Liquid-Phase Synthesis of Cyclic Diene Diepoxides Using Metal Halides and Hydrogen Peroxide

Kh. M. Alimardanov, O. A. Sadygov, N. I. Garibov, and M. Ya. Abdullaeva

Mamedaliev Institute of Petrochemical Processes, National Academy of Sciences of Azerbaijan, pr. Khodzhaly 30, Baku, AZ 1025 Azerbaijan e-mail: omar.sadiqov@gmail.com

Received November 17, 2011

Abstract—Optimal conditions were found for induced hydroxyhalogenation of cyclic dienes (tetrahydroindene, 4-vinylcyclohexene and 5-vinyl- and 5-cyclohexenylbicyclo[2.2.1]hept-2-enes) in the system [MHlg–HA or HHlg]–H₂O₂ (or NaClO). Dehydrohalogenation of the chloro- and bromohydrins thus obtained with powdered potassium carbonate gave the corresponding diepoxy derivatives, and their hydrolysis led to mixtures of stereoisomeric tetrahydric alcohols.

DOI: 10.1134/S1070428012100077

Development of efficient methods for the preparation of aliphatic and alicyclic diepoxides is important from both theoretical and practical viewpoints. These compounds are widely used as monomers in the manufacture of heat-resistant epoxy resins and specialty rubbers [1–5]. Polyols and their esters, as well as amino alcohols derived therefrom, are used in pharmacology, perfume and cosmetic industries [6, 7], and manufacture of paint-and-lacquer materials [8].

The most common methods for the synthesis of diepoxides are based on oxidation of diene hydrocarbons with peroxo acids [5, 9, 10] or hydroperoxides [11–13]. Analysis of numerous published data showed that introduction of a second or third oxygen atom into di- or polyene molecule requires more severe conditions and is often complicated by secondary transformations of the oxirane fragments [10].

Selective diepoxidation of dienes has become possible after large-scale implementation of the synthesis of epoxides from C_2 - C_4 unsaturated hydrocarbons with the use of hydroperoxides and transition metal compounds [14]. However, despite extensive studies performed in this field, the problem of selective epoxidation of mono-, di-, and polycyclic dienes remains unresolved so far [15–18]. Attempted one-step diepoxidation of dienes, including cyclic ones, under more severe conditions were often accompanied by oligomerization, and the yields of the target compounds were poor [19]. In view of the above stated, search for more efficient methods of synthesis of epoxy derivatives of cyclic dienes is important now. From this viewpoint, hydroxyhalogenation of the above hydrocarbons and subsequent dehydrohalogenation of halohydrins thus formed may provide an alternative synthetic approach to mono- and diepoxides with a desired structure.

There are published data on the use of $HCl-H_2O_2$ (or $HBr-H_2O_2$) in hypohalogenation of unsaturated compounds having only one double bond [20, 21]. We previously showed that hypohalogenation of alkenylarenes [21], enynes [22], alkyl cyclohexyl ketones [23], and alkyl-, vinyl-, and allylacetylenes of the bicyclo[2.2.1]heptene series can be performed, and the corresponding epoxides can be synthesized [24, 25], in aqueous solution of metal halides or hydrohalic acids.

The present article reports on the results of our studies on the synthesis of halohydrins and diepoxides from cyclic non-conjugated dienes, namely 4-vinyl-cyclohexene (Ia), 3a,4,7,7a-tetrahydro-1*H*-indene (Ib), 5-vinylbicyclo[2.2.1]hept-2-ene (Ic), and 5-(cyclohex-3-en-1-yl)bicyclo[2.2.1]hept-2-ene (Id, adduct of 4-vinylcyclohexene with cyclopentadiene), by one-pot oxidation using a system generating electrophilic reagents HOX (X = Cl, Br) (Scheme 1).

Treatment of dienes **Ia–Id** with dilute solutions of metal or hydrogen halides in the presence of oxidants under mild conditions (10–40°C) resulted in the formation of the corresponding halohydrins **IIa–IId** and

Scheme 1.



M = H, Na, K, Co; $A = HSO_4^-$, NO_3^- , RSO_3^- ; II, Hlg = Cl; III, Hlg = Br.

IIIa–IIId in fairly high yields (Scheme 1). Dehydrohalogenation of **IIa–IIId** and **IIIa–IIId** without isolation in alkaline medium gave diepoxides **IVa–IVd** and tetraols **Va–Vd** (Scheme 2).

With a view to determine the relative reactivity of the double bonds in the substrates we examined the effect of various parameters on the reaction selectivity and yield of chloro(bromo)hydrins. The rate of accumulation of halohydrins in the reaction mixture strongly depended on the temperature, concentration of metal halide or hydrohalic acid and oxidant, and intensity of stirring (Tables 1, 2).

Initial dienes **Ia–Id** are poorly soluble in water; therefore, the reaction in heterogeneous liquid–liquid system occurs at the phase boundary. In a stationary mode without strong stirring of the reaction mixture (500–600 rpm), transfer of hypohalous acids generated *in situ* from the aqueous phase to organic is considerably hindered, and the yield is reduced. At 0–20°C the oxidation involves mainly the double bond charac-

1

Table 1.	Temperature	effect on t	ne yield o	r chloro(bromojny	drins IIa-	-IId and IIIa-	1110

Compound no	Yield, %							
Compound no.	0°C	10°C	20°C	30°C	40°C	50°C		
IIa	40.6	48.4	76.5	86.4	89.6	80.7		
IIIa	36.5	43.6	72.4	81.5	86.5	74.6		
IIb	37.8	44.5	74.6	82	86.6	81		
IIIb	32.6	40.8	71.5	79	85.7	74.6		
IIc	34.6	42.8	72.6	80	87	68		
IIIc	31.7	38.6	67.5	78.4	84	64.8		
IId	36.7	43.6	73.6	78.5	85.6	71		
IIId	33.5	41.8	68.7	73.8	81.8	68		

^a Molar ratio substrate–MHlg (HHlg)–H₂O₂ (NaOCl) 0.1:0.24:0.24; HCl, 10%; HBr, 8%; NaBr or CoBr₂, 10%; rate of addition of H₂O₂ 10 g/h (NaOCl, 25 g/h); reaction time 7 h.

	Yield, %								
Concentration of HCl. %	chlorohydrins				bromohydrins				Concentration of HBr %
,,,,	IIa	IIb	IIc	IId	IIIa	IIIb	IIIc	IIId	011121, 70
6	78	74.6	79	71.5	76.5	71.6	70.5	68	6
10	89.6	86.6	87	85.4	86.5	85.7	84	81.8	8
15	72.5	70.4	71.6	64.5	72	70	73	64.5	15
25	54.6	50.8	51.5	46.4	48.5	46	43.6	44	25
36	42.4	40.5	41.6	38.6	42	40	38	39	33
					36	34	31	32.8	46

Table 2. Effect of concentration of hydrohalic acid on the yield of chloro(bromo)hydrins **Ha–Hd** and **HIa–Hd** (40°C, ratio substrate–MHlg–oxidant 1:0.24:0.24)

terized by higher electron density, and the products are the corresponding monohalohydrins. As the temperature rises from 20 to 40°C, the second double bond also undergoes oxidation, and bis-halohydrins are obtained. Raising the temperature to 50°C and higher considerably reduces the yield as a result of increased contribution of unproductive decomposition of hypohalous acids and oxidants (H₂O₂ and NaOCl).

The reaction direction and the yield of chloro-(bromo)hydrins also depended on the concentration of hydrohalic acid or metal halide (Table 2). Fairly high yields of chlorohydrins (up to 85%) were attained with the use of 6-10% aqueous HCl. Further raising the acid concentration (15-36%) reduced the yield of chlorohydrins to 32%. Analogous results were obtained with hydrobromic acid and its salts (NaBr, CoBr₂). The use of 8% aqueous HBr (NaBr) ensured fairly high yields (up to 82%) of bromohydrins, whereas the yield decreased to 35–50% when the concentration of HBr was higher than 8–10%; presumably, this is the result of side formation of molecular halogen (Cl₂ and Br₂) which is involved in other processes.

The structure of chloro- and bromohydrins **IIa–IId** and **IIIa–IIId**, as well as of diepoxides **IVa–IVd** and tetraols **Va–Vd** obtained therefrom, was confirmed by elemental analysis, IR and ¹H NMR spectroscopy, and independent synthesis, i.e., epoxidation of dienes **Ia– Id** with a 30% solution of H₂O₂ and acetic acid in



RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 48 No. 10 2012

the presence of chlorine-containing acidic cation exchanger Ku-2-8 (Cl 9.5%), the substrate– H_2O_2 –AcOH molar ratio being 1:1.2:0.5.

The IR spectra of **IIa–IId** and **IIIa–IIId** contained absorption bands at 3615, 3625, 3550, 3200 and 1150, 1100, 850–650 cm⁻¹, typical of secondary and tertiary O–H groups and C–Cl (C–Br) bonds, respectively, while bands assignable to vibrations of double C=C bonds in cyclohexene (680, 1650 cm⁻¹) or bicycloheptene fragments (720, 1670, 3030 cm⁻¹) were absent. The IR spectra of **IIa**, **IIc**, **IIIa**, and **IIIc** lacked absorption bands at 910, 990, and 3040 cm⁻¹, typical of vinyl group.

Compounds **IIa–IId** and **IIIa–IIId** displayed in the ¹H NMR spectra signals from CH protons at δ 3.46–3.49 ppm and a broadened singlet at δ 4.78–4.81 ppm due to CHOH fragment in the bicycloheptane or cyclopentane fragment or side hydroxyethyl group.

Both chloro- and bromohydrins **IIa–IId** and **IIIa–IId** readily underwent dehydrohalogenation to the corresponding diepoxides **IVa–IVd** on heating with powdered KOH (yield 79–96%), whereas treatment of these compounds with aqueous alkali afforded 80–94% of tetraols **Va–Vd** (Scheme 2).

Thus chloro- and bromohydrins derived from cyclic dienes can be used to obtain the corresponding diepoxides and various polyfunctionalized derivatives of alicyclic hydrocarbons.

EXPERIMENTAL

The IR spectra were recorded from thin films on a UR-20 spectrometer. The ¹H NMR spectra were measured from solutions in carbon tetrachloride on a Bruker spectrometer operating at 300 MHz; hexamethyldisiloxane was used as internal reference. Initial 5-vinylnorbornene [bp 60–61°C (6.5 mm), d_4^{20} = 1.4819, n_D^{20} = 0.8867] was prepared by thermal condensation of buta-1,3-diene with cyclopentadiene [26].

4-Vinylcyclohexene (purity 99.1%, bp 130°C, $d_4^{20} = 0.8363$, $n_D^{20} = 1.4648$) and bicyclo[4.3.1.0^{1.6}]nona-3,8diene (purity 99.3%, bp 148°C, $d_4^{20} = 0.8344$, $n_D^{20} = 1.4658$) were isolated by fractional distillation of a mixture of 70% of 4-vinylcyclohexene and 30% of bicyclo[4.3.1.0^{1.6}]nona-3,8-diene. 5-(Cyclohex-3-enyl)bicyclo[2.2.1]hept-2-ene [bp 99–101°C (4 mm), $d_4^{20} = 0.9768$, $n_D^{20} = 1.5158$] was prepared by condensation of cyclopentadiene with 4-vinylcyclohexene [19]. The purity and isomeric composition of the initial compounds and products were checked by TLC on Silufol UV-254 plates and by GLC on an LKhM-8MD-5 chromatograph equipped with a thermal conductivity detector [3000×0.3 -cm column packed with 5% of XE-60 on Chromaton N-AW-DMCS, oven temperature 140°C, carrier gas helium, flow rate 40 ml/min; or 8% of poly(ethylene glycol adipate) on Chromosorb W (110–130 mesh), carrier gas nitrogen, oven temperature 160°C (for products)].

Halohydrins IIa–IId and IIIa–IIId (general procedure). A 26–30% solution of hydrogen peroxide (0.25 mol) in water or dioxane or a 18.5% solution of NaOCl (containing 110 mol/l of active chlorine) was added dropwise (10 g/h) under stirring to a mixture of 0.2 mol of diene Ia–Id and 0.25 mol of a 6–8% solution of MBr (or HBr) or a 8–10% solution of MCl (or HCl), adjusted to a required temperature (0–40°C). The mixture was stirred for 5.5–7 h until complete consumption of the oxidant (according to the data of redox titration). Chloro- and bromohydrins thus obtained were then converted into the corresponding diepoxides by adding potassium (or sodium) hydroxide to the reaction mixture.

The organic phase containing compound II or III was separated, the aqueous phase was extracted with diethyl ether $(2 \times 50 \text{ ml})$, and the extracts were combined with the organic phase, neutralized with a 10% solution of sodium carbonate, dried over magnesium sulfate, and evaporated to isolate isomeric halohydrins IIa–III and IIIa–IIIId.

2(1)-Chloro-4-(1-chloro-2-hydroxyethyl)cyclohexan-1(2)-ol (IIa) was obtained from 21.6 g (0.2 mol) of diene Ia. Yield 36.8 g (86%), mp 61–64°C. IR spectrum, v, cm⁻¹: 3625, 1150, 1100 (CH–OH, CH₂–OH), 830, 745, 665 (C–Cl) [27]. ¹H NMR spectrum, δ , ppm: 3.47 t (1-H), 3.51 t (2-H), 3.76 br.s (8-OH), 3.91 d (7-H), 4.60 br.s (1-OH) [28, 29]. Found, %: C 45.12; H 6.72; Cl 33.41. C₈H₁₄Cl₂O₂. Calculated, %: C 45.07; H 6.57; Cl 33.33.

2(1),5(6)-Dichloroperhydroindene-1(2),6(5)-diol (IIb) was obtained from 24 g (0.2 mol) of diene **Ib**. Yield 36.9 g (82%), mp 136–140°C. IR spectrum, v, cm⁻¹: 3625, 3550, 3200, 1100 (CH–OH), 850, 830, 745, 660 (C–Cl). ¹H NMR spectrum, δ , ppm: 1.43 d (2-H), 1.49 d (1-H), 1.41–1.83 m (6H, CH₂), 3.47 d (8-H), 3.51 d (7-H), 3.53 t (3-H), 3.56 d (4-H), 3.71 br.s (8-OH), 4.70 br.s (3-OH). Found, %: C 48.23; H 6.38; Cl 31.83. C₉H₁₄Cl₂O₂. Calculated, %: C 48.0; H 6.22; Cl 31.56. **3(2)-Chloro-5-(1-chloro-2-hydroxyethyl)bicyclo-**[2.2.1]heptan-2(3)-ol (IIc) was obtained from 24 g (0.2 mol) of diene Ic. Yield 36.0 g (80%), mp 98–101°C. IR spectrum, v, cm⁻¹: 3625, 3615, 1150, 1100 (CH–OH, CH₂–OH), 830, 745, 660 (C–Cl). ¹H NMR spectrum, δ , ppm: 1.23–1.56 m (4H, CH₂), 1.78 t (4-H), 2.72 d (5-H), 3.46 t (2-H), 3.49 t (3-H), 3.50 d (8-H), 3.63–3.88 d.d (2H, 9-H), 3.76 br.s (9-OH), 4.78 br.s (2-OH). Found, %: C 48.12; H 6.33; Cl 31.70. C₉H₁₄Cl₂O₂. Calculated, %: C 48.0; H 6.22; Cl 31.56.

3(2)-Chloro-5-[3(4)-chloro-4(3)-hydroxycyclohexyl]bicyclo[2.2.1]heptan-2(3)-ol (IId) was obtained from 34.8 g (0.2 mol) of diene **Id**. Yield 43.8 g (79%), mp 158–161°C. IR spectrum, v, cm⁻¹: 3625, 3615, 1100 (CH–OH), 830, 745, 660–650 (C–Cl). ¹H NMR spectrum, δ , ppm: 0.89 d (2'-H, 6'-H), 1.11 d (5'-H), 1.57 t (2'-H, 6'-H), 1.79 t (5'-H), 3.32 t (4'-H), 4.77 br.s (4'-OH) 4.79 t (3'-H), 1.23–1.55 m (4H, CH₂), 1.73 t (4-H), 3.45 d (2-H), 3.49 d (3-H), 4.76 br.s (2-OH). Found, %: C 56.08; H 7.24; Cl 25.57. C₁₃H₂₀Cl₂O₂. Calculated, %: C 55.97; H 7.17; Cl 25.45.

2(1)-Bromo-4-(1-bromo-2-hydroxyethyl)cyclohexan-1(2)-ol (IIIa) was obtained from 21.6 (0.2 mol) of diene **Ia**. Yield 49.2 g (82%), mp 116–120°C. IR spectrum, v, cm⁻¹: 3625, 3615, 1150, 1100 (CH–OH, CH₂–OH), 745, 660–650 (C–Br). ¹H NMR spectrum, δ , ppm: 1.46–1.98 m (6H, CH₂), 3.49 t (2-H), 3.59 d (1-H), 3.86–4.11 d.d (2H, 8-H), 4.76–4.78 br.s (2H, OH). Found, %: C 31.96; H 4.8; Br 53.12. C₈H₁₄Br₂O₂. Calculated, %: C 31.79; H 4.64; Br 52.98.

1(2),5(6)-Dibromoperhydroindene-2(1),6(5)-diol (**IIIb**) was obtained from 24.0 g (0.2 mol) of diene **Ib**. Yield 43.6 g (79%), mp 173–176°C. IR spectrum, v, cm⁻¹: 3625, 3550, 3200, 1100 (CH–OH), 830, 750, 660 (C–Br). ¹H NMR spectrum, δ , ppm: 1.46 d (2-H), 1.49–1.98 m (6H, CH₂), 3.33 br.s (8-OH), 3.49 d (7-H), 3.52 d (4-H), 3.63 t (3-H), 4.78 br.s (3-OH). Found, %: C 34.43; H 4.52; Br 51.04. C₉H₁₄Br₂O₂. Calculated, %: C 34.39; H 4.46; Br 50.96.

3(2)-Bromo-5-(1-bromo-2-hydroxyethyl)bicyclo-[2.2.1]heptan-2(3)-ol (IIIc) was obtained from 24.0 g (0.2 mol) of diene **Ic**. Yield 49.2 g (78%), mp 160–163°C. IR spectrum, v, cm⁻¹: 3615, 1115, 1100 (CH–OH, CH₂–OH), 750, 680 (C–Br). ¹H NMR spectrum, δ , ppm: 1.23–1.54 m (4H, CH₂), 3.48 t (2-H), 3.50 t (3-H), 3.53 d (8-H), 3.63–3.89 d.d (2H, 9-H), 4.76 br.s (9-OH), 4.78 br.s (2-OH). Found, %: C 34.47; H 4.54; Br 51.16. C₉H₁₄Br₂O₂. Calculated, %: C 34.39; H 4.46; Br 50.96. **3(2)-Bromo-5-[3(4)-bromo-4(3)-hydroxycyclohexyl]bicyclo[2.2.1]heptan-2(3)-ol (IIId)** was obtained from 34.8 g (0.2 mol) of diene Id. Yield 54.3 g (74%), mp 182–187°C. IR spectrum, v, cm⁻¹; 3625, 1100 (CH–OH), 750, 680–670 (C–Br). ¹H NMR spectrum, δ , ppm: 0.89 d (2'-H, 6'-H), 1.11 d (5'-H), 1.58 t (2'-H, 6'-H), 1.79 t (5'-H), 3.32 t (4'-H), 4.78 br.s (4'-OH), 4.79 t (3'-H), 1.23–1.55 m (5H, 1-H, CH₂), 1.83 t (4-H), 3.46 d (3-H), 3.58 d (2-H), 4.80 br.s (2-OH). Found, %: C 42.43; H 5.51; Br 43.46. C₁₃H₂₀Br₂O₂. Calculated, %: C 42.39; H 5.43; Br 43.48.

Compounds IVa–IVd and Va–Vd (*general procedures***).** *a*. Powdered potassium hydroxide, 8.5 g (0.075 mol), was added under stirring to a solution of 0.025 mol of compound **IIa–IIId** or **IIIa–IIId** in 50 ml of diethyl ether, cooled to 8–10°C. The mixture was stirred for 2.5 h at 20°C, the solvent was distilled off, and the residue was subjected to vacuum distillation or chromatography on aluminum oxide (using hexane as eluent) to isolate mixtures of isomeric mono- and diepoxides.

b. Compound **Ha–Hd** or **HIa–Hd** was treated (without preliminary isolation from the reaction mixture; see above) with a cold (5–10°C) 20–22% aqueous solution of sodium hydroxide; mixtures of isomeric compounds **Va–Vd** were isolated as described in [11].

5-(Oxiran-2-yl)-2-oxabicyclo[4.1.0]heptane (IVa) was synthesized from 5.3 g (0.025 mol) of **Ha**. Yield 3.2 g (92%), bp 49–51°C (10 mm), $n_D^{20} = 1.4738$, $d_4^{20} = 1.0917$. IR spectrum, v, cm⁻¹: 3010–3028 (C–H) [27]; 1260, 1250, 945, 840 (oxirane). ¹H NMR spectrum, δ , ppm: 1.31–1.71 m (6H, CH₂), 1.74 d (5-H), 2.38 d.d and 2.63 d.d (9-H), 2.87 q (1-H, 3-H), 5.52 d (8-H) [28, 29]. Found, %: C 68.82; H 8.71. C₈H₁₂O₂. Calculated, %: C 68.57; H 8.57.

2,7-Dioxatetracyclo[6.3.2.0^{1.3}0^{5.10}0^{6.8}]**undecane** (**IVb**) was synthesized from 9.6 g (0.025 mol) of **IIb**. Yield 3.3 g. According to the GLC data, the product contained 84.2% of diepoxide **IVb** [bp 73–75°C (10 mm), $n_D^{20} = 1.4908$, $d_4^{20} = 1.1062$] and 15.8% of monoepoxide [bp 53–55.5°C (14 mm), $n_D^{20} = 1.5188$, $d_4^{20} = 0.9812$]. IR spectrum, v, cm⁻¹: 1265, 1260, 930, 940, 860, 865 (oxirane ring fused to the six-membered ring), 850–835 (oxirane ring fused to the five-membered ring). ¹H NMR spectrum, δ , ppm: 1.39–1.77 m (6H, CH₂), 2.82 q (1-H, 3-H), 3.53–3.51 d (6-H, 8-H). Found, %: C 71.15; H 7.93. C₉H₁₂O₂. Calculated, %: C 71.05; H 7.89. **6-(Oxiran-2-yl)-3-oxatricyclo[3.2.1.0**^{2.4}**]octane (IVc)** was synthesized from 7.9 g (0.025 mol) of **IIIc**. Yield 3.5 g (93%), mp 42–44°C, bp 111–113°C (10 mm), $d_4^{20} = 1.1182$; the product crystallized in a receiver. IR spectrum, v, cm⁻¹: 1265, 1260, 940, 850 (oxirane). ¹H NMR spectrum, δ, ppm: 1.24–1.56 m (4H, CH₂), 1.74–1.86 t (1-H, 5-H, 6-H), 2.53 d.d (9-H), 2.39–2.65 d.d (10-H), 2.77 q (2-H, 4-H). Found, %: C 70.95; H 8.5 C₉H₁₂O₂. Calculated, %: C 71.05; H 7.89.

6-(7-Oxabicyclo[4.1.0]hept-3-yl)-3-oxatetracyclo-[3.2.1.0^{2.4}]octane (IVd) was synthesized from 9.2 g (0.025 mol) of **IIId**. Yield 4.8 g (94%), bp 96–98°C (1 mm), $n_D^{20} = 1.5182$, $d_4^{20} = 1.1084$. IR spectrum, v, cm⁻¹: 1265, 1260, 858, 840 (oxirane). ¹H NMR spectrum, δ, ppm: 1.25–1.77 m (9H), 2.81 q (2-H, 4-H), 2.89 q (2H). Found, %: C 76.03; H 8.10. C₁₃H₁₈O₂. Calculated, %: C 71.05; H 7.89.

4-(1,2-Dihydroxyethyl)cyclohexane-1,2-diol (Va) was synthesized from 5.3 g (0.025 mol) of **Ha**. Yield 3.7 g (87%), mp 128–133°C. Found, %: C 54.51; H 8.97. $C_8H_{16}O_4$. Calculated, %: C 54.54; H 9.09.

Perhydroindene-1,2,5,6-tetraol (Vb) was synthesized from 7.9 g (0.025 mol) of **IIIb**. Yield 4.1 g (88%), mp 164–168°C. Found, %: C 57.46; H 8.56. $C_9H_{16}O_4$. Calculated, %: C 57.45; H 8.57.

5-(1,2-Dihydroxyethyl)bicyclo[2.2.1]heptane-2,3diol (Vc) was synthesized from 3.6 g (0.025 mol) of **IIc.** Yield 4.3 g (91%), mp 160–164°C. IR spectrum, v, cm⁻¹: 3625, 3615, 1150, 1100 (CH–OH, CH₂–OH). ¹H NMR spectrum, δ , ppm: 3.24 d (2-H, 3-H), 3.29 (8-H), 3.56–3.81 t (2H, 9-H), 4.78 br.s (CH₂OH), 4.81 br.s (CHOH). Found, %: C 57.43; H 8.56. C₉H₁₆O₄. Calculated, %: C 57.47; H 8.51.

5-(3,4-Dihydroxycyclohexyl)bicyclo[2.2.1]heptane-2,3-diol (Vd) was synthesized from 7.9 g (0.025 mol) of **IIId**. Yield 5.4 g (89%), mp 218– 222°C. Found, %: C 64.46; H 9.17. $C_{13}H_{22}O_2$. Calculated, %: C 64.47; H 9.09.

REFERENCES

- 1. Paquin, A.M., *Epoxydverbindungen und Epoxydharze*, Berlin: Springer, 1958.
- 2. Korshak, V.V., *Termostoikie polimery* (Heat-Resistant Polymers), Moscow: Nauka, 1969.
- Kameyama, A., Watanabe, Sh., Kobayashi, E., and Nishikubo, T., *Macromolecules*, 1992, vol. 25, no. 9, p. 2307.

- 4. Wu, S., Jorgensen, J.D., and Soucek, M.D., *Polymer*, 2000, vol. 41, p. 81.
- 5. Wang, Z., Xie, M., Zhoo, Y., Yu, Y., and Fang, S., *Polymer*, 2003, vol. 44, p. 923.
- Kheifits, L.A. and Dashunin, V.M., *Dushistye veshchestva i drugie produkty dlya parfyumerii* (Fragrance Substances and Other Materials for Perfumery), Moscow: Khimiya, 1994.
- Mashkovskii, K.L., *Lekarstvennye sredstva* (Medicines), Moscow: Novaya Volna, 2002, 15th ed., vols. 1, 2.
- Livshchits, R.M. and Vobrvinskii L.A., Zameniteli rastitel'nykh masel v lakokrasochnoi promyshlennosti (Vegetable Oil Substitutes in Paint-and-Lacquer Industry), Moscow: Khimiya, 1987.
- Prilezhaeva, E.N., *Reaktsiya Prilezhaeva. Elektrofil'noe* okislenie (Prilezhaev Reaction. Electrophilic Oxidation), Moscow: Nauka, 1974; Kas'yan, L.I., Seferova, M.F., and Okovityi, S.I., *Alitsiklicheskie epoksidnye soedi*neniya. Metody sinteza (Alicyclic Epoxy Compounds. Methods of Synthesis), Dnepropetrovsk: Dnepropetr. Gos. Univ., 1996.
- 10. Guiard, S., Giorgi, M., Santelli, M., and Parrain, J.-L., *J. Org. Chem.*, 2003, vol. 68, p. 3319.
- 11. Tolstikov, G.A., *Reaktsiya gidroperoksidnogo okisleniya* (Hydroperoxide Oxidation), Moscow: Nauka, 1976.
- Nozhnin, I.A., Mel'nik, L.V., Egorova, L.M., and Kryukov, S.I., *Neftekhimiya*, 1997, vol. 37, no. 2, p. 160.
- Leonov, V.N., Katalizatory epoksidirovaniya olefinov organicheskimi gidroperoksidami (Catalysts for Olefin Epoxidation with Organic Hydroperoxides), Moscow: TsNIIENeftekhim, 1993.
- Landau, R., Brown, D., Russel, J.L., and Collar, R., Book of Synopses, 7th World Petroleum Congress, Mexico, 1967.
- Sheng, M.N. and Zajacek, J.G., J. Org. Chem., 1970, vol. 35, p. 1839.
- 16. Lazurin, E.A., Voronenkov, V.V., and Osokin, Yu.G., Usp. Khim., 1997, vol. 46, p. 1739.
- 17. Antonova, T.N., Izv. Vyssh. Uchebn. Zaved., Ser. Khim. Khim. Tekhnol., 2008, vol. 51, no. 4, p. 38.
- Kas'yan, L.I., Kas'yan, A.O., Okovityi, S.I., and Tarabara, I.N., *Alitsiklicheskie epoksidnye soedineniya. Reaktsionnaya sposobnost*' (Alicyclic Epoxy Compounds. Reactivity), Dnepropetrovsk: Dnepropetr. Gos. Univ., 2003.
- Alimardanov, Kh.M., Sadygov, O.A., Gadzhiev, T.A., Abdullaeva, M.Ya., Asirova, R.B., and Babaev, N.R., *Prots. Neftekhim. Nefteper.*, 2007, no. 5, p. 66.
- Muganlinskii, F.F., Treger, Yu.A., and Lyushin, M.M., *Khimiya i tekhnologiya galogenorganicheskikh soedinenii* (Chemistry and Technology of Organohalogen Compounds), Moscow: Khimiya, 1991.
- 21. Sadygov, O.A. and Alimardanov, Kh.M., *Russ. J. Org. Chem.*, 2007, vol. 43, p. 1661.

RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 48 No. 10 2012

- 22. Veliev, M.G., Sadygov, O.A., Alimardanov, Kh.M., and Shatirova, M.I., *Russ. J. Org. Chem.*, 2007, vol. 43, p. 1604.
- 23. Sadygov, O.A. and Alimardanov, Kh.M., *Russ. J. Org. Chem.*, 2009, vol. 45, p. 166.
- 24. Sadygov, O.A., Alimardanov, Kh.M., and Abbasov, M.F., *Russ. J. Gen. Chem.*, 2009, vol. 79, p. 1698.
- Veliev, M.G., Sadygov, O.A., Shatirova, M.I., and Alimardanov, Kh.M., *Russ. J. Org. Chem.*, 2008, vol. 44, p. 1282.
- 26. Plate. A.F. and Belikova, N.A., Zh. Obshch. Khim., 1960, vol. 30, p. 3945.
- 27. Bellamy, L.J., *The Infra-red Spectra of Complex Molecules*, London: Methuen, 1958.
- Ionin, B.I. and Ershov, B.A., YaMR spektry v organicheskoi khimii (NMR Spectra in Organic Chemistry), Leningrad: Khimiya, 1967.
- 29. Gordon, A.J. and Ford, R.A., *The Chemist's Com*panion, New York: Wiley, 1972.