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Synthesis of Halohydrines of 5-Alkylbicyclo[2.2.1]heptene Series Using the Systems Inducing Electrophilic Reagents

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Abstract—The reactions of induced hydroxyhalogenation of alkylnorbornenes with the use of a mixture of aqueous solutions of hydrochloric or hydrobromic acids (or sodium, potassium and cobalt bromides) and hydrogen peroxide or sodium hypochloriteare are studied. The reaction are established to proceed through the addition at the double bond of the ring of the electrophilic reagent HOBr or HOCl formed *in situ* yielding of *cis*-vicinal halohydrines. By dehydrohalogenation of the latter in the presence of alkali are obtained *endo*-6-alkyl-*endo*-3-oxatricyclo[3.2.1^{1,5}.0 ^{2,4}]octanes and by their oxidation are synthesized respective haloketones in a high yield.

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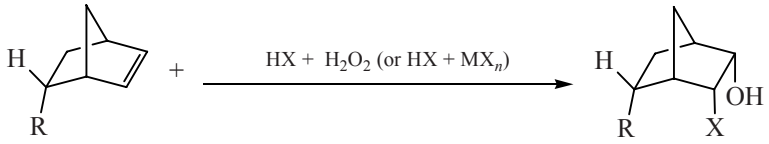
In recent years increased interest to the bicyclic unsaturated hydrocarbons and their derivatives caused by high reactivity of the strained multiple bond of the ring, stereoselectivity of the occurring reactions, stability and biological activity of the compounds synthesized on their basis. The direct halogenation of norbornene with molecular chlorine, bromine, iodine or mixed halides has been considered in detail [1–4]. The synthesized halo-substituted norbornenes were proposed as initial compounds for obtaining α-diketones [5] or cyclic halo-substituted ketones, easily converted further into the phenol trihalo-derivatives [6, 7]. It is established that at the bromination of norbornene and its alkyl derivatives depending on the reaction conditions are formed either bromides or bromohydrines, with the rearrangement of the initial hydrocarbon [6, 7]. However, the reaction of the induced halogenation or hydroxyhalogenation of the norbornene alkyl derivatives which proceeds without a change in the structure of initial hydrocarbon has not been described so far. Meanwhile the realization of the reaction of 1,2-addition to these hydrocarbons of the elements of hypohalogenous acids induced in a special system makes it possible to obtain vicinal hydroxyhalides appropriate for the synthesis of *endo*-oxiranes or halo-substituted ketones of bicyclic series [9–11]. The halogenation of norbornene derivatives by chloro(bromo)succinimide in a water–ether medium and the subsequent epimerization of the obtained products with sodium methylate is known to lead to the formation of *exo*-chloro(bromo)hydrines. The by-products of the reaction are nortricyclene derivatives [9].

The purpose of this work is to study the addition reaction of the elements of hypohalogenous acids to 5-R-bicyclo[2.2.1]hept-2-enes under the conditions that induce formation of electrophilic reagent HOCl, HOBr and transformation of the obtained compounds into appropriate haloketones. As the inducing system we used a mixture HX–H_2O_2 or (HX–MX_n)–H_2O_2, M = Na, K, Co (Scheme 1).

It is established that 5-alkylbicyclo[2.2.1]hept-2-enes at 20–40ºC smoothly react with HOCl and HOBr at the moment of their formation (*in situ*). In the IR spectra of the compounds **Ia**–**Ie** and **IIa**–**IIe** the absorption bands in the region of 745, 780 cm^{-1} (C–Cl bond); 623, 640 cm^{-1} (C–Br bond), and 1100–1170, 3615 cm^{-1} (OH group) are common, and the bands at 1378, 1420, 1443 cm^{-1} correspond to the deformation vibrations of CH_2 and CH_3 groups of the ring and alkyl radical [12].

In the ^{1}H NMR spectra of compounds **Ia–Ie** there are doublets at δ 1.53–1.75 ppm with J = 5 Hz corresponding to two bridgehead protons at C^1 and C^4. The signal of one of them is split into a doublet with J = 5 Hz and overlaps the signal of the other. The

Scheme 1.



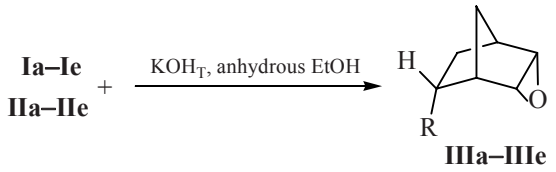
Ia–Ie, IIa–IIe

M = Na, K, Co; n = 1, 2. X = Cl (**I**); Br (**II**); R = CH_3 (**a**); C_2H_5 (**b**); C_3H_7 (**c**); C_4H_9 (**d**); C_5H_{11} (**e**).

protons at C^1 and C^4 of compounds **IIa – IIe** also give doublet signals, in the region of δ 1.53–1.85 ppm. The doublet signals at δ 3.46–3.48 ppm and δ 3.36–3.58 ppm can be assigned to the protons at C^2 and C^3 of compounds **Ia**–**Ie** and **IIa**–**IIe**, respectively. The proton at the C^5 carbon atom of compounds **Ia** and **IIa** gives rise to the triplet at δ 1.61 ppm, and of compounds **Ic**–**Ie** and **IIc**–**IIe,** at δ 1.42 ppm. The signals of protons of OH group of compounds **I** and **II** are observed in the region of δ 4.81 ppm as broad singlets [13, 14].

It is established that in the case of dehydrohalogenation of halohydrines **I** and **II** with alkali solution in alcohol the main reaction products are *endo*-6-alkyl-*endo*-3-oxatricyclo[3.2.$1^{1.5}$.$0^{2,4}$]octanes, with *cis*-vicinal arrangement of OH groups and atoms Cl (Br) in the halohydrides:

Scheme 2.



IIIa–IIIe

R = CH_3 (**a**); C_2H_5 (**b**);C_3H_7 (**c**); C_4H_9 (**d**); C_5H_{11} (**e**).

The structure of the obtained epoxies **IIIa**–**IIIe** is confirmed by the data of IR and ^{1}H NMR spectroscopy and by independent oxidation of alkylnorbornenes with 30% dioxane solution of H_2O_2 and CH_3COOH in the presence of the chlorine-bearing acidic cation-excahnger KU-2×8 [15].

In the IR spectra of *endo*-6-alkyl-*endo*-3-oxatricyclo[3. 2.$1^{1.5}$.$0^{2,4}$]octanes **III** the bands at 853 cm^{-1} related to C–O bond and the bands of stretching vibrations of C–H bonds at 3028–3010 cm^{-1} in the epoxy fragments are common. In the ^{1}H NMR spectra appear a triplet at δ 1.77 ppm of the protons at C^1 and C^5, a doublet at δ 2.87 ppm (C^2 and C^4), multiplets at δ 1.25–1.56 ppm related to CH_2 groups of norbornane and alkyl fragments. The doublets at δ 1.07 ppm in the spectrum of epoxyde **IIIa** belongs to the CH_3 protons of alkyl fragment. With an increase in the length of alkyl fragment these signals are shifted upfield and appear as a triplet at δ 0.97 ppm. [13,14].

For the optimization of conditions of synthesis of chloro(bromo)hydroxyhalides we studied the influence of different parameters on the yield of the reaction products. It was found that the yield of the final product depended mainly on the temperature and concentration of the hydrohalic acid (Tables 1 and 2). As can be seen from the data in Table 1, at increase in

Table 1. Influence of temperature on the yield of halohydrines. Ratio 5-R-bicyclo [2.2.1] hept-2-ene : HX : H_2O_2 = 0.1 : 0.14 : 0.14, acid solutions concentration 10% (HCl) and 6% (HBr), reaction duration 6.5 h, H_2O_2 feeding rate 10 g h^{-1}

Temperature, °C	Yield of halohydrines, %									
	I					**II**				
	a	**b**	**c**	**d**	**e**	**a**	**b**	**c**	**d**	**e**
20	72.5	71.8	70.6	70.3	71.5	72.6	73.6	69.4	71.6	70.3
30	80.6	79.7	78.5	78.2	77.6	79.5	79.2	78.8	78.3	77.8
40	86.4	86.8	85.4	84.3	84.6	85.5	85.6	86.3	84.7	83.8
50	92.5	90.6	89.5	88.7	88.2	88.4	87.2	88.7	86.5	85.6

Table 2. Dependence of halohydrine yield on the concentration of hydrochloric (hydrobromic) acid. Ratio 5-R-bicyclo[2.2.1] jept-2-ene : HX : H_2O_2 = 0.2 : 0.22 : 0.24, temperature 30°C, H_2O_2 feeding rate 10 g h^{-1}, reaction duration 7.0 h

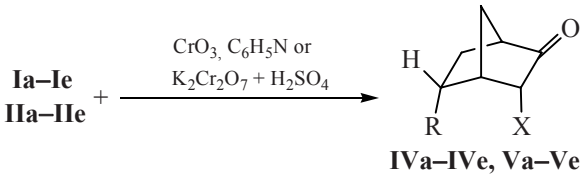
HCl concentration, %	Yield of hydroxychloride **I**					Yield of hydroxybromide **II**					HBr concentration, %
	a	**b**	**c**	**d**	**e**	**a**	**b**	**c**	**d**	**e**	
6.0	74.3	72.5	70.6	71.0	69.5	68.6	70.3	67.6	68.5	69.2	6.0
10	80.6	79.7	78.5	78.2	77.6	79.5	79.2	78.8	78.3	77.8	10
15	72.6	70.4	69.4	67.5	64.8	69.2	68.5	67.2	66.4	65.3	20
25	63.4	65.6	53.2	50.6	51.5	53.4	50.6	48.5	46.8	47.6	30
35	40.6	39.6	39.5	38.7	40.7	39.5	40.4	41.6	39.0	39.2	45

temperature from 20 to 50°C the chloro- and bromohydrines yield increases approximately by 10–15%. The highest yields of chlorohydrines (81%) and bromhydrines (79%) are reached at the temperature 30–40°C at the use of 6–10% aqueous solution of hydrohalic acids (Table 2). An increase in the acid concentration in the range of 15–35% (HCl) or 20–46% (HBr) leads to decrease in the yield of chloro (bromo)hydrines to 40%, which evidently is connected with the intensification of the formation of molecular halogen (Cl_2 or Br_2). The electrophilic addition of the formed halides to the multiple bond of norbornene fragment leads to the formation of certain amount of dichloro- or dibromo-derivatives (38–40%), whose structure we did not establish. It should be noted that addition to the solutions of HCl or HBr up to 3–7 wt % of MX_n, M=Na, K, Co, also contributes to an increase in the yield of chloro(bromo)hydroxyhalides.

In the literature there is practically no information on the synthesis of chlorine(bromine)-containing ketones of bicyclo[2.2.1]heptane series. An exception is [9], where the reaction is examined of oxidation of bromohydrin obtained by the epimerization of *endo*-nitrile group in the molecule of *anti*-7-bromo-*exo*-2-cyanobicyclo[2.2.1]heptane-5-one at the action of sodium methoxide. At the oxidation of halohydrines with the Brown mixture (or a mixture of CrO_3 with H_2SO_4) with a high selectivity are formed the corresponding haloketones according to Scheme 3.

Thus, the use of the induction of electrophilic reagents (HOCl or HOBr) in the highly acidic medium makes it possible to synthesize *cis*-vicinal halohydrines. Dehydrhalogenation and oxidation of the latter leads to the formation of *endo*-6-alkyl-*endo*-3-oxatricyclo[3. $2.1^{1.5}.0^{2,4}$]octanes and 3-chloro(bromo)-5-alkylbicyclo[2.2.1] heptan-2-ones with a high selectivity.

Scheme 3.



IVa–IVe, Va–Ve

X = Cl (**IV**); Br (**V**); R = CH_3 (**a**); C_2H_5 (**b**); C_3H_7 (**c**); C_4H_9 (**d**); C_5H_{11} (**e**).

EXPERIMENTAL

The IR spectra of the synthesized compounds were taken on a UR-20 spectrometer in the range 400–3600 cm^{-1} from thin films. The ^1H NMR spectra were registered on a Bruker spectrometer with operating frequency 300 MHz from the solutions in deuterochloroform, internal reference HMDS. The TLC data were otained with the use of Silufol UV-254 plates, the eluent ether, developing in iodine vapors.

The composition of the reaction products was monitored by GLC on a chromatograph LKhM-8 MD-5 with the detector on thermal conductivity, the column 200×0.4 cm filled with 0.5 wt % of silicone elastomer SE-30 on the carrier Chromoton-N-Super, the carrier gas nitrogen (υ = 60 cm^3 min^{-1}), the column temperature 140°C.

Initial cycloolefins were obtained by the known procedure [16]. Their physicochemical constants coincided with literature data [16, 17]. The experiments were carried out in a glass reactor under temperature control within ±0.2°C. To the reactor at a given temperature was loaded 0.12–0.22 mol of 6% aqueous solution of HBr or 6–10% solution of HCl (or their mixture with MX_n, M = Na, K, Co; X = Cl, Br, n = 1; 2; 3–8 wt %) and 1 mol of norbornene alkyl

derivative. To the reaction mixture at stirring through a dropping funnel was introduced 0.24 mol of 26–30% aqueous solution of hydrogen peroxide (feed rate 10 g h^{-1}). Stirring was continued for 6–7 h. The reaction was completed after total consumption of H_2O_2, HOCl or HOBr (tested by permanganometric and iodometric methods). Organic layer was separated from the aqueous layer. Aqueous layer was extracted with ether (2×50 ml). The ether extracts were joined with the organic layer, neutralized with 10% solution of Na_2CO_3 and dried over magnesium sulfate. Halohydrines **Ia**–**Ie**, **IIa**–**IIe** were separated by distillation. The purity of the synthesized compounds was estimated by GLC analysis.

3-Chloro-5-methylbicyclo[2.2.1]heptan-2-ol (Ia) was obtained from 10.8 g of 5-methylbicyclo[2.2.1] hept-2-ene. Yield 13.8 g (86.4%), bp 94–95°C (3 mm Hg) n_D^{20} 1.0983, d_4^{20} 1.4763. IR spectrum, ν, cm^{-1}: 745, 780, (CCl), 3320, 3615 (COH) [12]. ^1H NMR spectrum, δ, ppm: 1.53 d (1H, C^1), 3.48 t (2H, C^2, C^3), 1.73 d (1H, C^4), 1.61 t (1H, C^5), 1.23–1.48 d.d (2H, C^6), 1.29–1.54 d.d (2H, C^7), 1.07 d (3H, C^8, alkyl) and 4.81 br.s (1H, OH). Found, %: C 60.08; H 8.35; Cl 22.32. $C_8H_{23}ClO$. Calculated, %: C 59.81; H 8.16; Br 22.07 [13,14].

3-Chloro-5-ethylbicyclo[2.2.1]heptan-2-ol (Ib) was obtained from 12.2 g (0.1 mol) of 5-ethylbicyclo[2.2.1]-hept-2-ene. Yield 6.4 g (85.2%), bp 101–103°C (3 mm Hg) n_D^{20}1.0988, d_4^{20} 1.4783. IR spectrum, ν, cm^{-1}: 745, 780, (CCl), 3320, 3615 (COH) [12]. ^1H NMR spectrum, δ, ppm: 1.53 d (1H, C^1), 3.48 t (2H, C^2, C^3), 1.73 d (1H, C^4), 1.41 so-called (C^5), 1.23–1.48 d.d (2H, C^6), 1.29–1.54 d.d (2H, C^7), 4.81 br.s. (1H, OH), 1.28 (2H, C^8), 0.95 t (3H, C^9, alkyl). Found, %: C 62.12; H 8.92; Cl 21.08. $C_9H_{815}ClO$. Calculated, %: C 61.89; H 8.66; Cl 20.30 [13,14]. Identical spectral characteristics are obtained for the products **Ic** and **Id**.

3-Chloro-5-propylbicyclo[2.2.1]heptan-2-ol (Ic) was obtained from 15 g (0.1 mole) of 5-propylbicyclo [2.2.1]hept-2-ene. Yield 15.4 g (81.4%), bp 113–114° C (3 mm Hg), n_D^{20} 1.0998, d_4^{20} 1.4875. Found, %: C 64.06; H 9.26; Cl 19.08. $C_{10}H_{17}ClO$. Calculated, %: C 63.65; H 9.08; Cl 18.797.

3-Chloro-5-butylbicyclo[2.2.1]heptane-2-ol (Id) was obtained from 15 g (0.1 mole) of 5-butylbicyclo [2.2.1]hept-2-ene. Yield 15.2 g (70.2%), bp 134–136° C (2 mm Hg), n_D^{20} 1.1086, d_4^{20} 1.4876. Found, %: C 65.34; H 9.83; Cl 17.86. $C_{11}H_{21}ClO$. Calculated, %: C 65.17; H 9.45; Cl 17.49.

Analogously were synthesized bromohydrines **IIa**–**IIe**.

3-Bromo-5-methylbicyclo[2.2.1]heptan-2-ol (IIa) was obtained from 10.8 g of 5-methylbicyclo[2.2.1] hept-2-ene. Yield 17.1 g (83.5%), mp 47–49°C. IR spec-trum, ν, cm^{-1}: 623, 640, 930 (CBr), 1380, 1410, 3320, (COH) [12]. ^1H NMR spectrum, δ, ppm: 1.51 d (1H, C^1), 3.44–3.56 d.d (2H, C^2, C^3), 1.83 d (1H, C^4), 1.61 d (1H, C^5), 1.23–1.48 d. (2H, C^6), 1.29–1.54 d. (2H, C^7), 1.07 d (3H, C^8, alkyl) and 4.81 br.s (1H, OH) [13, 14]. Found, %: C 47.08; H 6.58; Br 22.32. $C_8H_{13}BrO$. Calculated, %: C 46.85; H 6.39; Br 38.96 [13,14]

3-Bromo-5-ethylbicyclo[2.2.1]heptan-2-ol (IIb) was obtained from 12.2 g (0.1 mol) of 5-ethylbicyclo[2.2.1] hept-2-ene. Yield 17.6 g (80.6%), mp 57–59.5°C. IR spectrum, ν, cm^{-1}: 623, 780, (CBr), 3320, 3615 (COH) [12]. ^1H NMR spectrum, δ, ppm: 1.53 d (1H, C^1), 3.48 t (2H, C^2, C^3), 1.73 d (1H, C^4), 1.41 so-called C^5), 1.23–1.48 d.d (2H, C^6), 1.29–1.54 d.d (2H, C^7), 4.81 br.s. (1H, OH), 1.28 (2H, C^8), 0.95 t (3H, C^9, alkyl). Found, %: C 62.12; H 8.92; Br21.08. $C_9H_{15}BrO$. Calculated, %: C 61.89; H 8.66; Br 20.30 [13,14]. Identical spectral data were found for the compounds **IIc** and **IIe**.

3-Bromo-5-propylbicyclo[2.2.1]heptan-2-ol (IIc) is obtained from 13.6 g (0.1 mol) of 5-propylbicyclo [2.2.1]hept-2-ene. Yield 17.8 g (76.3%) mp 68–70°C. Found, %: C 51.86; H 7.67; Br 34.46. $C_{10}H_{17}BrO$. Calculated, %: C 51.52; H 7.35; Br 34.27.

3-Bromo-5-pentylbicyclo[2.2.1]heptane-2-ol (IIe) was obtained from 16.4 g (0.1 mol) of 5-pentylbicyclo-[2.2.1]hept-2-ene. Yield 17.8 g (68.2%), mp 91–94°C. Found, %: C 55.62; H 8.44; Br 30.85. $C_{12}H_{21}BrO$. Calculated, %: C 55.18; H 8.10; Br 30.59. At working up the synthesized halohydrines with alcohol solution of KOH are obtained respective *endo*-epoxies (yield 83.6–94.7%).

***endo*-6-Methyl-*endo*-3-oxatricyclo[3.2.1$^{1.5}$.0$^{2.4}$]octane (IIIa)** was obtained from 16 g of **Ia**. Yield 11.5 g (92.6%), bp 143°C, n_D^{20} 1.4657, d_4^{20} 0.9724. IR spectrum, ν, cm^{-1}: 865, 873, 880 [12]. ^1H NMR spectrum, δ, ppm: 1.75 t (2H, C^1, C^5), 2.87 d (2H, C^2, C^4), 1.59 d (1H, C^6), 1.41 so-called C^5), 1.23–1.48 d. (2H, C^7), 1.29–1.54 d. (2H, C^8), 1.07 t (3H, C^9). [13,14]. Found, %: C 77.85; H of 10.03 Br21. $C_8H_{12}O$. Calculated, %: C 77. 38; H 9.74.

***endo*-6-Ethyl-*endo*-3-oxatricyclo[3.2.1$^{1.5}$.0$^{2.4}$]octane (IIIb)** was obtained from 11 g (0.05 mol) of **IIb**. Yield

6.2 g (90.5%), bp 166°C, n_D^{20} 1.4682, d_4^{20} 0.9701. IR spectrum, ν, cm^{-1}: 865, 873, 880 [12]. ^1H NMR spectrum, δ, ppm: 1.75 t (2H, C^1, C^5), 2.87 d (2H, C^2, C^4), 1.59 d (1H, C^6), 1.23–1.48 d (2H, C^7), 1.29–1.54 d, (2H, C^8), 1.24 d (3H, C^9), 0.97 t (3H, C^{10}) [13,14]. Found, %: C 78.67; H 10.76. $C_9H_{14}O$. Calculated, %: C 78. 21; H 10.21.

Analogous spectral data were found for other epoxies **IIIc**–**IIIe**.

***endo*-6-Propyl-*endo*-3-oxatricyclo[3.2.1$^{1.5}$.0$^{2.4}$]octane (IIIc)** was obtained from 9.4 g (0.05 mol) of **Ic**. Yield 6.7 g (88.6%), bp 71–73°C (14 mm Hg), n_D^{20} 1.4751, d_4^{20} 0.9692. Found, %: C 79.08; H 10.83. $C_{10}H_{16}O$. Calculated, %: C 78. 90; H 10.59.

***endo*-6-Butyl-*endo*-3-oxatricyclo[3.2.1$^{1.5}$.0$^{2.4}$]octane (IIId)** was obtained from 12.7 g (0.05 mol) of **IId**. Yield 7.6 g (85.8%), bp 64–66°C (14 mm Hg), n_D^{20} 1.4826, d_4^{20} 0.9823. Found, %: C 79.84; H 11.07. $C_{12}H_{18}O$. Calculated, %: C 79. 46; H 10.91.

***endo*-6-Pentyl-*endo*-3-oxatricyclo[3.2.1$^{1.5}$.0$^{2.4}$]octane (IIIe)** was obtained from 10.8 g (0.05 mol) of **Ie**. Yield 7.5 g (83.7%), bp 83–75°C (3 mm Hg), n_D^{20} 1.4952, d_4^{20} 0.9823. Found, %: C 80.06; H 11.26. $C_{10}H_{20}O$. Calculated, %: C 79. 94; H 11.18.

3-Chloro(bromo)-5-alkylbicyclo[2.2.1]heptan-2-ones (I, II) (*general procedure*). To 0.025 mol of 3-chloro-5-alkylbicyclo[2.2.1]heptan-2-ol in 40 ml of ether was added dropwise 16 ml of Brown reagent obtained by dissolving 20 g of potassium bichromate in 20 ml of concentrated sulfuric acid with the subsequent dilution by water to a volume of 55 ml. The reaction proceeds at room temperature (18–20°C) at stirring, for 20–30 min (according to the data of GLC). The ether layer was separated, aqueous layer was extracted with ether (2×50 ml), joined extracts were dried, the solvent was removed, and the ketone was separated.

3-Chloro-5-methylbicyclo[2.2.1]heptan-2-one (IVa) was obtained from 4 g of **Ia**. Yield 3.3 g (82%), bp 69–71°C (3 mm Hg), d_4^{20} 0.9962, n_D^{20} 1.4472. IR spectrum, ν, cm^{-1}: 1723, 1745 (C=O), 710, 745 (CCl4) [12,14]. The ^1H NMR spectrum, δ, ppm: 2.06 d (1H, C^1), 4.04 d (1H, C^3), 2.32 d (1H, C^4), 1.68 d (1H, C^5), 1.60–1.85 d.d (2H, C^6), 1.81–2.06 d.d (2H, C^7), 1.07 d (3H, CH_3, alkyl) [13,14]. Found, %: C 60.75; H 7.12; Cl 22.74. $C_8H_{11}ClO$. Calculated, %: C 60.57; H 6.99; Cl 22.35. Analogously were obtained compounds **IVb**–**IVe**, the chloroketones, with the same spectral characteristics.

3-Chloro-5-ethylbicyclo[2.2.1]heptane-2-one (IVb) was obtained from 4.4 g (0.025 mol) of **Ib**. Yield 3.4 g (79.3%), bp 94–95°C (3 mm Hg), d_4^{20} 0.9932, n_D^{20} 1.4512. Found, %: C 62.07; H 8.93; Cl 20.76. $C_9H_{13}ClO$. Calculated, %: C 61.89; H 8.66; Cl 20.30.

3-Chloro-5-propylbicyclo[2.2.1]heptane-2-one (IVc) was obtained from 4.7 g (0.025 mol) of **Ic**. Yield 3.6 g (78.4%), mp 53–55°C. Found, %: C 64.67; H 8.43; Cl 19.12. $C_{10}H_{15}ClO$. Calculated, %: C 64.34; H 8.10; Cl 18.99.

3-Chloro-5-butylbicyclo[2.2.1]heptane-2-one (IVd) was obtained from 5.1 g (0.025 mol) of **Id**. Yield 3.7 g (75.6%), mp 63–65°C. Found, %: C 66.03; H 8.82; Cl 18.10. $C_{11}H_{17}ClO$. Calculated, %: C 65.83; H 8.54; Cl 17.66.

3-Chloro-5-pentylbicyclo[2.2.1]heptan-2-onet (IVe) was obtained from 5.4 g (0.025 mole) of **Ie**. Yield 3.8 g (70.8%), mp 74–76°C. Found, %: C 67.53; H 9.06; Cl 17.03. $C_{12}H_{19}ClO$. Calculated, %: C 67.12; H 8.92; Cl 16.51.

Bromoketones (Va–Ve) were obtained similarly to the chloroketones. To 0.025 mole of 3-bromo-5-alkylbicyclo[2.2.1]heptan-2-ol in 30 ml of pyridine was added 9.8 g of chromium trioxide. The reaction mixture was stirred at 30–45°C till completion (according to the data of TLC), then pyridine was removed in a vacuum. The residue was worked up with water and the product was extracted with chloroform. The organic layer was washed with diluted sulfuric acid and water, then dried, the solvent was removed and the ketone was isolated.

3-Bromo-5-methylbicyclo[2.2.1]heptan-2-one (Va) was obtained from 5.1 g (0.025 mol) of **IIa**. Yield 8.2 g (80.7%), mp 58–60°C. IR spectrum, ν, cm^{-1}: 1723, 1745 (C=O), 680, 750 (CBr) [12,14]. The ^1H NMR spectrum, δ, ppm: 2.06 d (1H, C^1), 3.97 d (1H, C^3), 2.42 d (1H, C^4), 1.68 t (1H, C^5), 1.60–1.85 d.d (2H, C^6), 1.81–2.06 d.d (2H, C^7), 1.07 d (3H, CH_3, alkyl) [13,14]. Found, %: C 47.66; H 5.83; Br 39.87. $C_8H_{11}BrO$. Calculated, %: C 47.32; H 5.46; Br 39.35.

Identical spectral data were obtained for the bromoketones **Vb**–**Ve**.

3-Bromo-5-ethylbicyclo[2.2.1]heptan-2-one (Vb) was obtained from 5.5 g (0.025 mol) of **IIb**. Yield 4.3 g (79.3%), mp 69–71°C. Found, %: C 50.08; H 6.35; Br 37.12. $C_9H_{13}BrO$. Calculated, %: C 49.79; H 6.04; Br 36.80.

3-Bromo-5-propylbicyclo[2.2.1]heptan-2-one (Vc) was obtained from 5.8 g (0.025 mol) of **IIc**. Yield 4.5 g (77.5%), mp 81–83°C. Found, %: C 52.10; H 6.78; Br 35.08. $C_{10}H_{15}BrO$. Calculated, %: C 51.97; H 6.54; Br 34.57.

3-Bromo-5-butylbicyclo[2.2.1]heptan-2-one (Vd) was obtained from 6.2 g (0.025 mol) of **IId**. Yield 4.6 g (75.6%), mp 92–94°C. Found, %: C 54.06; H 7.11; Br 33.11. $C_{11}H_{17}BrO$. Calculated, %: C 53.89; H 6.99; Br 32.59.

3-Bromo-5-pentylbicyclo[2.2.1]heptan-2-one (Ve) was obtained from 6.5 g (0.025 mol) of **IIe**. Yield 4.4 g (68.3%), mp 102–104°C. Found, %: C 55.93; H 7.76; Br 31.12. $C_{12}H_{19}BrO$. Calculated, %: C 55.61; H 7.39; Br 30.83.

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