysts were substantially different. The spectrum of the unsupported sample contained strong absorption bands at 1020–1067 and 869–962 cm^{-1}, characteristic of the PO_4^{3-} group and the Mo–O–Mo + Mo=O bonds, respectively; the Gd–O bond vibration gave rise to a strong band at 1461 cm^{-1} and weaker bands at 400–720 cm^{-1}. In the case of the supported sample, intensity of the PO_4^{3-} group absorption band substantially decreased, whereas the Mo–O–Mo and Mo=O bands grew stronger. Additional absorption band at 1568 or 1617 cm^{-1} appeared, assigned to the C–O–Mo(Gd) bond.

ESR spectra of the catalyst contained the signals with $g_{\|} = 2.094$ and $g_{\perp} = 1.941$ [$A_{\|}$(Mo) = 82 Gs and $A_{\perp}$(Mo) = 31 Gs] suggesting the presence of the MoO^{3+} fragments in the complex. Investigation of ESR signal intensity as function of the catalyst concentration in ethanol solution showed that the catalyst existed predominantly in the dimeric state.

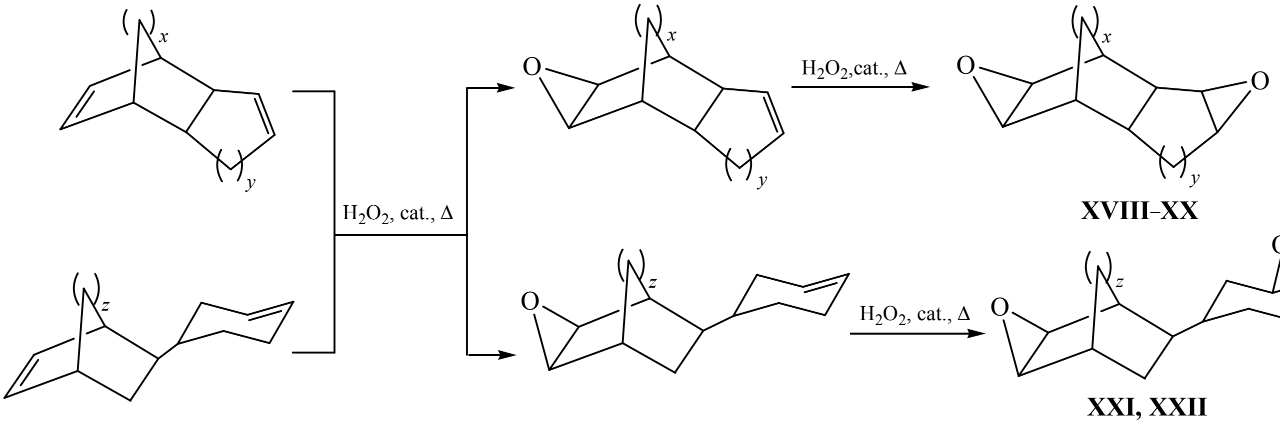
Adduct of hydrogen peroxide with urea was used as oxidizer. The epoxidation proceeded via the *in situ* formation mixture of Gd(III) or Nd(III)-containing polyoxoperoxomolybdate complexes (Scheme 5).

In Scheme 5, the initially formed peroxyacid participated in the formation of the active peroxometalate complex, further taking part in addition of electrophilic oxygen at the double bond of the tricyclic unsaturated hydrocarbons. The epoxidation products structure was confirmed by IR, ^{1}H, and ^{13}C NMR spectroscopy as well as mass spectrometry.

The second epoxidation method consisted in the reaction without any carboxylic acid. The initial Gd(III) polyoxophosphorus molybdenum complex was pretreated with 30% solution of H_2O_2 during 0.5 h at 40°C [12]. The so obtained peroxometalate complex exhibited high activity in electrophilic addition of oxygen atom at the double bond of the substrate.

Reactivity of the studied codimers under conditions of the induced epoxidation strongly depended on

Scheme 5.



XVIII–XX

XXI, XXII

$x = y = 1$ (**XVIII**); $x = 2, y = 1$ (**XIX**); $x = y = 2$ (**XX**); $z = 1$ (**XXI**), 2 (**XXII**).

spatial orientation of the methyl group and hydrogen atoms at the double bond. In particular, in the case of *trans*-orientation of the methyl group and the hydrogen atom at the double bond of the five-membered fragment of the product of codimerization of dienes **I** and **II**, attack of the double bond with active electrophilic oxygen of the polyoxoperoxometalate complex was hindered, and oxygen atom was majorly added at the double bond of the bicyclooctene fragment. On the contrary, epoxidation of the hardly separable mixture of adducts of cocondensation of methylcyclohexa-1,3-diene with diene **IV**, occurred at the cyclopentene fragment due to the shielding of the double bond of the bicyclooctene group. The highest yield of epoxides (80–85%) was attained at 50–70°C after 2–2.5 h. Further heating to 70–90°C and longer reaction time caused the reaction of the oxirane ring with unreacted molecules of the substrate to form the cooligomerization products. The IR spectra of oligomeric fractions contained typical absorption bands of hydroxyl (3400–3640 cm^{-1}) and ethereal (1075–1160 cm^{-1}) groups as well as of double bonds (1620–1640 cm^{-1}).

Oligomers **XXIII–XXV** obtained, respectively, via oxidation of tricyclo[5.2.1.0^{2,6}]deca-3,8-diene (**V**), tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene (**VI**), tricyclo[6.2.2.0^{2,7}]dodeca-3,9-diene (**VII**), and the product of cooligomerization of **XXIII** with styrene (the **XXIII** : styrene ratio of 1 : 4) **XXVI** were tested as film-forming materials. Preliminary results have shown the produced coatings can be used as thermoreactive film-forming materials (see table).

Parameters of coatings obtained from oligomeric fractions of epoxidation of tricyclic diene hydrocarbons

Parameter	Oligomer				Oligodivinylstyrene varnish
	XXIII	**XXIV**	**XXV**	**XXVI**	
color	dark-brown	dark-brown	light-brown	light-brown	light-brown
Time of drying to grade “3”	4 h at 100°C	3 h at 80°C	3 h at 80°C	2 h at 80°C	24 h at 20°C
Specific viscosity with B 3–4 at 20°C, s	26	20	19	19	20–30
Shock resistance, cm	50	50	50	≥50	50
Film elasticity in bending, mm	Not more than 1	Not more than 1	Not more than 1	Not more than 1	Not more than 1
Adhesion by the method of lattice cuts, score	Not more than 1	Not more than 1	Not more than 1	Not more than 1	Not more than 1

EXPERIMENTAL

IR spectra of suspensions in Vaseline oil or pellets with KBr were recorded using an Alpha FTIR spectrometer at 400–4000 cm^{-1} or a Vertex (Bruker) spectrometer at 100–700 cm^{-1}. ESR spectra were registered with a Bruker-BioSpin radiospectrometer at 25°C. Tuning to the internal field reference was performed using ultradisperse diamond ($g = 2.0036$).

X-ray phase analysis was performed with a Miniflex diffractometer (Rigaku) Analysis of interlayer distances calculated from the 2θ values showed the presence of $GdPO_4{\cdot}H_2O$ phase with d = 4.04; 2.978; 2.79; 2.63; 2.057; 1.82 Å, corresponding to 2θ = 22.3°; 29.8°, and 32.0° and $(MoO_2)P_{0.5}Mo_{14}O_{42}$ phase with d = 3.30; 6.325; 2.74; 2.50 Å [20, 21].

Crystal structure of the prepared catalysts was determined using an S–3400 N scanning electron microscope equipped with an Oxford Instruments Nano Analysis microanalysis system.

GC analysis of composition and purity of the starting reagents and epoxidation products was performed using a Tsvet-500 chromatograph with a flame-ionization detector (a 2000 × 3 mm column, 5 wt % of polyethylene glycol succinate on chromosorb as a stationary phase, nitrogen as carrier gas, column temperature 160°C, injector temperature 280°C). Chromato-mass spectra were recorded using a GC 7890A-MSD 5975C Agilent Technologies instrument (column: HP5-MS, temperature program 40–280°C, helium as carrier gas).

Concentration of H_2O_2 was determined by redox titration with permanganate. Content of epoxide groups was determined by thiosulfate method [22]. Cyclohexadiene-1,3, a mixture of its methyl-substituted derivatives [23], 4-vinylcyclohexene [24], and dimer of cyclopentadiene isolated by vacuum distillation from industrial fraction (99.0%, GC) were used as starting hydrocarbons.

Preparation of catalysts. Natural clinoptilolite (Ai-Dag deposit, Azerbaijan) or synthetic mordenite (SiO_2/Al_2O_3 = 10) were used as catalysts for dimerization after 4× treatment with 10% aqueous solution of NH_4Cl, drying at 120°C during 2 h, and calcination at 500–550°C during 4 h. Degree of decationization was 75 wt %.

Catalysts for epoxidation were prepared by refluxing aqueous solutions of $(NH)_6Mo_7O_{24}{\cdot}4H_2O$ (2.447 g, 1.98 mmol), $Gd(NO_3)_3{\cdot}5H_2O$ (0.5 g, 1.155 mmol) and H_3PO_4 (0.113 g, 1.155 mmol) during 5–6 h. The product was then cooled to room temperature, filtered off, dried at 110–120°C, and heated at 220–250°C during 2–3 h; dark-yellow powder. The catalyst of the same composition supported on highly dispersed carbon material (AG-3) was prepared similarly. The catalyst was added to the reaction mixture as a suspension in acetic or formic acid.

Peroxometalate complexes were prepared by stirring of the above quantity of the catalytic system with 30% aqueous H_2O_2 (3.14 g, 0.0923 mol) during 1 h at 40°C. The prepared complex was introduced into the system without any carboxylic acid.

***endo*-Tricyclo[5.2.2.0^{2,6}]undecadiene-3,8 (VI).** A 1 L autoclave was charged with 132 g of the dimer of cyclopentadiene, 200 g of catalyzate prepared by dehydration of cyclohexene oxidation product at 180°C over γ-Al_2O_3 promoted with 2% NaOH (cyclohexadiene-1,3 content of 40 wt %) and 20 g of H-form of ground clinoptilolite. The reaction mixture was stirred during 3 h at 200°C. Cyclohexene and benzene contained in the hydrocarbon mixture acted as solvent during cocondensation. After the reaction, autoclave was cooled with water, unreacted part of hydrocarbons was distilled off at normal pressure, and the residue was distilled in vacuum. Yield 103.4 g (70.8% with respect to cyclohexa-1,3-diene), bp 71–73°C (13 mmHg), d_4^{20} 0.9878, n_D^{20} 5.5158, MR_D 44.8, calc. 45. IR spectrum, ν, cm^{-1}: 1611, 1649, 3020 [24]. ^1H NMR spectrum, δ, ppm: 6.28 d.d (1H, H^8, $J_{9,8}$ = 9.9 Hz, $J_{8,7}$ = 6.5 Hz), 6.25 d.d (1H, H^9, $J_{9,8}$ = 9.9 Hz, $J_{9.1}$ = 6.5 Hz), 6.24 d.d (1H, H^3, $J_{4,3}$ = 9.9 Hz, $J_{3,2}$ = 6.6 Hz), 5.59 m (1H, H^4), 3.18 m (1H, H^1), 2.59 m (1H, H^7), 2.38 m (1H, H^{5y}), 2.28 m (1H, H^2), 2.14 m (1H, H^{5x}), 1.76 m (1H, H^{10x}), 1.51 m (1H, H^{10y}) [26, 27]. ^{13}C NMR spectrum, δ_C, ppm: 37.9 (C^1); 42.8 (C^2); 133.7 (C^3); 131.5 (C^4); 38.7 (C^5); 58.9 (C^6); 39.8 (C^7); 134.6 (C^8); 133.5 (C^9); 30.9 (C^{10}); 29.9 (C^{11}) [16–18]. Mass spectrum, *m/z* (relative intensity, %): 146 (4.4), 117 (4.3), 118 (6.9), 91 (11.4), 89 (2.7), 80 (100), 79 (59.6), 78 (9.9), 77(23.3), 68(13.7), 67(5.4), 66 (29.3), 65(19.0). Found, %: C 89.66, H 10.13. $C^{11}H_{14}$. Calculated, %: C 90.40; H 9.59.

Tricyclo[6.2.2.0^{2,7}]dodecadiene-3,9 (VII) was obtained similarly from 200 g of the product of dehydration of cyclohexene oxidation product with diene **II** content of 40%. Yield 63.4 g (79.2%) (*exo* : *endo* = 17 : 83). bp 75–77°C (4 mmHg), d_4^{20} 0.9963, n_D^{20} 1.5245, MR_D 49.2, calc. 49.6. IR spectrum, ν, cm^{-1}:

1610, 1650, 3020. ^{1}H NMR spectrum, δ, ppm: 5.91 d.d (1H, H^{10}, $J_{10,9}$ = 9.9 Hz, $J_{10,1}$ = 6.6 Hz), 5.89 d.d (1H, H^9, $J_{10,9}$ = 9.9 Hz, $J_{9,8}$ = 5.9 Hz), 5.89 d.d (1H, H^3, $J_{3,4}$ = 9.9 Hz, $J_{3,2}$ = 5.9 Hz), 5.60 m (1H, H^4), 2.12–2.16 m (3H, H^{1,2,8}), 2.03 m (1H, H^{5x}), 1.75 m (1H, H^{6x}), 1.93 m (1H, H^{5y}), 1.51 m (1H, H^7), 1.48 m (1H, H^{6y}),1.58 m (2H, H^{11x,12x}), 1.33 m (2H, H^{11y,12y}). ^{13}C NMR spectrum, δ$_C$, ppm: for *endo*-isomer: 40.9 (C^1); 37.5 (C^2); 133.3 (C^3); 132.6 (C^4); 27.9 (C^5); 24.0 (C^6); 37.9 (C^7); 39.7 (C^8); 134.1 (C^9); 128.2 (C^{10}); 26.9 (C^{11}); 25.9 (C^{12}). Found, %: C', 89.72, H', 10.24. $C^{12}H_{16}$. Calculated, %: C 89.94, H 10.06.

5-(Cyclohexen-3-yl)bicyclo[2.2.1]hepten-2-ene (Xa) was obtained similarly from 132 g (2 mol) of cyclopentadiene and 108 g (1 mol) of 4-vinylcyclohexene-1. 137.5 g (79%) of **Xa** was obtained, bp 99–101°C (4 mmHg), d_4^{20} 0.9768, n_D^{20} 1.5158, MR_D 53.8, calc. 54.2. ^{1}H NMR spectrum, δ, ppm: in bicycloheptene fragment: 6.28 d.d (1H, H^2, $J_{3,2}$ = 11 Hz, $J_{2,1}$ = 7.8 Hz), 6.25 d.d (1H, H^3, $J_{3,2}$ = 11 Hz, $J_{3,4}$ = 7.8 Hz), 2.59 m (1H, H^4), 2.29 m (1H, H^1), 1.76 m (1H, H^{7x}), 1.62 m (1H, H^{6x}), 1.53 m (1H, H^5), 1.51 m (1H, H^{7y}), 1.37 m (1H, H^{6y}); in cyclohexene fragment: 5.61 d.d (1H, H^4, $J_{4,3}$ = 10.6 Hz, $J_{4,5}$ = 6.7 Hz), 5.60 d.d (1H, H^3, $J_{3,4}$ = 10.6 Hz, $J_{3,2}$ = 6.7 Hz), 2.06 m (1H, H^{2x}), 2.03 m (1H, H^{5x}), 1.93 m (1H, H^{5y}), 1.80 m (1H, H^{2y}), 1.75 m (1H, H^{6x}), 1.49 m (1H, H^{6y}). Mass spectrum, *m/z* (relative intensity, %): 174 (8.5), 136 (2.3), 134 (4.7), 91 (5.8), 105 (1.6), 103 (1.8), 91 (6.8), 81 (10.7), 80 (100), 79 (50.6), 67 (1.5), 66 (21.8). Found, %: C 88.55; H 11.63. $C^{13}H_{18}$. Calculated, %: C 89.66; H 10.34.

5-(Cyclohexen-3-yl)bicyclo[2.2.2]oct-2-ene (Xb) was prepared similarly from 200 g of the product of dehydration of cyclohexene oxidation product diene **II** content of 40% and 108 g (1 mol) of 4-vinylcyclohexene-1. Yield 122.2 g (65%), bp 109–111°C (4 mmHg), d_4^{20} 0.9695, n_D^{20} 1.5165, MR_D 57.4, calc. 57.9. IR spectrum, ν, cm^{-1}: 1630–1635, 3010, 3045. ^{1}H NMR spectrum, δ, ppm: in bicyclooctene fragment: 5.89 d.d (1H, H^2, $J_{3,2}$ = 9.9 Hz, $J_{2,1}$ = 6.7 Hz), 5.89 d.d (1H, H^3, $J_{3,2}$ = 9.9 Hz, $J_{3,4}$ = 6.7 Hz), 2.14 m (1H, H^1), 2.12 m (1H, H^4), 1.58 m (2H, H^{7x,8x}), 1.53 m (1H, H^{6x}), 1.33 m (2H, H^{7y,8y}), 1.28 m (1H, H^{6y}); in cyclohexene fragment: 5.58 d.d (1H, H^3, $J_{3,4}$ = 10.6 Hz, $J_{3,2}$ = 6.7 Hz), 5.58 d.d (1H, H^4, $J_{4,3}$ = 10.6 Hz, $J_{4,5}$ = 6.7 Hz), 2.06 m (1H, H^{2x}), 2.03 m (1H, H^{5x}), 1.93 m (1H, H^{5y}), 1.80 m (1H, H^{2y}), 1.75 m (1H, H^{6x}), 1.49 m (1H, H^{6y}). ^{13}C NMR spectrum, δ$_C$, ppm: for *endo*-isomer: 44.4 (C^1); 136.9 (C^2); 132.5 (C^3); 49.8 (C^4); 42.8 (C^5); 32.1 (C^6); 28.7 (C^7); 28.6 (C^8); 45.9 (C^9); 31.9 (C^{10}); 127.2 (C^{11}); 126.9 (C^{12}); 39.4 (C^{13}); 38.8 (C^{14}); for *exo*-isomer: 44.3 (C^1); 135.9 (C^2); 132.5 (C^3); 49.4 (C^4); 42.5 (C^5); 32.1 (C^6); 28.1 (C^7); 25.2 (C^8); 45.6 (C^9); 31.2 (C^{10}); 127.5 (C^{11}); 127.6 (C^{12}); 39.4 (C^{13}); 38.8 (C^{14}). Found, %: C 89.11; H 10.76. $C^{14}H_{20}$. Calculated, %: C 89.36; H 10.64.

4,10-Dioxapentacyclo[6.3.1.0^{3,5}.0^{2,7}.0^{9,11}]dodecane (XVIII) was prepared similarly from 13.2 g (0.1 mol) of dimer **V**. Yield 14.3 g (87% from GC), bp 50°C (7.5 mmHg), d_4^{20} 1.4956, n_D^{20} 1.5206. IR spectrum, ν, cm^{-1}: 832, 858, 1250, 1260 (epoxide) 3010–3040. ^{1}H NMR spectrum, δ, ppm: in tricyclooctane fragment: 2.86 m (1H, H^4), 2.85 m (1H, H^2), 2.28 m (1H, H^1), 2.14 d (1H, H^{8s}, $J_{8s,8a}$ = 8.5 Hz), 1.89 d (1H, H^{8a}, $J_{8s,8a}$ = 8.5 Hz), 1.76 m (1H, H^5), 1.51 m (1H, H^{7x}), 1.42 m (1H, H^6), 1.26 m (1H, H^{7y}); in bicycloheptane fragment: 2.88 m (2H, H^{3,5}), 1.72 m (1H, H^{6x}), 1.68 m (1H, H^{2x}), 1.54 m (1H, H^{7x}), 1.47 m (1H, H^{6y}), 1.40 m (1H, H^{2y}), 1.29 m (1H, H^{7y}). ^{13}C NMR spectrum δ$_C$, ppm: 65.4 (C^{2,4}), 62.6 (C^7), 57.2 (C^9), 48.9 (C^6), 46.0 (C^1), 39.4 (C^5), 33.6 (C^{10}), 28.6 (C^{11}), 21.2 (C^{12}). Found, %: C 73.10; H 7.32. $C_{10}H_{12}O_2$. Calculated, %: C 73.15; H 7.37.

4,10-Dioxapentacyclo[6.3.2.0^{3,5}.0^{2,7}.0^{9,11}]tridecane (XIX) was prepared similarly from 14.6 g (0.1 mol) of codimer **VI**. Yield 16.0 g (89.6% from GC), bp 102°C (7.5 mmHg), d_4^{20} 1.5016, n_D^{20} 1.5214, IR spectrum, ν, cm^{-1}: 835, 842, 860 (epoxide), 3050–3070. ^{1}H NMR spectrum, δ, ppm: in tricyclononane fragment: 2.85 m (1H, H^2), 2.86 m (1H, H^4), 1.76 m (1H, H^1), 1.74 m (1H, H^5), 1.52 m (2H, H^{8x,9x}), 1.50 m (1H, H^{7x,}), 1.42 m (1H, H^6), 1.28 m (2H, H^{8y,9y}) 1.26 m (1H, H^{7y,}); in bicycloheptane fragment: 2.88 m (2H, H^{3,5}), 1.72 m (1H, H^{6x}), 1.68 m (1H, H^{2x}), 1.54 m (1H, H^{7x}), 1.47 m (2H, H^{6y}), 1.40 m (1H, H^{2y}), 1.29 m (1H, H^{7y}). ^{13}C NMR spectrum δ$_C$, ppm: 62.9 (C^{2,4,7}), 58.1 (C^9), 48.9 (C^6), 32.3 (C^{10,12}), 30.1 (C^{11}), 19.9 (C^{12,13}). Found, %: C 74.10; H 7.87. $C_{11}H_{14}O_2$. Calculated, %: C 74.13; H 7.92.

4,11-Dioxapentacyclo[7.3.2.0^{3,5}.0^{2,8}.0^{10,12}]tetradecane (XX). A constant-temperature 100 mL glass reactor equipped with thermometer, dropping funnel, and condenser was charged with gadolinium phosphorus molybdenum complex (0.05 mmol) and treated with 30% solution of H_2O_2 (0.1–1.0 mmol) during 0.5–1.0 h at 40–50°C. Then, 16.0 g of compound **VII** (0.1 mol) and 30% solution of H_2O_2 in dioxane (0.2–0.25 mol) were added dropwise, and the mixture was stirred at 50–70°C during 2–4 h. Similar experiments were also performed with urea peroxide in acetic acid. 16 g of compound **XX** was obtained. Yield 82% (from GC), bp 118°C (7.5 mmHg), d_4^{20} 1.5028, n_D^{20} 1.5235. IR spectrum, ν, cm^{-1}: 850, 862, 3050–3070. ^{1}H NMR spectrum, δ, ppm: 2.85–2.89 m (4H, H^{3,4,10,12}), 1.24–1.73 m (16H, ring protons). ^{13}C NMR spectrum, δ_C, ppm: 63.2 (C^{2,4}), 58.1 (C^{8,9}), 38 (C^{6,12}), 31.0 (C^{7,11}), 29.8 (C^{1,5}), 20.2 (C^{13,14}). Found, %: C 74.93; H 8.35. $C_{12}H_{16}O_2$. Calculated, %: C 74.97; H 8.39.

6-(4-Oxabicyclo[4.1.0]heptyl-3-*exo*-oxatricyclo-[3.2.1.0^{2,4}]octane (XXI) was prepared similarly from 17.4 g (0.1 mol) of compound **Xa**, yield 16.5 g (80% from GC), bp 138°C (8 mmHg), d_4^{20} 1.1084, n_D^{20} 1.5182. IR spectrum, ν, cm^{-1}: 835, 858, 3010–3030. ^{1}H NMR spectrum, δ, ppm: 2.88 m (1H, H^5), 2.86 m (1H,H^3), 2.85 m (1H, H^4), 2.83 m (1H, H^2), 1.22–1.74 m (18H, ring protons). ^{13}C NMR spectrum, δ_C, ppm: 67.9 (C^2), 65.7 (C^4), 44.1 (C^5), 39.6 (C^6), 37.5 (C^1), 31.9 (C^7), 24.3 (C^8); signals of the cyclohexane fragment: 60.0 (C$^{5'}$), 57.8 (C$^{3'}$), 34.1 (C$^{1'}$), 33.1 (C$^{2'}$), 28.0 (C$^{6'}$), 27.6 (C$^{7'}$). Found, %: C 75.66; H 8.78. $C_{13}H_{18}O_2$. Calculated, %: C 75.69; H 8.80.

6-(4-Oxabicyclo[4.1.0]heptyl-3-*exo*-4-oxatricyclo-[4.2.1.0^{2,4}]nonane (XXII) was prepared similarly from 18.8 g of compound **XIa**. Yield 19.2 g (78.5%), bp 146°C (5 mmHg), d_4^{20} 1.1068, n_D^{20} 1.5146. IR spectrum, ν, cm^{-1}: 850, 858, 862, 3010–3030. ^{1}H NMR spectrum, δ, ppm: 2.86–2.88 m (4H, H$^{2–5}$), 1.24–1.76 m (20H, ring protons). ^{13}C NMR spectrum, δ_C, ppm: 65.4 (C^2), 63.4 (C^4), 39.6 (C^9), 30.4 (C^5), 28.8 (C^1), 27.6 (C^7), 22.4 (C^8), 20.2 (C^9); signals of the cyclohexane fragment: 60.0 (C$^{5'}$), 57.8 (C$^{3'}$), 34.1 (C$^{1'}$), 33.4 (C$^{2'}$), 28.0 (C$^{6'}$), 27.6 (C$^{7'}$). Found, %: C 76.28; H 9.23. $C_{14}H_{20}O_2$. Calculated, %: C 76.33; H 9.15.

Similarly, a hardly separable mixture of the isomers of the corresponding diepoxides of 3-methyl- and 5-methyl-3.8-dioxapentacyclo[6.3.2.0$^{2.7}$.0$^{3.5}$0$^{9.11}$]tridecane and 1-methyl and 8-methyl-3.8-dioxapentacyclo [6.3.2.0$^{2.7}$.0$^{3.5}$.0$^{9.11}$]tridecane was obtained from the mixture of the isomers of 3- and 4-methyltricyclo-[5.2.2.0$^{2.6}$]undecadiene-3.8 and 1- and 8-methyl-tricyclo[5.2.2.0$^{2.6}$]undecadiene-3.8. GC analysis of the oxidation products of those dienes isomeric mixture revealed the presence of four products differing in the retention time beside the starting reagents [28].

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