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Epoxidation and Oxidative Dihydroxylation of C_{10}–C_{13} Unsaturated Bridged Hydrocarbons Involving Hydrogen Peroxide and Modified Forms of Heteromolybdic Compounds

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Abstract—Induced oxidation of C_{10}–C_{13} tricyclic bridged olefins synthesized from C_5–C_8 cyclodiene hydrocarbons using hydrogen peroxide has been studied. It has been shown that phosphomolybdic heteropoly compounds supported on a finely divided carbon material and additionally modified with HBr and $CoCO_3$ or Gd_2O_3 exhibit high activity in this reaction. Depending on the conditions of the experiments, the main reaction products are the corresponding oxiranes and diols that retain the structure of the reactant hydrocarbons.

Keywords: tricyclodecene, tricycloundecene, tricyclododecene, cyclohexenylnorbornane, phenylnorbornene, modified forms of heteromolybdic compounds, epoxidation, cyclic vicinal glycols

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Oxidative functionalization of cyclic hydrocarbons (HCs) remains one of the priority areas of petrochemical and organic synthesis. To introduce the oxygen function into substrates with different structures, liquid-phase autooxidation using air oxygen as an oxidant or the insertion of oxygen-containing units by means of various oxidants and polyvalent metal compounds is currently preferred [1, 2]. Among the latter oxidants and metal compounds, hydrogen peroxide as a cheap and environmentally more appropriate oxidant and heteropoly compounds in combination with quaternary ammonium compounds as phase transfer catalysts gain the most attention in application to catalytic processes [3–6]. The selectivity of these processes largely depends on the carrier of active oxygen to the multiple bond of the substrate and also on the catalytic system itself, which ensures the desired conversion of the reactants and the yields of products with a desired structure. However, the unresolved problem in these processes is the isolation and reuse of the catalyst systems.

It is known that mono- and diepoxy derivatives of bridged bi- and tricyclic unsaturated hydrocarbons can be used as binders and additives to create polymeric compositions for various purposes, such as heat-resistant glass-reinforced plastics, coatings, molded articles, and insulating materials [7, 8]. In addition, these products have an independent value and are used to produce biologically active substances and pharmaceuticals [9], as well as fragrances [10].

An increased amount of unsaturated alicyclic hydrocarbons from industrial sources [11, 12] and improvements in their condensation methods [13–19] create real prerequisites for the synthesis of the aforementioned oxygen-containing compounds.

In earlier studies on the synthesis of epoxides of unsaturated hydrocarbons, peroxo acids [8, 20] and peroxides or alkyl hydroperoxides [20, 21] were mainly used. To date, procedures for the oxidation of organic compounds with aqueous hydrogen peroxide solutions under phase-transfer catalysis conditions using phase transfer catalysts have been developed [22–25].

High selectivity for epoxides is achieved in the case of hydroxyhalogenation of bridged unsaturated hydrocarbons followed by dehydrohalogenation of the products with potassium hydroxide [26].

In this paper we present the results of epoxidation and dihydroxylation of tricyclic bridged monoolefins with hydrogen peroxide. The catalyst used was a phosphomolybdic heteropoly compound (PMHC) supported to a finely divided carbon material that was additionally modified with hydrobromic acid and cobalt(II) carbonate or gadolinium oxide.

EXPERIMENTAL

Samples of PMHC catalysts for the oxidation of cycloolefins with hydrogen peroxide were synthesized according to the procedure developed previously [28]. IR spectra of these samples in the form of white-oil mull or KBr tablets were taken on an Alpha FTIR spectrometer in the region of 400–4000 cm^{-1} or a Vertex (Bruker) instrument in the range of 100–700 cm^{-1}.

Reactant Preparation Procedure

Unsaturated bridged C_{10}–C_{13} hydrocarbons were obtained via the [4 + 2]-cycloaddition reaction of cyclopentadiene with cyclohexadiene-1,3, 4-vinylcyclohexene, vinylcyclohexane, and styrene in the presence of the H-form of clinoptilolite ($SiO_2/Al_2O_3 = 5.4$) or mordenite ($SiO_2/Al_2O_3 = 10$) at T = 180–200°C over 2 to 3 h [28]. The addition reaction of cyclopentadiene with styrene was carried out in the presence of 5 wt % hydroquinone [30]. The main products were the corresponding *endo*-isomers (*endo*- to *exo*-isomer molar ratio was 80–83 : 17–20).

General Procedure for Isomerization and Hydrogenation of C_{10}–C_{13} Bi- and Tricyclic Dienes

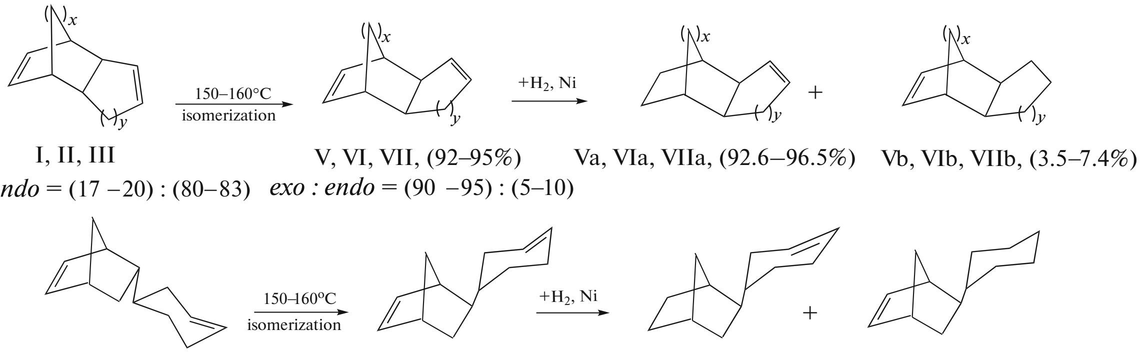
A predetermined amount of a synthesized diene hydrocarbon (in an *endo*- to *exo*-isomer ratio of the dimers or codimers of 4–5 : 1) and a 5% $AlCl_3$ solution in hexane ($AlCl_3$ content of 10–15% of the total weight of the isomer mixture) were charged to an autoclave and heated at 150–160°C for 6–8 h [29]. The reactor was then cooled to room temperature; the products were washed with an aqueous KCl solution; and the organic phase was separated from the aqueous phase, diluted with toluene, and fed with a microdoser into a flow reactor for hydrogenation to the corresponding cycloolefins over a fixed bed of kieselguhr-supported nickel at T = 80–85°C, $V = 0.5$ h^{-1}, and a diene : H_2 molar ratio of 1 : 2 [28]. A mixture of *exo*- and *endo*-isomers of cycloolefins with a molar ratio of 90–95 : 5–10 is mainly formed in this case. After vacuum distillation of the catalyzate, corresponding cycloolefins were obtained in a yield of 96–98.5%.

exo-5-Cyclohexyl- and *exo*-5-phenylbicyclo[2.2.1]hept-2-enes used in the epoxidation reaction were obtained from the respective *endo*-isomers according to the procedure described in [29, 30]. Physicochemical and spectral parameters given below for the compounds synthesized are consistent with relevant published data [30–37].

^1H and ^{13}C NMR spectra were recorded in a deuterated chloroform solution at room temperature on a Bruker Fourier-transform pulsed spectrometer operating on a frequency of 300.18 MHz. The relative abundance of protons in different structural moieties was determined by integrating the corresponding resonance absorption bands [32, 35].

Mass chromatograms were recorded on an Agilent Technologies GC 7890A-MSD 5975C instrument using an HP5-MS column, temperature programming within 40–280°C, and helium as the carrier gas. Elemental analysis was performed with a Leco TruSpes Micro analyzer. The molecular weights of some oxidation products were determined cryoscopically. Cryoscopic benzene was used as the solvent. The relative error was 1.0–1.5%.

Cycloolefins were synthesized according to the following scheme:



I, II, III
exo : endo = (17 –20) : (80–83)

V, VI, VII, (92–95%)
exo : endo = (90 –95) : (5–10)

Va, VIa, VIIa, (92.6–96.5%)

Vb, VIb, VIIb, (3.5–7.4%)

IV
vexo : endo = (20–80)

VIII, (93%)
exo : endo = 93 : 7

VIIIa, (96%)

VIIIb, (4.0%)

$x = y = 1$ (I, V, mixture of Va and Vb); $x = 2$, $y = 1$ (II, VI, mixture of VIa and VIb);
$x = 2$, $y = 2$ (III, VII, mixture of VIIa and VIIb), *exo* : *endo* = (90–95) : (5–10), *exo* : *endo* = 93: 7

Scheme 1. Synthesis of cycloolefins.

***exo*-Tricyclo[5.2.1.0^{2,6}]dec-3(8)-ene (Va, Vb)** was prepared from 26.4 g (0.2 mol) of the cyclopentadiene dimer (I). Yield 25.9 g (96.6 wt %, Va : Vb = 96.5 : 3.5). Bp 71–72°C (2.13 kPa), d_4^{20} 0.9986, n_D^{20} 1.4988 (published data: bp 179–181°C, 101 kPa [31]). IR spectrum, ν, cm^{-1}: 3060–3050 (CH=, ν^s), 2860–2850 (CH_2, ν^s), 1670–1630 (C=C, ν), 1470–1465 (CH_2, δ^{as}), 1360, 1345 (CH, δ). ^1H NMR, δ, ppm: 1.34–

1.59 m (7H, H^1, H^6, H^7, H^8_B, H^8_A, H^9_A, H^9_B), 1.91–2.40 m (5H, H^2, H^5_A, H^5_B, H^{10}_A, H^{10}_B), 5.64 d.d. (1H, H^4, $^2J_{4.3}$ 11.1 Hz, $^3J_{4.5}$ 6.5Hz), 6.35 d.d. (1H, H^3, $^2J_{4.3}$ 11.1 Hz, $^3J_{3.2}$ 6.5 Hz) [33]. ^{13}C NMR, δ, ppm: 132.4 (C^4), 132.2 (C^3), 53.4 (C^2), 43.2 (C^6), 41.3 (C^7), 40.0 (C^1), 39 (C^5), 32.6 (C^{10}) , 28.8 (C^8), 26.5 (C^9). Mass spectrum, *m/z* (abundance, %): 134$[M]^{+\bullet}$ (8.6), 120 $[C_9H_{12}]^{+\bullet}$ (6.7) 119 $[C_9H_{11}]^+$ (4.4), 91 $[C_7H_7]^+$ (12.4), 80 $[C_6H_8]^{+\bullet}$ (100), 79 $[C_6H_7]^+$ (60.1), 78 $[C_6H_6]^{+\bullet}$ (8.9), 77 $[C_6H_5]^+$ (21.4), 68 $[C_5H_8]^{+\bullet}$ (14.2), 67 $[C_5H_7]^+$ (4.4), 66 $[C_5H_6]^{+\bullet}$ (25.6), 65$[C_5H_5]^+$ (15.4).

***exo*-Tricyclo[5,2.2.0$^{2.6}$]undec-3(8)-ene (VIa, VIb)** was obtained by hydrogenation of 29.2 g (0.2 mol) of *exo*-tricyclo[5.2.2.0$^{2.6}$]undeca-3,8-diene (VI). Yield 27.4 g (92.6 wt %, VIa : VIb = 94.0 : 6.0). Bp 76–78°C (1.73 kPa), d_4^{20} 0.9983, n_D^{20} 1.4963. IR spectrum, ν, cm^{-1}: 3050–3030 (CH=, ν^s), 2860–2855 (CH_2, ν^s), 1640–1635 (C=C, ν), 1470–1465(CH_2, δ^{as}), 1365, 1345 (CH, δ). ^1H NMR, δ, ppm: 1.29–1.54 m [12H, H^1, H^5_A, H^6, H^7, $H^{(8-11)}_{A,\,B}$], 2.13–2.39 m (2H, H^2, H^5_B), 5.62 d.d. (1H, H^4, $^2J_{4.3}$ 11.1Hz, $^3J_{4.5}$ 6.4 Hz), 6.28 d.d. (1H, H^3, $^2J_{4.3}$ 11.1 Hz, $^3J_{3.2}$, 6.4 Hz). ^{13}C NMR, δ, ppm: 132.2 (C^4), 132 (C^3), 39.4 (C^5), 38.2 (C^2), 31.2 (C^1), 31.0 (C^7), 29.2 (C^6), 24.2 ($C^{10,\,11}$), 22.9 (C^9). Mass spectrum, *m/z* (abundance, %):148 $[M]^{+\bullet}$ (4.8), 120 $[C_9H_{12}]^{+\bullet}$ (6.8), 92 $[C_7H_8]^{+\bullet}$ (11.4), 82 $[C_6H_{10}]^{+\bullet}$ (10), 81 $[C_6H_9]^+$ (9.2), 80 $[C_6H_8]^{+\bullet}$ (100), 79 $[C_6H_7]^+$ (59.6), 78$[C_6H_6]^{+\bullet}$ (9.9), 77$[C_6H_5]^+$ (23.6), 68 $[C_5H_8]^{+\bullet}$ (13.7). 66 $[C_5H_6]^{+\bullet}$ (29.3), 65 $[C_5H_5]^+$(19.0).

***exo*-Tricyclo[6,2.2.0$^{2.7}$]dodec-3(9)-ene (VIIa, VIIb)** was prepared by hydrogenation of 32.0 g (0.2 mol of *exo*-tricyclo[6.2.2.0$^{2.7}$]dodeca-3,9-diene (VII). Yield 29.1 g (89.3 wt %, VIIa : VIIb = 92.6 : 7.4). Bp. 78–80°C (0.53 kPa), d_4^{20} 0.9852, n_D^{20} 1.4946. IR spectrum, ν, cm^{-1}: 3050–3040 (CH=, ν^s), 2860–2855 (CH_2, ν^s), 1640–1630 (C=C, ν), 1460–1470 (CH_2, δ^{as}), 1360, 1345 (CH, δ). ^1H NMR, δ, ppm: 1.30–1.77 m [13H, H^1, $H^6_{A,\,B}$, H^7, H^8, $H^{(9-12)}_{A,\,B}$], 1.94–2.14 m (3H, H^2, $H^5_{A,\,B}$), (1H, 5.62 dd (1H, H^4, $^2J_{4.3}$ 11.1 Hz, $^3J_{5.4}$ 6.5 Hz), 5.93 dd (1H, H^3, $^2J_{4.3}$ 11.2 Hz, $^3J_{3.2}$ 6.5 Hz) . ^{13}C NMR, δ, ppm: 129.2 (C^3), 128 (C^4), 34.1 (C^7), 31.6 (C^1), 31.1 (C^2), 28.6 (C^8), 24.5 ($C^{9,\,12}$), 23.8 (C^5), 22.8 ($C^{10,\,11}$), 19.2 (C^6). Mass spectrum, *m/z* (abundance, %): 162 $[M]^{+\bullet}$ (4.8), 134 $[C_{10}H_{14}]^{+\bullet}$ (4.9), 119 $[C_9H_{11}]^+$ (4.7), 91 $[C_7H_7]^+$ (11.3), 82 $[C_6H_{10}]^{+\bullet}$ (10), 81 $[C_6H_9]^+$ (10.3), 80 $[C_6H_8]^{+\bullet}$ (100), 79 $[C_6H_7]^+$ (57.4), 78$[C_6H_6]^{+\bullet}$ (10.3), 77 $[C_6H_5]^+$ (23.6), 68 $[C_5H_8]^{+\bullet}$ (13.7). 65 $[C_5H_5]^{+\bullet}$ (9.3).

A mixture of *exo*-2-(cyclohex-3^{l}-en-l^{l}-yl)bicyclo[2.2.1]-heptane (VIIIa) and *exo*-5-cyclohexylbicyclo[2.2.1]hept-2-ene (VIIIb) was obtained by hydrogenation of 34.8 g (0.2 mol) of *exo*-5-(cyclohex-3^{l}-en-l^{l}-yl)bicyclo[2.2.1]hept-2-ene (VIII). Yield: 31.8 g (90.3 wt %, VIIIa : VIIIb = 96.0: 4.0). Bp 103–105°C (0.53 kPa), d_4^{20} 0.9878, n_D^{20} 1.4887. IR spectrum, ν, cm^{-1}: 3050–3040 (CH=, ν^s), 2860–2855 (CH_2, ν^s), 1655–1628 (C=C, ν), 1470–1465 (CH_2, δ^{as}), 1360, 1345 (CH, δ). ^1H NMR, δ (ppm) in bicycloheptane: 1.26–1.62 m (8H, H^2, $H^3_{A,\,B}$, H^4, $H^5_{A,\,B}$, $H^6_{A,\,B}$), 1.91–2.15 m (2H, $H^7_{A,\,B}$); in cyclohexene: 1.52–2.07 m (7H, H^1, $H^2_{A,\,B}$, $H^5_{A,\,B}$, $H^6_{A,\,B}$), 5.61 dd (1H, H^3, $^2J_{4.3}$ 11.2 Hz, $^3J_{3.2}$ 6.5 Hz), 6.63 dd (1H, H^4, $^2J_{4.3}$ 11.2Hz, $^3J_{5.4}$ 6.5Hz): ^{13}C NMR, δ (ppm) in bicycloheptane: 44.3 (C^2), 40.5 (C^7), 38.1 (C^4) , 35.9 (C^1), 29.5 (C^5), 29.1 (C^6), 26.7 (C^3); in cyclohexene: 126.3 (C^3), 126 (C^4), 33.1 (C^1), 32.2 (C^2), 29.0 (C^6), 23.6 (C^5). Mass spectrum, *m/z* (abundance, %): 176$[M]^{+\bullet}$ (8.5), 148 $[C_{11}H_{16}]^{+\bullet}$ (2.3), 134 $[C_{10}H_{14}]^{+\bullet}$ (4.7), 91 $[C_7H_7]^{+\bullet}$ (6.8), 81 $[C_6H_9]^+$ (10.7), 80 $[C_6H_8]^{+\bullet}$ (100), 79 $[C_6H_7]^{+\bullet}$ (50.6), 66 $[C_5H_6]^{+\bullet}$ (2.8).

***exo*-5-Cyclohexylbicyclo[2.2.1]hept-2-ene (VIIIb)** was prepared by condensation of 22.0 g (0.2 mol) of vinylcyclohexane and 33.0 g of the dimer fraction of cyclopentadiene (dimer content, 80% or 0.2 mol) followed by isomerization of the endo-addition product according to a procedure reported in [29]. Yield 21.9 g (62.3%). Bp 100–101°C (0.53 kPa) d_4^{20} 0.9693, n_D^{20} 1.5123 (published data [30] 100–101°C [0.53 kPa], d_4^{20} 0.9695, n_D^{20} 1.5120). IR spectrum, ν, cm^{-1}3045–3040 (CH=, ν^s), 2920–2890 (CH_2, ν^s), 1635–1625 (C=C, ν), 1470–1465 (CH_2, δ^{as}), 1360, 1345 (CH, δ). ^1H NMR, δ (ppm) in bicycloheptene: 1.37–1.63 m (4H, H^5, $H^6_{A,\,B}$, H^7_B), 1.77–2.60 m (3H, H^1, H^4, H^7_A), 6.27 d (1H, H^2, $^2J_{3.2}$ 11.3 Hz, $^2J_{2.1}$ 6.5 Hz), 6.29 d (1H, H^3, $^2J_{3.2}$ 11.3 Hz, $^3J_{4.3}$ 6.5 Hz); in cyclohexane: 1.29–1.48 m (6H, H^1, H^2_B, H^3_B, H^4_B, H^5_B, H^6_B), 1.50–1.56 m (5H, H^2_A, H^3_A, H^4_A, H^5_A, H^6_A). ^{13}C NMR, δ (ppm) in bicycloheptene: 136.2 (C^2, C^3), 49.0 (C^5), 47.8 (C^7), 43.8 (C^1), 37.3 (C^4), 31.6 (C^6); in cyclohexane: 37.6 (C^1), 33.3 (C^2 and C^6), 26.4 (C^3 and C^5), 26.2 (C^4). $M_{\text{found}} = 174.3$, $M_{\text{calc}\cdot} = 176$.

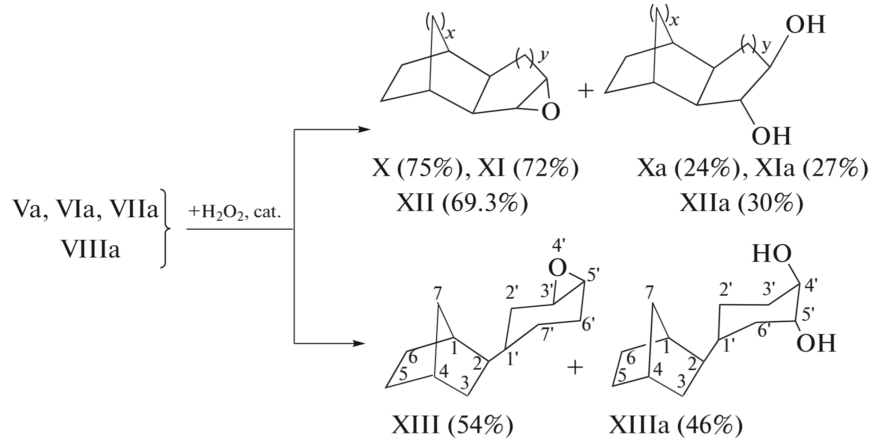
***exo*-5-Phenylbicyclo[2.2.1]hept-2-ene (IX)** was prepared by condensation of 104 g of freshly distilled styrene (1 mol), 165 g of the dimer fraction of cyclopentadiene (dimer content of 80% or 1 mol), and 5 wt % hydroquinone in an autoclave at a temperature of 200°C followed by isomerization of the endo-addition product according to the procedure reported in [29]. Yield 111.4 g (65.5%). Bp. 135–136°C (1.2 kPa), d_4^{20} 1.0272, n_D^{20} 1.5481 (published data [30]: d_4^{20} 1.0270, n_D^{20}

1.5480). IR spectrum, ν, cm^{-1}: 785–680 (C_6H_5, δ), 1650–1640 (C=C, ν), 3050–3040 (CH=, $ν^s$), 1470–1465 (CH_2 $δ^{as}$), 1360, 1345 (CH, δ). ^1H NMR, δ (ppm) in bicycloheptene: 1.52–1.96 m (4H, $H^6_{A, B}$, $H^7_{A, B}$), 2.30–2.85 m (3H, H^1, H^4, H^5), 6.25 (2H, H^2, H^3, $^2J_{3.2}$ 6.5 Hz), 7.28–7.39 m (5H, Ar). ^{13}C NMR, δ, ppm: 132.4 (C^2), 131.3 (C^3), 53 (C^4), 50.8 (C^7), 43 (C^1), 35.8 (C^5), 31.7 (C^6); in the C_6H_5 moiety: 144.7 (C^1), 128.5 (C^3 and C^5), 127 (C^2 and C^6), 126 (C^4). Mass spectrum, *m/z* (abundance, %): 170 $[M]^{+\cdot}$, 141 $[C_{11}H_9]^+$ (3.2), 115$[C_9H_7]^+$ (3.1), 10 $[C_8H_7]^+$ (55.6), 102 $[C_8H_6]^{+\cdot}$ (5.6), 91 $[C_7H_7]^+$ (7.8), 79 $[C_6H_7]^+$ (45.3), 78 $[C_6H_6]^{+\cdot}$ (100), 77 $[C_6H_5]^+$ (10.2), 66 $[C_5H_6]^{+\cdot}$ (4.7).

General Procedure for Oxidation of Bridged Unsaturated Hydrocarbons

The reaction was carried out in the liquid phase at atmospheric pressure in a laboratory unit with a glass reactor equipped with an oxidant (hydrogen peroxide solution) supply system. The reactor was simultaneously charged with cycloolefin (0.1 mol), catalyst, and toluene (or dichloroethane) as a solvent (15 mL). A measured amount of the oxidant (0.2 mol) was introduced into the reactor at 50°C within 1 h, with the temperature being raised to 70–75°C. The reaction mixture was stirred for 3 h. The H_2O_2 consumption was monitored using permanganatometric titration, and the composition of the oxidation products was determined by GLC on a Tsvet-500 chromatograph with a flame ionization detector, using a 2000 × 3 mm column packed with polyethylene glycol succinate-coated (5 wt %) Chromosorb, nitrogen as a carrier gas, a column temperature of 160°C, and an evaporator temperature of 280°C. The reactivity of the substrates was determined as the time dependence of the yield of corresponding epoxides and diols. The IR spectra of the epoxides and diols were recorded on an Alpha spectrometer in the region of 400–4000 cm^{-1}. The assignment of their absorption bands was made on the basis of published data [32].

Scheme 2 shows the oxidation products of the main isomers of cycloolefins contained in the mixture (Va, VIa, VIIa, VIIIa).



$x = y = 1$(X, Xa); $x = 2, y = 1$(XI, XIa); $x = y = 2$(XII, XIIa)

Scheme 2. Oxidation of isomeric cycloolefins.

***endo*-4-Oxa-*exo*-tetracyclo[6.2.1.0$^{3.5}$0$^{2.7}$]undecane (X)** was prepared from 13.4 g (0.1 mol) of Va; oxidant: $H_2O_2 \cdot CO(NH_2)_2$. Yield 11.3 g (75.3 wt %). Bp 44–45°C (0.24 kPa), d_4^{20} 1.0235, n_D^{20}1.4876. IR spectrum, ν, cm^{-1}: 3040 (HC, $ν^s$, oxirane), 2890 (CH, ν), 2860 (CH_2, $ν^s$), 1458 (CH_2, $δ^{as}$), 1340 (CH, δ), 1260 (HC—O—CH, $ν^s$), 975, 910, 860, 845(HC—O—CH, $ν^{as}$). ^1H NMR, δ (ppm): 1.36–1.76 m (10H, H^1, H^2, $H^6_{A, B}$, H^7, H^8, $H^9_{A, B}$, $H^{10}_{A, B}$), 1.91–2.57 m (4H, H^3, H^5, $H^{11}_{A, B}$). ^{13}C NMR, δ (ppm): 61.9 (C^5), 53.4 (C^3), 52.2 (C^2), 37.6 (C^8), 36.7 (C^1), 34.8 (C^{11}), 34.0 (C^6), 32.6 (C^7), 28.9 (C^9), 28.7 (C^{10}). Mass spectrum, *m/z* (abundance, %): 150 $[M]^{+\cdot}$ (3.8), 132 $[C_{11}H_{14}]^{+\cdot}$ (6.6), 120 $[C_9H_{12}]^{+\cdot}$ (4.4), 119 $[C_9H_{11}]^+$ (4.3), 118$[C_9H_{10}]^{+\cdot}$ (6.0), 92 $[C_7H_8]^{+\cdot}$ (10.7), 91 $[C_7H_7]^+$ (4.5), 81$[C_6H_9]^+$ (51.8), 80 $[C_6H_8]^{+\cdot}$ (100), 78 $[C_6H_6]^{+\cdot}$ (9.1), 68 $[C_5H_6]^{+\cdot}$ (14.0), 66 $[C_5H_6]^{+\cdot}$ (29.4).

***endo*-4-Oxa-*exo*-tetracyclo[6.2.2.0$^{3.5}$0$^{2.7}$]dodecane (XI)** was obtained from 14.8 g (0.1 mol) of VIa;

oxidant: $H_2O_2 \cdot CO(NH_2)_2$. Yield 11.8 g (72.0 wt %). Bp. 75–77°C (0.66 kPa) 1.0426, 1.4906. IR spectrum, ν, cm^{-1}: 3035 (HC, ν^{s}, oxirane), 2892 (CH, ν), 2855 (CH_2, ν^{s}), 1450 (CH_2, δ^{as}), 1350 (CH, δ), (1245 ($\underset{\text{O}}{\text{HC——CH}}$, ν^{s}), 985, 910, 870, 845 ($\underset{\text{O}}{\text{HC——CH}}$,$\nu$ ^{as}). ^{1}H NMR, δ (ppm): 1.29–1.56 (12H, H^1, H^6_B, H^8, H^7, $H^{(9-12)}_{A,B}$), 1.67–2.73 m (4H, H^2, H^3, H^5, H^6_A). ^{13}C NMR, δ (ppm): 62.3 (C^5), 53.8 (C^3), 52.9 (C^2), 34.3 (C^7) , 32.6 (C^6), 31.0 (C^8), 24.4 ($C^{(9-12)}$), 24.0 (C^1). Found: C, 80.15; H, 9.97. Calculated for $C_{11}H_{16}O$: C, 80.49; H, 9.76; $M_{\text{found}} = 162.0$, $M_{\text{calc}} = 164$.

***endo*-4-Oxa-*exo*-tetracyclo[7.2.2.0$^{3.5}$0$^{2.8}$]tridecane (XII)** was prepared from 16.2 g (0.1 mole) of VIIa, oxidant: $H_2O_2 \cdot CO(NH_2)_2$, yield 12.3 g (69.3%). Bp 92–93°C (0.5 kPa) 1.0745, 1.4914. IR spectrum, ν, cm^{-1}: 3030 (CH, ν^{s}, oxirane), 2890 (CH, ν), 2855 (CH_2, ν^{s}), 1455 (CH_2, δ^{as}), 1340 (CH, δ), (1250 ($\underset{\text{O}}{\text{HC——CH}}$, ν^{s}), 900, 870, 850 ($\underset{\text{O}}{\text{HC——CH}}$, ν^{as}). ^{1}H NMR, δ, ppm: 1.29–1.56 m [14H, H^1, H^2, H^6_B, H^7_B, H^8, H^9, $H^{(10-13)}_{A,B}$], 1.67–2.89 m (H^3, H^5, H^6_A, H^7_A). ^{13}C NMR, δ, ppm: 54.5 (C^5), 51.2 (C^3), 42.3 (C^8), 32.8 (C^2) 29.3 (C^7), 28.4 (C^9), 24.5 (C^1, C^{10}, C^{13}), 24.2 (C^{11}, C^{12}), 24.0 (C^6). Found: C 81.11, H 10.28. Calculated for $C_{12}H_{18}O$: C, 80.90; H 10.11, $M_{\text{found}} = 176.2$, $M_{\text{calc}} = 178$.

***exo*-2-(4^{l}-Oxabicyclo[4.1.0]heptyl)bicyclo[2.2.1]heptane (XIII)** was obtained from 17.6 g (0.1 mol) of VIIIa; oxidant: $H_2O_2 \cdot CO(NH_2)_2$. Yield: 10.4 g (54.0 wt %). Bp 90–92°C (0.2 kPa), mp 46–48°C. IR spectrum, ν, cm^{-1}: 3030–3040 (HC, νs, oxirane), 2890 (CH, ν), 2850 (CH_2, ν^{s}), 1430 (CH_2, δ^{as}), 1348 (CH, δ), 1265 ($\underset{\text{O}}{\text{HC——CH}}$, ν^{s}), 990, 910, 870($\underset{\text{O}}{\text{HC——CH}}$, ν^{as}). ^{1}H NMR, δ (ppm) in bicycloheptane: 1.27–2.16 m [11H, H^1, H^2, $H^3_{A,B}$, H^4, $H^5_{A,B}$, $H^6_{A,B}$, $H^7_{A,B}$], in epoxycyclohexane: 1.29–2.89 m (9H, H^1, $H^2_{A,B}$, H^3, H^5A, $H^6_{A,B}$, $H^7_{A,B}$). ^{13}C NMR, δ (ppm) in norbornane: 42.4 (C^2), 40.6 (C^7), 38.0 (C^4), 36.0 (C^1), 29.5 (C^5), 29.1 (C^6), 26.5 (C^3) Epoxycyclohexane: 62.3 (C5), 52.5 (C3), 34.2 (C2), 33.3 (C1), 30.8 (C7), 21.8 (C6). Found: C, 81.44; H 10.63. Calculated for $C_{13}H_{20}O$: C, 81.95; H, 10.42.

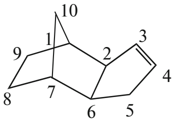
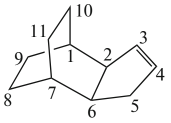
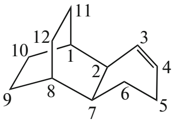
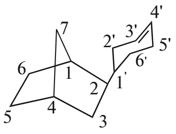
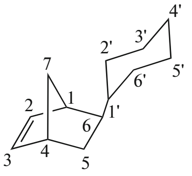
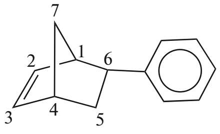
***endo*-3-Oxa-*exo*-6-cyclohexyltricyclo[3.2.1.0$^{2.4}$]octane (XIV)** was obtained from 17.6 g (0.1 mol) of VIIIb; oxidant $H_2O_2 \bullet CO(NH_2)_2$. Yield 14.7 g (76.4 wt %). Bp 94–95°C (0.2 kPa), 1.0683, 1.4926. IR spectrum, ν, cm^{-1}: 3050 (HC, νs, oxirane), 2890 (CH, ν), 2850 (CH_2, ν^{s}), 1440 (CH_2, δ^{as}), 1345 (CH, δ), 1260 ($\underset{\text{O}}{\text{HC——CH}}$, ν^{s}), 990, 903, 870, 850 ($\underset{\text{O}}{\text{HC——CH}}$, ν^{as}). ^{1}H NMR, δ (ppm) in tricyclooctane: 1.23–1.78 m (6H, H^1, H^5, H^6, $H^7_{A,B}$, H^8_B), 1.91–2.90 m (3H, H^2, H^4, H^8_A) 2.29 m; in cyclohexane: 1.29 m (2H, H^2_B, H^6_B), 1.44 m (1H, H^1), 1.46 m (2H, H^3_B, H^5_B); 1.48 m (1H, H^4_B), 1.51 m (1H, H^4_A), 1.56 m (4H, H^2_A, H^3_A, H^5_A). ^{13}C NMR, δ (ppm) in bicyclooctane: 53.9 (C^2), 53.4 (C^4), 43.0 (C^6), 37.8 (C^1), 32.0 (C^5), 26.0 (C^7), 24.5 (C^8); in cyclohexane: 40.8 (C^1), 33.2 (C^2, C^6), 26.3 (C^3, C^5), 26.1 (C^4). Found: C, 81.54; H 10.28. Calculated for $C_{13}H\ _{20}O$: C, 81.25; H 10.42, $M_{\text{found}} = 190.2$, $M_{\text{calc}} = 192$.

5-*exo*-Cyclohexyl-*exo,endo*-2,3-dihydroxybicyclo[2.2.1]heptane (5-cyclohexylnorbornane-2,3-diol) (XIVa) was obtained from 17.6 g (0.1 mol, VIIIb); oxidant: 30% H_2O_2 aqueous solution. Yield 12.2 g (58.6 wt %). Mp 108–110°C. IR spectrum ν, cm^{-1}: 3620 (OH, ν), 3580 (OH, ν), 2905 (CH, ν), 2860 (CH_2, ν^{s}), 1440 (CH_2, δ^{as}), 1355 (CH, δ), 1125 (OH, δ). ^{1}H NMR, δ (ppm): 1.26–2.16 m (1H, H^1, H^4, H^5, $H^6_{A,B}$, $H^7_{A,B}$), 3.27 d (2H, H^2 and H^3, $J_{3.2}$, 7.2 Hz) 3.61 br.s (2H, 2OH); in cyclohexane: 1.44–1.55m (11H). ^{13}C NMR, δ (ppm) in bicycloheptane: 82 (C^2), 79.6 (C^3), 45.8 (C^4), 41 (C^5), 39.4 (C^1), 28 (C^7), 24.3 (C^6); in cyclohexane: 41.3 (C^1), 33.2 (C^2 and C^6), 26.3 (C^3 and C^5), 26.1 (C^4). Found: C, 74.54; H 10.36. Calculated for $C_{13}H_{22}O_2$: C, 74.29; N 10. 48, $M_{\text{found}} = 207.2$, $M_{\text{calc}} = 210$.

***endo*-3-Oxa-*exo*-6-phenyltricyclo[3.2.1.0$^{2.4}$]octane (XV)** was obtained from 17.0 g (0.1 mol) of IX; oxidant: $H_2O_2 \cdot CO(NH_2)_2$. Yield 10.1 g (54.2 wt %). Mp 63–65°C. IR spectrum, ν, cm^{-1}: 3040 (HC, ν^{s}, oxirane), 2890 (CH, ν), 2855 ($CH_{2,}$ ν^{s}), 1660 (C_6H_5, ν), 1430 (CH_2, δ^{as}), 1265 ($\underset{\text{O}}{\text{HC——CH}}$, ν^{s}), 845($\underset{\text{O}}{\text{HC——CH}}$, ν^{as}), 975, 910, 778–685 (C_6H_5, δ). ^{1}H NMR, δ (ppm): 1.58 m (1H, H^7_B), 1.83 m (1H, H^7_A), 1.91 m (1H, H^8_B), 2.15 m (2H, H^5, H^8_A), 2.30 m (1H, H^1), 2.88 d (1H, H^2, H^4, $J_{4.2}$ 7.2 Hz), 7.28–7.39 m (5H, Ar). ^{13}C NMR, δ (ppm): 67.2 (C^4), 54 (C^2), 43 (C^6), 39.8 (C^7), 39.4 (C^5), 37 (C^1), 23.8 (C^8), in C_6H_5: 146.5 (C^1), 1(8.6 (C^3 and C^5), 126.7 (C^2 and C^6), 126 (C^4). Found: C, 83.51; H, 7.38. Calculated for $C_{13}H_{14}O$: C, 83.87; H, 7.53; $M_{\text{found}} = 184.4$, $M_{\text{calc}} = 186$.

***exo*-5-Phenyl-*exo,endo*-2,3-dihydroxybicyclo [[2, 2, 1]heptane (5-phenylnorbornane-2,3-diol) (XVa)** was obtained from 17.0 g (0.1 mol) of IX; oxidant: 30% H_2O_2 aqueous solution. Yield 8.9 g (44.0 wt %). Mp 228–230°C. IR spectrum ν, cm^{-1}: 3580 (OH, ν), 3550 (OH, ν), 2890 (CH, ν), 2850 (CH, νs), 1640 (C_6H_5,

Table 1. Results of experiments on the oxidation of cycloolefins with a 30% H_2O_2 aqueous solution in the presence of modified forms of the phosphomolybdic heteropoly compound (PMHC)* (olefin : H_2O_2 molar ratio = 1 : 2, 50 mmol of olefin, 15 mL of $C_2H_4Cl_2$, $T = 70°C$, $\tau = 6$ h)

Cycloolefin		Conversion, %	Yield, wt % **	
			epoxide	diol
Va		$\frac{91}{90}$	X – $\frac{21.3}{20.5}$	Xa – $\frac{60}{65.3}$
VIa		$\frac{89}{82}$	XI – $\frac{23}{25.4}$	XIa – $\frac{60}{50.6}$
VIIa		$\frac{82}{80}$	XII – $\frac{18.6}{22.0}$	XIIa – $\frac{55}{52}$
VIIIa		$\frac{61}{59}$	XIII – $\frac{7.4}{10.3}$	XIIIa – $\frac{74.2}{74.5}$
***VIIIb		$\frac{75}{91}$	XIV – $\frac{29}{30.4}$	XIVa – $\frac{58.5}{58.6}$
IX		$\frac{52}{63}$	XV – $\frac{11}{43}$	XVa – $\frac{78}{44}$

In Tables 1 and 2:

* PMHC : HBr : $CoCO_3$ molar ratio is 1 : 0.8 : 3.5, the support is a carbon material.

** The value in the numerator refers to the yield of the product of the reaction in the presence of a sample modified with HBr and $CoCO_3$ and that in the denominator, over PMHC modified with HBr and Gd_2O_3.

*** The catalyst was used without pretreatment with hydrogen peroxide.

δ), 1460 (CH_2, δ^{as}), 1360 (CH, δ), 778–685 (C_6H_5, δ). ^1H NMR, δ ppm: 1.58 m (1H, $H^6{}_B$), 1.83 m (1H, $H^6{}_A$), 1.89 m (1H, $H^7{}_B$), 1.91 m (1H, H^4), 2.05 m (1H, $H^7{}_A$), 2.73 m (1H, H^5), 3.26 d (2H, H^2 and H^3, $J_{3.2}$ 7.2 Hz), 3.60 br.s (2H, 2OH), 7.28–7.39 m (5H C_6H_5). ^{13}C NMR, δ (ppm) in bicycloheptane: 81.8 (C^2), 78.9 (C^3), 41.2 (C^5), 39.8 (C^4), 38.0 (C^6), 37.3 (C^1); in the C_6H_5 moiety: 146.5 (C^1), 128.6 (C^3 and C^5), 126.7 (C^2 and C^6). m/z (abundance, %):186 $[C_{13}H_{14}]^{+\bullet}$(3.4), 145 $[C_{11}H_{14}]^+$ (6.3), 144 $[C_{11}H_{12}]^{+\bullet}$ (11.2), 121 $[C_9H_{13}]^+$ (3.2), 120 $[C_9H_{12}]^{+\bullet}$ (5.8), 106 $[C_7H_{10}]^{+\bullet}$ (56.8), 92 $[C_7H_8]^{+\bullet}$ (11.6), 79 $[C_6H_7]^+$ (51.0), 78 $[C_6H_6]^{+\bullet}$ (100), 77 $[C_6H_5]^+$ (10.3), 66 $[C_5H_6]^{+\bullet}$ (21.4), 65 $[C_5H_5]^{+\bullet}$ (5.0), 66 $[C_5H_6]^{+\bullet}$. Found: C, 76.24; H 7.97. Calculated for $C_{13}H_{16}O_2$: C, 76.47; H, 7.84.

The reactivity of the cycloolefins was determined by comparing their conversion and the yield of the corresponding epoxides or diols under the conditions adopted as standard ($T = 70°C$; $\tau = 6$ h; olefin : H_2O_2

molar ratio = 1: 2; olefin amount, 50 mmol; solvent $C_2H_4Cl_2$, 15 mL) (Tables 1, 2).

RESULTS AND DISCUSSION

Epoxidation (or dihydroxylation) of tricyclic unsaturated hydrocarbons with hydrogen peroxide in the two-phase water–organic solvent system selectively proceeds at 65–85°C according to Scheme 2.

In contrast to the norbornene epoxidation reaction, the Wagner–Meerwein rearrangement in tricyclic hydrocarbons does not occur under these conditions,.

The results of the study are presented in Tables 1 and 2.

According to published data [36, 37], acid groups preliminarily introduced into the composition of peroxo complexes under the conditions of oxidation of unsaturated compounds successfully compete with substrate conversion products (diols in this case) for coordination sites at the MeO^{4+} ion, thereby preventing the peroxo complexes from washing out of the surface of the carbon material.

The activation of H_2O_2 and the product composition in the oxidation of mono- and polycyclic olefins in a pseudohomogeneous system largely depend on the nature of the solvent used, the oxidizing agent, and the reaction-mixture stirring speed. In particular, it is known that solvents actively participate in the solvation of the initial catalytic system, the forming peroxo complexes, and other components of the reaction mixture [38, 39]. Depending on the solvent nature, the substrate conversion and selectivity for the products can vary over a wide range. The results of experiments on the oxidation of *exo*-tricyclo[5.2.1.$0^{2,6}$]dec-3(8)-ene with a 30% H_2O_2 solution in dioxane show that there is no distinct dependence of the initial oxidation rate of this cycloolefin on the dielectric constant (ε) of the solvent. The highest epoxide yields were obtained using dioxane (93%), toluene (92%), and dichloroethane (85%) with a cycloolefin conversion of 90–97%. In the case of basic polar solvents (dimethylformamide, acetonitrile), the yields of the oxidation products were significantly lower to be as small as 72.8–82%. On passing from the dioxane solution of H_2O_2 to an aqueous or alcohol solution of the H_2O_2 adduct with urea, both the active-oxygen consumption rate, calculated by graphical differentiation of the curves in the product yield–reaction time coordinates, and the product composition are changed. In the case of the dioxane solution of H_2O_2 or the [$H_2O_2 \cdot CO(NH_2)_2$] adduct in ethanol, the main product of the reaction is a mixture of *endo*-4-oxa-*exo*-tetracyclo[6.2.1.$0^{3.5}0^{2.7}$]- and *exo*-3-oxa-*exo*-tetracyclo[5.3.1.$0^{2.4}$.$0^{6.10}$]undecanes (yield 69.5–82.8%). However, the oxidation of this hydrocarbon with the 30% H_2O_2 aqueous solution leads mainly to the formation of a hardly separable mixture of tricyclodecanediol isomers. Probably, in the case of the H_2O_2 adduct with urea or its dioxane solution, the isomers bind the released water molecules to form hydrates, thereby precluding the hydrolysis of the primary oxidation products, namely, the epoxides.

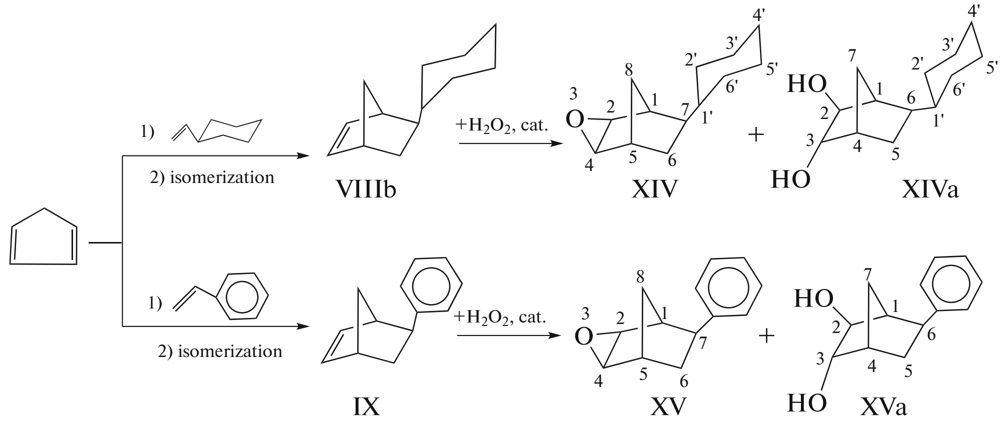
Table 2. Results of experiments on the oxidation of cycloolefins with 30% H_2O_2 solution in dioxane or with the adduct $H_2O_2 \cdot CO(NH_2)_2$ in the presence of PMHC (I) modified with HBr and $CoCO_3$ (II) or HBr and Gd_2O_3 (III)* (olefin : H_2O_2 molar ratio= 1 : 2, 50 mmol of olefin, 15 mL of $C_2H_4Cl_2$, $T = 70$°C, $\tau = 6$ h)

Cycloolefin	Conversion, %	Yield, wt %**	
		epoxide	diol
Va	$\frac{81.0}{86.0}$	$\frac{60}{75.3}$	$\frac{12.5}{4.4}$
VIa	$\frac{84}{85.0}$	$\frac{67.2}{72.0}$	$\frac{12}{7.4}$
VIIa	$\frac{80}{79.0}$	$\frac{64.5}{69.3}$	$\frac{9.7}{8.7}$
VIIIa	$\frac{58}{62}$	$\frac{43.3}{54.0}$	$\frac{10.5}{5.9}$
VIIIb	$\frac{79}{83.0}$	$\frac{51.6}{76.4}$	$\frac{20.4}{6.8}$
IX	$\frac{64}{67.0}$	$\frac{52.0}{54.2}$	$\frac{8.4}{6.1}$

The temperature and time of the reaction have a significant effect on the yields and the epoxide to diol molar ratio; in the case of aqueous solution, the speed of stirring of the reaction mixture has an effect as well. Since cycloolefins are practically insoluble in the aqueous medium, the reaction proceeds in the heterogeneous system. Oxidation of the reduced forms of PMHC occurs in the aqueous phase, and the oxidation of the substrate occurs either in the organic phase or at the interface. Therefore, in the case of an aqueous H_2O_2 solution, a high conversion of cycloolefins is achieved using intense stirring of the reaction mixture at a rate of 600–700 rpm. In the case of dioxane or alcoholic solutions of the oxidant, the stirring speed does not exceed 150–200 rpm. With an increase in temperature from 40 to 70°C, the total yield of epoxides and glycols (depending on the oxidant used) increases from 26.5 to 95.4%. A further increase in temperature leads to an increase in the amount of oligomerization products and a decrease in the amount of epoxides and glycols in the oxidate.

The yield of epoxides and diols also depends on the structure of the substrates, the reactivity of which varies in the order: VIIIb > Va ~ VIa ~ VIIa > VIIIa > IX.

Higher selectivity for epoxides and diols is observed in the case of oxidation of compounds with a multiple bond in the bicycloheptene moiety (Scheme 3):



Scheme 3. Oxidation of compounds with a multiple bond.

Note that after completing the oxidation experiments, the catalysts are easily separated from the liquid phase by filtration. Fivefold reuse of these systems has shown that their activity in the oxidation reaction remains almost unchanged.

In summary, the study of the oxidation of C_{10}–C_{13} bridged unsaturated hydrocarbons with the participation of a molybdenic heteropoly compound modified with HBr and $CoCO_3$ (or Gd_2O_3) and supported on a carbon material has shown that in the case of a 30% H_2O_2 aqueous solution or the H_2O_2–carbamide adduct as an oxidant, the main products of the reaction are respectively corresponding vicinal glycols or epoxides.

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