

Induced Halogenation of Alkyl Cyclohexenyl Ketones Involving Metal Halides, Hydrohalogenic Acids, and Hydrogen Peroxide

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Abstract—The induced halogenation and hydroxyhalogenation of alkyl cyclohexenyl ketones in a system [MHlg + HHLg or HHLg]–H₂O₂ or in NaOCl was performed and optimum reaction conditions were established. Under mild conditions the electrophilic addition of the halogen or the acid occurred at the multiple bond of the ring with the formation of the corresponding dihalo or hydroxyhalo derivatives of cycloaliphatic ketones. From the compounds obtained epoxy- and dioxyketones of aliphatic series were prepared. Chloro(bromo)hydrins of ketones from the alkylcyclohexane series and oxiranes based thereon are reactive compounds and can be employed as synthons in the organic synthesis.

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Halogen-substituted ketones and their derivatives are convenient synthons for the synthesis of organic compounds, and they are used in the production of insecticides, antihelmintic agents and other biologically active compounds [1–3]. These compounds can also be employed as modifiers of epoxy resins [4] and antifreeze additives to lubricants [5, 6].

The halogenation of various unsaturated compounds is sufficiently thoroughly described in reviews [7–10] and a monograph [11]. However the data on the induced halogenation of unsaturated ketones, especially of cycloaliphatic series, were practically absent.

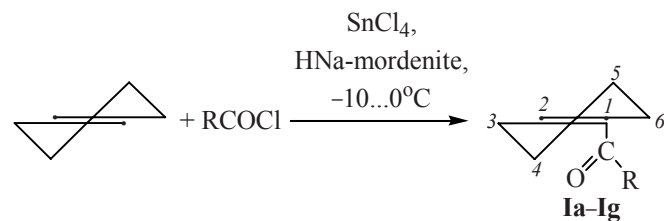
In the present study in extension of the research on the induced halogenation of aromatic [12] and alkenyl-

aromatic compounds [13] and also of conjugated enyne systems [14] results are reported of the halogenation and hydroxyhalogenation of unsaturated ketones from the cycloaliphatic series under the conditions of the formation of Hlg₂ and HOHlg in situ. We used as inducing system [HHLg or MHlg + HHLg]–H₂O₂ (or NaOCl).

The synthesis of initial unsaturated ketones was performed by acylation of cyclohexene with acid chlorides of C₂–C₈ carboxylic acids by the known procedure [15, 16]. The use in this reactions as catalyst of highly dispersed AlCl₃ and SnCl₄ on a solid carrier (HNa-mordenite) instead of usually applied soluble salts (ZnCl₂, AlCl₃) made it possible to carry out the reaction selectively at –10...0°C instead of –3...–25°C [16] (Scheme 1).

The composition and structure of obtained alkyl cyclohexenyl ketones **Ia–Ig** was established by elemental analysis and IR and ¹H NMR spectroscopy. In the IR spectra these compounds have common absorption bands in the region 1660 and 1703 cm^{–1} characteristic of the stretching vibrations of the C=O group of α,β-unsaturated ketones. The bands in the region 752, 836, 965, 1634, 1640, 1654 cm^{–1} correspond to the C=C bonds of the cyclohexene ring, and the bands at 1377, 1420, 1445 cm^{–1},

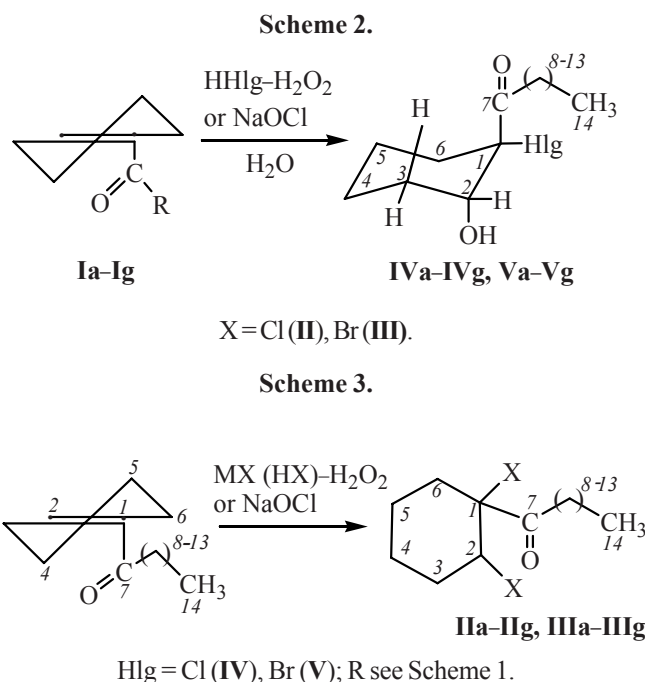
Scheme 1.



to the bending vibrations of groups CH_2 and CH_3 [17]. In the ^1H NMR spectra of compounds **Ia–Ig** appeared a triplet from the fragment $=\text{CH}$ (6.71 ppm) and multiplets at 1.65–1.96 ppm from the CH_2 groups of the cyclohexene ring. The singlet at 2.31 ppm in the spectrum of ketone **Ia** belongs to the CH_3 group of the acyl fragment. With the growing length of the acyl residue the proton signals of the terminal methyl group shift upfield (in the ^1H NMR spectra of ketone **Ib** a doublet at 1.11 ppm, of ketones **Ic–Ig** a triplet at 0.97 ppm). The protons of the group $\text{CH}_2\text{C}=\text{O}$ in ketones **Ib–Ig** also give rise to a triplet at 2.46 ppm [18, 19].

It was established experimentally that alkyl cyclohexenyl ketones in the presence of concentrated water solutions of MHlg and H_2O_2 under the conditions of induced addition of electrophilic reagents were easily converted into 1,2-substituted dihalides **IIa–IIg** and **IIIa–IIIg** (Scheme 2).

The yield of dihaloketones **IIa–IIg** and **IIIa–IIIg** and the selectivity of the process depend on the temperature, the concentration of the water solutions of metal halides or hydrohalogenic acids, and the intensity of stirring of the reaction mixture. Inasmuch as the 1-(cyclohex-1-enyl)alkanones are sparingly soluble in water, the reaction proceeds in a heterophase system on the phase boarder, and in the stationary mode without vigorous stirring (the rate of the agitator 500–600 rpm) the transfer of the halogen from the water into the organic phase would be significantly hampered leading to the decrease in the yield of the products. The highest yield of 1-(1,2-dichlorocyclohexyl)- and 1-(1,2-dibromocyclohexyl)alkanones was obtained at 20–50°C and attained 73–94 and 72–89% respectively. Raising the temperature from 50 to 70°C resulted in decreased yield evidently due to the acceleration of a side reaction, electrophilic substitution of hydrogen atoms in CH_2 groups of the cyclohexane ring for halogen atoms. With rising concentrations of the water solutions of metal halides and hydrohalogenic acids (up to 33% for NaCl , HCl and 45% for NaBr , HBr) the yields of the target products increased up to 96 and 98% with respect to the consumed halogen. At low concentrations of salt and acid solutions (below 15%) the corresponding chloro- and bromohydrins were obtained. Thus the optimum conditions maximizing the yield of compounds **IIa–IIg** and **IIIa–IIIg** are as follows: molar ratio **Ia–Ig**– $\text{MHlg}(\text{HHlg})\text{–H}_2\text{O}_2$ (or NaOCl) 1:2:2, concentration of solutions of MHlg 25–30%, of hydrochloric and hydrobromic acids 20–33 and 30–45% respectively,



temperature 20–40°C. With growing length of the alkyl chain from CH_3 to C_7H_{15} the yields of the corresponding dihalides diminished to 69–71%, apparently due to the shielding of the double bond by the alkyl residues.

At the use of low concentrated solutions (HCl 10–15%, HBr 6–8%) the corresponding products of hydroxyhalogenation were obtained in sufficiently good yield (Scheme 3).

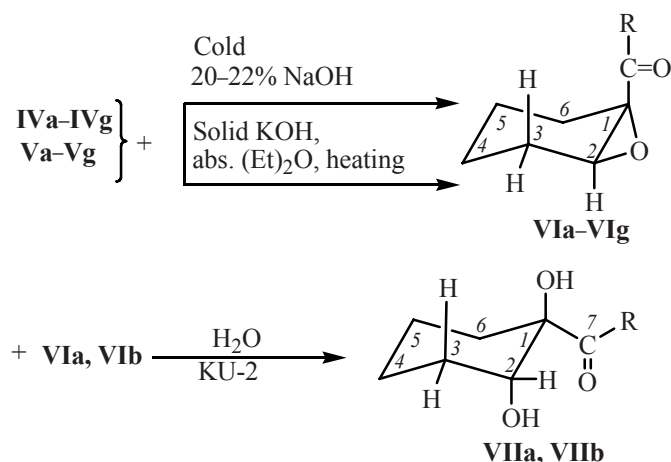
The addition to the solutions of HCl and HBr up to 3–7 wt % of MHlg also favored the increased yield of hydroxyhalides.

The composition and structure of compounds **IIa–IIg–IVa–IVg** were established from elemental analysis, IR and ^1H NMR spectra.

The hydroxyhalides and dihalides obtained from the cyclohexenylalkanones easily underwent dehydrohalogenation in the presence of powdered potassium hydroxide (or sodium hydroxide) giving epoxides **Vla–Vlg**, and the latter were converted into *trans*-diols **VIIa** and **VIIb** in 65–86% yield (Scheme 4).

The composition and structure of epoxides **Vla–Vlg** was confirmed by elemental analysis, IR and ^1H NMR spectra, and also by independent synthesis: by epoxidation of cyclohexenylalkanones **Ia–Ig** with 30% dioxane solution of H_2O_2 and CH_3COOH in the presence of chlorine-containing acidic cation-exchanger $\text{KU-2}\times 8$ or $\text{KU-2}\times 8\text{p}$ at the molar ratio substrate– H_2O_2 – CH_3COOH 1:1.2:0.5.

Scheme 3.



R see Scheme 1.

EXPERIMENTAL

IR spectra of compounds synthesized were recorded on a spectrophotometer UR-20, ^1H NMR spectra, on a spectrometer Bruker (300 MHz) from solutions in CCl_4 , internal reference HMDS. Cyclohexene was obtained by cyclohexanol dehydration followed by purification as described in [20]. Monocarboxylic acid $\text{C}_2\text{-C}_7$ chlorides were obtained by boiling the acids with the thionyl chloride by the known procedure till the end of HCl evolution (monitoring with litmus) [15]. The purity and isomeric composition of compounds was estimated from TLC on Silufol UV-254 plates (eluent benzene-ethyl ether, 3-5 : 1 v/v, development in iodine vapor) and from GLC on a chromatograph LKhM-8M8-5, detector catharometer, column 0.3×300 cm packed with Chromaton N-AW DMCS impregnated with 5% silicone XE-60, oven temperature 150°C , carrier gas helium, flow rate 40 ml/min.

1-(Cyclohex-1-enyl)ethanone (Ia). To a solution of 18.1 g (0.24 mol) of acetyl chloride in 30 ml of CCl_4 at -15 – 0°C was added while stirring 6.3 g of SnCl_4 or AlCl_3 dispersed on HNa-mordenite and afterwards within 0.5 h was added 16.4 g (0.2 mol) of cyclohexene. The reaction mixture was stirred for 60–90 min. Then the content of the reactor was charged into a beaker cooled with ice, the organic layer was separated and dried with Na_2SO_4 . A fraction of bp 60 – 90°C (1.5 mm Hg) was distilled off, 2–3 h treated with sodium methylate, then neutralized with 10% solution of hydrochloric acid, washed with water, dried, and distilled in a vacuum. Yield 20.2 g (81%), bp 65 – 67°C (5 mm Hg), d_4^{20} 0.9703,

n_D^{20} 1.4882. Found, %: C 77.12; H 10.05. $\text{C}_8\text{H}_{12}\text{O}$. Calculated, %: C 77.42; H 9.68. Likewise were synthesized compounds **Ib–Ig**.

1-(Cyclohex-1-enyl)propan-1-one (Ib) was obtained from 21.5 g (0.24 mol) of propionyl chloride and 16.4 g (0.2 mol) of cyclohexene. Yield 19.2 g (70%), bp 72 – 76°C (5 mm Hg), d_4^{20} 0.9636, n_D^{20} 1.4871. Found, %: C 78.12; H 10.36. $\text{C}_9\text{H}_{14}\text{O}$. Calculated, %: C 78.26; H 10.14.

1-(Cyclohex-1-enyl)butan-1-one (Ic) was obtained from 25.6 g (0.24 mol) of butanoyl chloride and 16.4 g (0.2 mol) of cyclohexene. Yield 17.7 g (58%), bp 78 – 81°C (5 mm Hg), d_4^{20} 0.9428, n_D^{20} 1.4793. Found, %: C 78.76; H 10.75. $\text{C}_{10}\text{H}_{16}\text{O}$. Calculated, %: C 78.95; H 10.53.

1-(Cyclohex-1-enyl)pentan-1-one (Id) was obtained from 28.9 g (0.24 mol) of pentanoyl chloride and 16.4 g (0.2 mol) of cyclohexene. Yield 16.2 g (49%), bp 86 – 89°C (5 mm Hg), d_4^{20} 0.9338, n_D^{20} 1.4780. Found, %: C 79.36; H 11.06. $\text{C}_{11}\text{H}_{18}\text{O}$. Calculated, %: C 79.52; H 10.84.

1-(Cyclohex-1-enyl)hexan-1-one (Ie) was obtained from 32.3 g (0.24 mol) of hexanoyl chloride and 16.4 g (0.2 mol) of cyclohexene. Yield 15.3 g (43%), bp 93 – 98°C (5 mm Hg), d_4^{20} 0.9248, n_D^{20} 1.4773. Found, %: C 78.86; H 11.28. $\text{C}_{12}\text{H}_{20}\text{O}$. Calculated, %: C 80.0; H 11.11.

1-(Cyclohex-1-enyl)heptan-1-one (If) was obtained from 35.5 g (0.24 mol) of a heptanoyl chloride and 16.4 g (0.2 mol) of cyclohexene. Yield 14.3 g (36%), bp 94 – 97°C (2 mm Hg), d_4^{20} 0.9138, n_D^{20} 1.4722. Found, %: C 79.32; H 11.16. $\text{C}_{13}\text{H}_{22}\text{O}$. Calculated, %: C 80.41; H 11.34.

1-(Cyclohex-1-enyl)octan-1-one (Ig) was obtained from 38.9 g (0.24 mol) of octanoyl chloride and 16.4 g (0.2 mol) of cyclohexene. Yield 13.2 g (33%), bp 112 – 115°C (2 mm Hg), d_4^{20} 0.9012, n_D^{20} 1.4653. Found, %: C 81.18; H 11.72. $\text{C}_{14}\text{H}_{24}\text{O}$. Calculated, %: C 80.71; H 11.54.

1-(1,2-Dichlorocyclohexyl)alkan-1-ones IIa–IIg. To 22.5 g (0.2 mol) of 33% HCl was added 0.1 mol of ketone **Ia–Ig**, then within 60 min was added 23 g (0.2 mol) of 30% water solution of H_2O_2 or 124.2 g (0.2 mol) of 18.5% solution of sodium hypochlorite (active chlorine content 110 g-ion l^{-1}). Then the temperature of the reaction mixture was raised to 30 – 50°C , and the stirring was continued for 4–5 h. On completion of the reaction (H_2O_2 consumption was monitored by potassium permanganate titration, NaOCl by iodometry [21]) the organic layer was separated from the water phase,

washed, dried with anhydrous Na_2SO_4 , and distilled in a vacuum.

1-(1,2-Dichlorocyclohexyl)ethanone (IIa) was obtained from 6.2 g (0.05 mol) of ketone **Ia**. Yield 9.1 g (94%), bp 90–92°C (5 mm Hg), d_4^{20} 1.2073, n_D^{20} 1.4961. IR spectrum, ν , cm^{-1} : 2870 (CH), 1720 (C=O), 745, 710 (C–Cl). ^1H NMR spectrum, δ , ppm: 1.39–1.79 m and 1.49–2.04 m (CH_2 of ring), 2.1 s (3H, CH_3), 3.96 t (1H, H^2). Found, %: C 49.88; H 6.15; Cl 36.06. $\text{C}_8\text{H}_{12}\text{Cl}_2\text{O}$. Calculated, %: C 49.23; H 6.50; Cl 36.41.

1-(1,2-Dichlorocyclohexyl)propan-1-one (IIb) was obtained from 6.9 g (0.05 mol) of ketone **Ib**. Yield 9.3 g (89%), bp 112–114°C (5 mm Hg), d_4^{20} 1.1632, n_D^{20} 1.4882. IR spectrum, ν , cm^{-1} : 2950 (CH), 1720 (C=O), 800, 745, 720 (C–Cl). ^1H NMR spectrum, δ , ppm: 1.08 t (3H, CH_3), 2.5 d (2H, C^8H_2), 3.95 t (1H, H^2). Found, %: C 49.84; H 7.13; Cl 34.25. $\text{C}_9\text{H}_{14}\text{Cl}_2\text{O}$. Calculated, %: C 51.67; H 6.69; Cl 33.77.

1-(1,2-Dichlorocyclohexyl)butan-1-one (IIc) was obtained from 7.6 g (0.05 mol) of ketone **Ic**. Yield 9.5 g (85%), bp 114–117°C (4 mm Hg), d_4^{20} 1.1437, n_D^{20} 1.4842. IR spectrum, ν , cm^{-1} : 2875 (CH), 1720 (C=O), 800, 745, 710 (C–Cl). ^1H NMR spectrum, δ , ppm: 0.97 t (3H, CH_3), 1.62 d (2H, C^9H_2), 2.46 t (2H, C^8H_2), 3.95 t (1H, H^2). Found, %: C 53.57; H 7.51; Cl 32.23. $\text{C}_{10}\text{H}_{16}\text{Cl}_2\text{O}$. Calculated, %: C 53.81; H 7.17; Cl 31.83.

1-(1,2-Dichlorocyclohexyl)pentan-1-one (IIId) was obtained from 8.3 g (0.05 mol) of ketone **Id**. Yield 9.7 g (82%), bp 123–125°C (4 mm Hg), d_4^{20} 1.0956, n_D^{20} 1.4732. IR spectrum, ν , cm^{-1} : 2960, 2880 (CH), 1720 (C=O), 800, 745, 710 (C–Cl). ^1H NMR spectrum, δ , ppm: 0.96 t (3H, CH_3), 1.34 d (2H, C^{10}H_2), 1.56 d (2H, C^9H_2), 2.46 d (2H, C^8H_2), 3.96 t (1H, H^2). Found, %: C 56.82; H 7.89; Cl 30.42. $\text{C}_{11}\text{H}_{18}\text{Cl}_2\text{O}$. Calculated, %: C 55.69; H 7.59; Cl 29.95. Identical spectral data were obtained for compounds **IIe–IIg**.

1-(1,2-Dichlorocyclohexyl)hexan-1-one (IIe) was obtained from 9 g (0.05 mol) of ketone **Ie**. Yield 9.4 g (75%), bp 139–142°C (5 mm Hg), d_4^{20} 1.0715, n_D^{20} 1.4672. Found, %: C 57.71; H 7.92; Cl 29.10. $\text{C}_{12}\text{H}_{20}\text{Cl}_2\text{O}$. Calculated, %: C 57.37; H 7.96; Cl 28.28.

1-(1,2-Dichlorocyclohexyl)heptan-1-one (IIIf) was obtained from 9.7 g (0.05 mol) of ketone **If**. Yield 9.8 g (74%), bp 145–148°C (5 mm Hg), d_4^{20} 1.0623, n_D^{20} 1.4583. Found, %: C 59.26; H 8.32; Cl 26.83. $\text{C}_{13}\text{H}_{22}\text{Cl}_2\text{O}$. Calculated, %: C 58.87; H 8.30; Cl 26.79.

1-(1,2-Dichlorocyclohexyl)octan-1-one (IIg) was obtained from 10.2 g (0.05 mol) of ketone **Ig**. Yield 10 g

(72%), bp 151–154°C (5 mm Hg), d_4^{20} 1.0562, n_D^{20} 1.4475. Found, %: C 61.34; H 8.35; Cl 25.82. $\text{C}_{14}\text{H}_{24}\text{Cl}_2\text{O}$. Calculated, %: C 60.22; H 8.60; Cl 25.45.

Likewise were obtained compounds **IIIa–IIIg**. To 33.5 g (0.2 mol) of 46% HBr or 20.6 g (0.2 mol) of NaBr or KBr was added 25 ml of H_2O and 22.5 g (0.2 mol) of 30% water solution of H_2O_2 and 0.1 mol of ketone **Ia–Ig**.

1-(1,2-Dibromocyclohexyl)ethanone (IIIa) was obtained from 12.4 g (0.1 mol) of ketone **Ia**. Yield 25.1 g (89%), bp 115–118°C (2 mm Hg), d_4^{20} 1.7634, n_D^{20} 1.5576. IR spectrum, ν , cm^{-1} : 2870 (CH), 1720, 1705 (C=O), 1654, 1634, 1445 (CH_2 , CH_3), 750, 680, 590 (C–Br). ^1H NMR spectrum, δ , ppm: 1.38 d (2H, C^4H_2), 1.48 d (2H, C^5H_2), 1.76, 2.01 d (2H, C^3H_2), 2.02–2.26 d (2H, C^6H_2), 2.11 s (3H, CH_3), 4.01 t (1H, H^2). Found, %: C 33.27; H 4.76; Br 56.98. $\text{C}_8\text{H}_{12}\text{Br}_2\text{O}$. Calculated, %: C 33.8; H 4.22; Br 56.34.

1-(1,2-Dibromocyclohexyl)propan-1-one (IIIb) was obtained from 13.8 g (0.1 mol) of ketone **Ib**. Yield 24.9 g (84%), bp 123–126°C (2 mm Hg), d_4^{20} 1.7617, n_D^{20} 1.5533. IR spectrum, ν , cm^{-1} : 2950 (CH), 1720, 1705 (C=O), 750, 680, 590 (C–Br). ^1H NMR spectrum, δ , ppm: 1.07 t (3H, CH_3), 1.38 d (2H, C^4H_2), 1.48 d (2H, C^5H_2), 1.77–2.02 d (2H, C^3H_2), 2.02, 2.77 d (2H, C^6H_2), 2.50 d (2H, C^8H_2), 4.02 t (1H, H^2). Found, %: C 36.87; H 4.92; Br 54.13. $\text{C}_9\text{H}_{14}\text{Br}_2\text{O}$. Calculated, %: C 36.24; H 4.69; Br 53.69.

1-(1,2-Dibromocyclohexyl)butan-1-one (IIIc) was obtained from 15.2 g (0.1 mol) of ketone **Ic**. Yield 25.6 g (82%), bp 128–132°C (2 mm Hg), d_4^{20} 1.7582, n_D^{20} 1.5465. IR spectrum, ν , cm^{-1} : 2875 (CH), 1720, 1705 (C=O), 750, 680, 590 (C–Br). ^1H NMR spectrum, δ , ppm: 0.97 t (3H, CH_3), 1.62 q (2H, C^9H_2), 2.85 t (2H, C^8H_2), 4.01 t (1H, H^2). Found, %: C 39.12; H 5.46; Br 52.32. $\text{C}_{10}\text{H}_{16}\text{Br}_2\text{O}$. Calculated, %: C 38.46; H 5.13; Br 51.28.

1-(1,2-Dibromocyclohexyl)pentan-1-one (IIIId) was obtained from 16.6 g (0.1 mol) of ketone **Id**. Yield 24.8 g (76%), bp 134–136°C (2 mm Hg), d_4^{20} 1.7526, n_D^{20} 1.5436. ^1H NMR spectrum, δ , ppm: 0.97 t (3H, CH_3), 1.34 q (2H, C^{10}H_2), 1.58 q (2H, C^9H_2), 2.46 t (2H, C^8H_2), 4.01 t (1H, H^2). Found, %: C 40.51; H 5.96; Br 49.86. $\text{C}_{11}\text{H}_{18}\text{Br}_2\text{O}$. Calculated, %: C 40.49; H 5.52; Br 49.08.

1-(1,2-Dibromocyclohexyl)hexan-1-one (IIIe) was obtained from 18 g (0.1 mol) of ketone **Ie**. Yield 25.4 g (75%), bp 138–139°C (2 mm Hg), d_4^{20} 1.7174, n_D^{20} 1.5412. ^1H NMR spectrum, δ , ppm: 0.97 t (3H, CH_3), 1.34 q (2H, C^{11}H_2), 1.29 q (2H, C^{10}H_2), 1.56 q (2H,

C^9H_2), 2.46 t (2H, C^8H_2), 4.02 t (1H, H²). Found, %: C 42.88; H 6.12; Br 48.15. $C_{12}H_{20}Br_2O$. Calculated, %: C 42.35; H 5.88; Br 47.06.

1-(1,2-Dibromocyclohexyl)heptan-1-one (III_f) was obtained from 19.4 g (0.1 mol) of ketone **If**. Yield 26.1 g (74%), bp 142–145°C (2 mm Hg), d_4^{20} 1.6883, n_D^{20} 1.5485. Found, %: C 46.38; H 7.17; Br 44.52. $C_{14}H_{24}Br_2O$. Calculated, %: C 45.65; H 6.52; Br 43.43.

1-(1,2-Dibromocyclohexyl)octan-1-one (III_g) was obtained from 20.8 g (0.1 mol) of ketone **Ig**. Yield 26.6 g (73%), bp 146–149°C (2 mm Hg), d_4^{20} 1.6748, n_D^{20} 1.5436. Found, %: C 46.38; H 6.97; Br 43.82. $C_{14}H_{24}Br_2O$. Calculated, %: C 45.65; H 6.52; Br 43.43.

A mixture of isomers **1-[1(2)-hydroxy-2(1)-chlorocyclohexyl]- and [1(2)-bromo-2(1)-hydroxycyclohexyl]alkan-1-ones**. Into a flask at desired temperature was charged 0.15–0.2 mol of 6–8% water solution of HBr or 6–10% solution of HCl and 0.1 mol of ketone **Ia–Ig**. At vigorous stirring of the reaction mixture was added 0.15–0.22 mol of 26–30% water solution of hydrogen peroxide at a rate 10 g per hour or 124.2 g (0.2 mol) of 18.5% solution of sodium hypochlorite (active chlorine content 110 g-ion l⁻¹). The mixture was stirred for 5–7 h. The completion of reaction was monitored by permanganometric or iodometric titration [21]. After total consumption of the oxidant the obtained chloro- and bromohydrins were further used in preparation of the corresponding epoxycyclohexylalkanones by adding into the reaction mixture potassium hydroxide. In order to establish the structure and physicochemical constants of the halohydrins the organic layer was separated from the water layer. The reaction products were extracted from the water layer into ethyl ether (2 × 50 ml). The combined organic solutions were neutralized with 10% solution of Na₂CO₃, dried with magnesium sulfate, and after distilling off the ether we isolated a mixture of halohydrins **IVa–IVg** and **Va–Vg**. According to the data of GLC, TLC, and IR spectroscopy the obtained 1-[chloro(bromo)hydroxy-cyclohexyl]alkan-1-ones are composed of two *cis*-isomers: 85–92% of 1-(2-hydroxy-1-chlorocyclohexyl)- and 6–12% of 1-(1-hydroxy-2-chlorocyclohexyl)alkan-1-ones, or 73–82% of 1-bromo-2-hydroxycyclohexyl)- and 17–23% of 1-(2-bromo-1-hydroxycyclohexyl)alkan-1-ones.

1-[1(2)-Hydroxy-2(1)-chlorocyclohexyl]ethanone (IV_a) was obtained from 6.2 g (0.05 mol) of ketone **Ia**. Yield 7.2 g (82%), bp 112–114°C (11 mm Hg), d_4^{20} 1.2368, n_D^{20} 1.5382. IR spectrum, ν , cm⁻¹: 3625, 1100 (C–OH), 2870 (CH), 1720 (C=O), 830, 745, 660 (C–Cl). ¹H NMR

spectrum, δ , ppm: 1.38–2.05 m (8H, CH₂ of ring), 2.10 s (3H, CH₃), 3.71 t (1H, H²), 4.81 ψ .C (1H, OH). Found, %: C 54.83; H 8.15; Cl 20.41. $C_8H_{13}ClO_2$. Calculated, %: C 54.39; H 7.37; Cl 20.11.

1-[1(2)-Hydroxy-2(1)-chlorocyclohexyl]propan-1-one (IV_b) was obtained from 6.9 g (0.05 mol) of ketone **Ib**. Yield 7.4 g (78%), bp 116–118°C (11 mm Hg), d_4^{20} 1.2335, n_D^{20} 1.5367. IR spectrum, ν , cm⁻¹: 3625, 1100 (C–OH), 2870 (CH), 1720 (C=O), 830, 745 (C–Cl). ¹H NMR spectrum, δ , ppm: 1.07 d (3H, CH₃), 2.48 d (2H, C^8H_2), 3.71 t (1H, H²), 4.81 br.s (1H, OH). Found, %: C 57.26; H 7.36; Cl 19.25. $C_9H_{15}ClO_2$. Calculated, %: C 56.69; H 7.87; Cl 18.64.

1-[1(2)-Hydroxy-2(1)-chlorocyclohexyl]butan-1-one (IV_c) was obtained from 7.2 g (0.05 mol) of ketone **Ic**. Yield 7.8 g (76%), bp 120–122°C (10 mm Hg), d_4^{20} 1.2286, n_D^{20} 1.5346. Found, %: C 57.49; H 8.62; Cl 17.82. $C_{10}H_{17}ClO_2$. Calculated, %: C 58.68; H 8.31; Cl 17.40.

1-[1(2)-Hydroxy-2(1)-chlorocyclohexyl]pentan-1-one (IV_d) was obtained from 8.3 g (0.05 mol) of ketone **Id**. Yield 8.1 g (75%), bp 125–126°C (10 mm Hg), d_4^{20} 1.2258, n_D^{20} 1.5278. Found, %: C 61.35; H 8.92; Cl 16.75. $C_{11}H_{19}ClO_2$. Calculated, %: C 60.41; H 8.69; Cl 16.25.

1-[1(2)-Hydroxy-2(1)-chlorocyclohexyl]hexan-1-one (IV_e) was obtained from 9 g (0.05 mol) of ketone **Ie**. Yield 8.4 g (72%), bp 128–130°C (10 mm Hg), d_4^{20} 1.2232, n_D^{20} 1.5256. Found, %: C 62.23; H 9.28; Cl 15.86. $C_{12}H_{21}ClO_2$. Calculated, %: C 61.95; H 9.03; Cl 15.27.

1-[1(2)-Hydroxy-2(1)-chlorocyclohexyl]heptan-1-one (IV_f) was obtained from 9.7 g (0.05 mol) of ketone **If**. Yield 8.7 g (70%), bp 132–134°C (8 mm Hg), d_4^{20} 1.2215, n_D^{20} 1.5194. Found, %: C 63.78; H 9.76; Cl 14.96. $C_{13}H_{23}ClO_2$. Calculated, %: C 63.29; H 9.33; Cl 14.40.

1-[1(2)-Hydroxy-2(1)-chlorocyclohexyl]octan-1-one (IV_g) was obtained from 10.4 g (0.05 mol) of ketone **Ig**. Yield 8.9 g (69%), bp 136–138°C (5 mm Hg), d_4^{20} 1.2208, n_D^{20} 1.5167. Found, %: C 65.18; H 9.84; Cl 14.18. $C_{14}H_{25}ClO_2$. Calculated, %: C 64.49; H 9.57; Cl 13.63.

1-[1(2)-Hydroxy-2(1)-bromocyclohexyl]ethanone (Va) was obtained from 12.4 g (0.1 mol) of ketone **Ia**. Yield 17.3 g (75%), bp 86–88°C (5 mm Hg), d_4^{20} 1.4295, n_D^{20} 1.5204. IR spectrum, ν , cm⁻¹: 3615, 1410, 1380 (OH), 1720 (C=O), 640, 623 (C–Br). ¹H NMR spectrum, δ , ppm: 2.10 s (3H, CH₃), 3.28 t (1H, H²), 4.82 C (1H, OH). Found, %: C 43.81; H 6.26; Br 36.84. $C_8H_{13}BrO_2$. Calculated, %: C 43.44; H 5.88; Br 36.2.

1-[1(2)-Hydroxy-2(1)-bromocyclohexyl]propan-1-one (Vb) was obtained from 13.8 g (0.1 mol) of ketone

Ib. Yield 17.3 g (74%), bp 90–91°C (5 mm Hg), d_4^{20} 1.4264, n_D^{20} 1.5296. IR spectrum, ν , cm^{-1} : 3615, 1410, 1380 (OH), 1720 (C=O), 648, 620 (C–Br). ^1H NMR spectrum, δ , ppm: 1.08 t (3H, CH_3), 2.51 q (2H, C^8H_2), 3.81 t (1H, H^2), 4.81 br.s (1H, OH). Found, %: C 46.43; H 6.91; Br 34.72. $\text{C}_9\text{H}_{15}\text{BrO}_2$. Calculated, %: C 45.96; H 6.38; Br 34.0.

1-[1(2)-Bromo-2(1)-hydroxycyclohexyl]-butan-1-one (Vc) was obtained from 15.2 g (0.1 mol) of ketone **Ic**. Yield 17.6 g (71%), bp 95–96°C (5 mm Hg), d_4^{20} 1.4186, n_D^{20} 1.5237. Found, %: C 48.73; H 7.26; Br 33.16. $\text{C}_{10}\text{H}_{17}\text{BrO}_2$. Calculated, %: C 48.19; H 6.83; Br 32.13.

1-[1(2)-Bromo-2(1)-hydroxycyclohexyl]pentan-1-one (Vd) was obtained from 8.3 g (0.05 mol) of ketone **Id**. Yield 9.2 g (70%), bp 101–107°C (5 mm Hg), d_4^{20} 1.3962, n_D^{20} 1.5218. Found, %: C 50.61; H 7.56; Br 30.71. $\text{C}_{11}\text{H}_{19}\text{BrO}_2$. Calculated, %: C 50.19; H 7.22; Br 30.42.

1-[1(2)-Bromo-2(1)-hydroxycyclohexyl]hexan-1-one (Ve) was obtained from 9 g (0.05 mol) of ketone **Ie**. Yield 9.6 g (69%), bp 105–108°C (5 mm Hg), d_4^{20} 1.3884, n_D^{20} 1.5206. Found, %: C 52.63; H 7.82; Br 29.25. $\text{C}_{12}\text{H}_{21}\text{BrO}_2$. Calculated, %: C 51.98; H 7.58; Br 28.88.

1-[1(2)-Bromo-2(1)-hydroxycyclohexyl]heptan-1-one (Vf) was obtained from 9.7 g (0.05 mol) of ketone **If**. Yield 10 g (68%), bp 110–112°C (5 mm Hg). Found, %: C 54.13; H 8.15; Br 28.26. $\text{C}_{13}\text{H}_{23}\text{BrO}_2$. Calculated, %: C 53.61; H 7.9; Br 27.49.

1-[1(2)-Bromo-2(1)-hydroxycyclohexyl]octan-1-one (Vg) was obtained from 10.4 g (0.05 mol) of ketone **Ig**. Yield 10.1 g (67%), bp 115–116°C (3 mm Hg). Found, %: C 56.13; H 8.74; Br 26.98. $\text{C}_{14}\text{H}_{25}\text{BrO}_2$. Calculated, %: C 55.08; H 8.2; Br 26.23.

1,2-Epoxyhexylalkanes VIa–VIg. To 0.05 mol of a solution of compounds **IVa–IVg** and **Va–Vg** in 60 ml of ether cooled to 5–10°C was added at vigorous stirring 8.4 g (0.15 mol) of powdered potassium hydroxide. The reaction mixture was stirred for 3 h at 18–25°C. After the common workup and removal of solvents products **Va–Vg** were isolated by a vacuum distillation. At the use of 28–30 g of 22% cooled solution of sodium hydroxide and after stirring the reaction mixture for 4–5 h we also obtained the corresponding epoxides.

1-(7-Oxabicyclo[4.1.0]hept-1-yl)ethanone (VIa) was obtained from 8.8 g (0.05 mol) of compound **IVa** or 11 g (0.05 mol) of compound **Va**. Yield 5.8 g (83%) from **IVa**, 12.5 g (90%) from **Va**, bp 83–84°C (10 mm Hg), d_4^{20} 1.1083, n_D^{20} 1.4812. IR spectrum, ν , cm^{-1} : 1730, 1722, 1704 (C=O), 1260, 1250, 920, 863 (epoxyd). ^1H NMR

spectrum, δ , ppm: 2.10 s (3H, CH_3), 3.10 t (1H, H^2). Found, %: C 68.85; H 8.82. $\text{C}_8\text{H}_{12}\text{O}_2$. Calculated, %: C 68.57; H 8.57.

1-(7-Oxabicyclo[4.1.0]hept-1-yl)propan-1-one (VIb) was obtained from 9.5 g (0.05 mol) of enone **IVb** or 13.3 g (0.05 mol) of compound **Vb**. Yield 6.1 g (80%) from **IVb**, 13.3 g (86%) from **Vb**, bp 90–91°C (10 mm Hg), d_4^{20} 1.0946, n_D^{20} 1.4682. IR spectrum, ν , cm^{-1} : 1730, 1722, 1704 (C=O), 1260, 1250, 920, 863 (epoxyd). ^1H NMR spectrum, δ , ppm: 1.07 t (3H, CH_3), 2.48 q (2H, CH_2CO), 3.10 t (1H, H^2). Found, %: C 70.84; H 9.32. $\text{C}_9\text{H}_{14}\text{O}_2$. Calculated, %: C 70.13; H 9.09.

1-(7-Oxabicyclo[4.1.0]hept-1-yl)butan-1-one (VIc) was obtained from 10.5 g (0.05 mol) of enone **IVc** or 12.5 g (0.05 mol) of enone **Vc**. Yield 6.4 g (80%) from **IVc**, 14.3 g (85%) from **Vc**, bp 97–98°C (10 mm Hg), d_4^{20} 1.0946, n_D^{20} 1.4686. IR spectrum, ν , cm^{-1} : 1730, 1722, 1704 (C=O), 1260, 1250, 920, 863 (epoxyd). ^1H NMR spectrum, δ , ppm: 3.10 t (1H, H^2), 2.46 t (2H, C^8H_2), 1.62 q (2H, C^9H_2), 0.97 q (3H, CH_3). Found, %: C 71.86; H 9.86. $\text{C}_{10}\text{H}_{16}\text{O}_2$. Calculated, %: C 71.43; H 9.52.

1-(7-Oxabicyclo[4.1.0]hept-1-yl)pentan-1-one (VIId) was obtained from 10.9 g (0.05 mol) of enone **IVd** or 13.2 g (0.05 mol) of enone **Vd**. Yield 6.7 g (73%) from **IVd**, 15 g (83%) from **Vd**, bp 105–106°C (10 mm Hg), d_4^{20} 0.9865, n_D^{20} 1.4663. IR spectrum, ν , cm^{-1} : 1730, 1722, 1704 (C=O), 1260, 1250, 920 (epoxyd). ^1H NMR spectrum, δ , ppm: 3.09 t (H^2), 2.48 t (2H, C^8H_2), 1.62 q (2H, C^9H_2), 1.57 t (2H, C^{10}H_2), 1.34 q (2H, C^{11}H_2), 0.97 t (3H, CH_3). Found, %: C 72.85; H 9.23. $\text{C}_{11}\text{H}_{18}\text{O}_2$. Calculated, %: C 72.53; H 8.89. Identical spectral characteristics were obtained for compounds **VIe–VIg**

1-(7-Oxabicyclo[4.1.0]hept-1-yl)hexan-1-one (VIe) was obtained from 11.6 g (0.05 mol) of enone **IVe** or 13.8 g (0.05 mol) of enone **Ve**. Yield 6.7 g (74%) from **IVe**, 15.8 g (81%) from **Ve**, bp 112–113°C (10 mm Hg), d_4^{20} 0.9736, n_D^{20} 1.4642. Found, %: C 73.85; H 10.6. $\text{C}_{12}\text{H}_{20}\text{O}_2$. Calculated, %: C 73.47; H 10.2.

1-(7-Oxabicyclo[4.1.0]hept-1-yl)heptan-1-one (VIIf) was obtained from 12.3 g (0.05 mol) of enone **IVf** or 14.6 g (0.05 mol) of enone **Vf**. Yield 7.2 g (68%) from **IVf**, 16.7 g (80%) from **Vf**, bp 120–121°C (10 mm Hg), d_4^{20} 0.9684, n_D^{20} 1.4625. Found, %: C 74.72; H 10.87. $\text{C}_{13}\text{H}_{22}\text{O}_2$. Calculated, %: C 74.29; H 10.48.

1-(7-Oxabicyclo[4.1.0]hept-1-yl)octan-1-one (VIg) was obtained from 13 g (0.05 mol) of enone **IVg** or 15.2 g (0.05 mol) of enone **Vg**. Yield 7.1 g (77%) from **IVg**, 17.5 g (78%) from **Vg**, bp 128–129°C (10 mm Hg),

d_4^{20} 0.9616, n_D^{20} 1.4584. Found, %: C 75.62; H 11.42. $C_{14}H_{24}O_2$. Calculated, %: C 75.0; H 10.71.

Diols VIIa and VIIb. To 7 g (0.05 mol) of compound **VIa** or **VIb** was added 9 g (0.05 mol) of water and 3.5 g of KU-2×8. The mixture obtained was stirred for 4 h at 50–60°C, further by extraction with ethyl acetate from a saturated solution of K_2CO_3 , by recrystallization from a mixture hexane–EtOAc, 7:3, or from CCl_4 along procedure [22] the corresponding diols were isolated.

1-(1,2-Dihydroxycyclohexyl)ethanone (VIIa). Yield 6.7 g (84%), mp 105–108°C, R_f 0.68 (hexane–EtOAc, 7:3). IR spectrum, ν , cm^{-1} : 3625, 3615, 1100, 974, 918 (OH), 1723 (C=O). 1H NMR spectrum, δ , ppm: 3.48 t (1H, H²), 2.1 br.s (C'OH), 4.81 br.s (C²OH), 2.1 s (3H, CH₃). Found, %: C 61.34; H 9.23. $C_8H_{14}O_3$. Calculated, %: C 60.76; H 8.86.

1-(1,2-Dihydroxycyclohexyl)propan-1-one (VIIb). Yield 6.9 g (80%), mp 110–112°C, R_f 0.68 (hexane–EtOAc, 7:3). IR spectrum, ν , cm^{-1} : 3625, 3615, 1100, 974, 918 (OH), 1723 (C=O). 1H NMR spectrum, δ , ppm: 3.48 t (1H, H²), 2.0 br.s (1H, C'OH), 4.81 br.s (1H, C²OH), 2.49 d (2H, C⁸H₂), 1.07 d (3H, CH₃). Found, %: C 63.25; H 9.64. $C_9H_{16}O_3$. Calculated, %: C 62.79; H 9.30.

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