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Synthesis of 3-Oxatricyclo[4.4.0.02,7]decene Derivatives

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Abstract—Unsaturated haloethers of norpinane structure were prepared by reaction of *N*-iodo- and *N*-bromosuccinimides with 1-phenyltricyclo[4.1.0.0^{2,7}]-heptane in the presence of unsaturated propargyl or allyl alcohol. The iodopropargyloxy derivative underwent reductive 6-*exo*-cyclization when treated with tributyltin hydride resulting in 5-methylene-3-oxa-2-phenyltricyclo[4.4.0.0^{2,7}]decane, and the iodoallyloxy derivative on heating in the presence of benzoyl peroxide suffered isomerization into 5-iodomethyl-3-oxa-2-phenyltricyclo[4.4.0.0^{2,7}]decene. Bromopropargyloxy and bromoallyloxy derivatives failed to undergo the reductive cyclization under the treatment with a system cobaloxime(III)–sodium borohydride, but suffered hydrogenetion at the multiple carbon–carbon bond.

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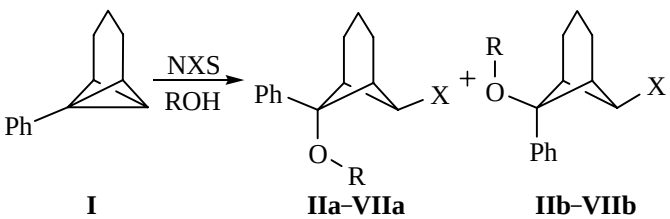
In extension of our research directed at application of tricyclo[4.1.0.0^{2,7}]heptane for building up the bridging system of tricyclo[4.*n*.0.0]alkane [1] we report on the present study of a two-stage synthesis of 3-oxa-2-phenyltricyclo-[4.4.0.0^{2,7}]-decene derivatives based on an available 1-phenyltricyclo[4.1.0.0^{2,7}]heptane (**I**). In the first stage we planned to perform a conjugate halogenation of initial hydrocarbon **I** at the central bicyclobutane C^{1}–C^{7} bond by treating with N-bromo(iodo)succinimide in the presence of unsaturated (propargyl or allyl) alcohol expecting that the addition would occur regio- and stereoselective providing the corresponding adducts **IIa–Va**, since according to the previously obtained results [2] hydrocarbon **I** reacts in the cold with N-bromosuccinimide in methanol giving in high yields diastereomeric adducts **VIa** and **VIb** in a ratio 15:1.

In the second stage it was necessary by any method to carry out a cyclization of the unsaturated haloderivative



I **IIa–VIIa** **IIb–VIIb**

R = $CH_2Ca"CH$ (**II, IV**), $CH_2CH{=}CH_2$ (**III, V**), CH_3 (VI), $CH_2CH_2CH_3$ (**VII**); X = Br (**II, III, VI, VII**), I (**IV, V**).

IIa–Va where the multiple bond and carbon atom attached to the halogen are spatially close favoring the formation of a system of 3-oxa-2-phenyltricyclo[4.4.0.0^{2,7}]decene.

The reactions of bromo(iodo)propargyloxy(allyloxy)-lation were carried out in dichloromethane using the corresponding N-halosuccinimide (NXS) in a slight excess and the unsaturated alcohol ROH in a large excess with respect to the initial hydrocarbon **I**. All reactions took the expected route and resulted in formation of two-component mixtures of stereoisomeric products of the conjugate halogenation **IIa, IIb–Va, Vb** with a high degree of *anti*-stereoselectivity.

The composition of the reaction mixture was analyzed by ^{1}H NMR spectroscopy, yields and isomers ratio are presented in the table. The main reaction products obtained with propargyl alcohol, compounds **IIa** and **IVa**, were isolated by crystallization from methanol, but the isolation of the main products of reaction with allyl alcohol, compounds **IIIa** and **Va**, required chromatographic separation on silica gel. As seen from the table, the yields obtained with propargyl alcohol are higher than with allyl alcohol*, and the iodination is less stereoselective than bromination.

^{1}H and ^{13}C NMR spectra were registered from all compounds **IIa, IIb–Va, Vb.** The spectral characteristics

* Bromoallyloxylation of alkenes using NBS practically failed for under these conditions the allyl alcohol was converted into epibromohydrin [6].

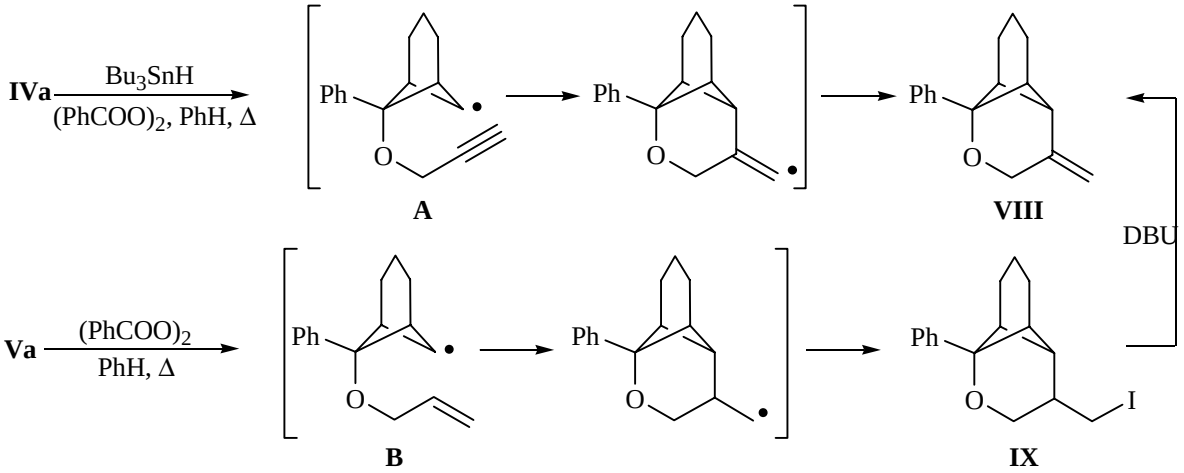
of each of the four stereoisoneris pairs as expected resemble the corresponding spectra of the known bromides **VIa** and **VIb** [2]. The norpinane structure of the carbon skeleton is reliably confirmed by the ^{13}C NMR spectra, and the spatial arrangement, by the data of ^{1}H NMR spectra. In particular, the *syn*-orientation of the halogen atom in all compounds **IIa, IIb–Va, Vb** corresponds to the appearance of a triplet signal (J 6 Hz) of H^7 atom [3], and the assumed configuration at the C^6 atom in compounds **IIa–VIa** is consistent with the high value of the chemical shift of H^7 (~ 5.5 ppm) and with the upfield shift of the signals of *endo*-H^3 (~ 0.6 ppm) [2]. The indication of a changed configuration at C^6 in epimers **IIb–VIb** is a strong upfield shift of the triplet signal from H^7 (~ by 1.2 ppm) and downfield shift of H^3 signals to 1.5–2 ppm [2] as compared with epimers **IIa–VIa**.

To achieve the cyclization of haloderivatives **IIa–Va** it was necessary first to perform the homolytic rupture of the carbon–halogen bond in the initial compound. The examples of radical cyclization of bromo- and iodo-derivatives of unsaturated organic compounds are well known [4]. First we attempted to carry out a cyclization catalyzed by cobaloxime [5] of the most available for us bromide **IIa** and followed the procedure recommended in [6] for the use with unsaturated vicinal bromoethers. However the only reaction product was bromide **IIIa**, namely, occurred the reduction of a triple bond C≡C into a double bond. When we carried out the same procedure with bromide **IIIa**, the double bond C=C suffered reduction to give bromide **VIIa**, identical to the product of an independent sysnthesis by reaction of hydrocarbon **I** with NBS in the presence of propanol. Thus contrary to expectations the C–Br bond in bromides **IIa** and **IIIa** proved to be stable with respect to a system cobaloxime(III)–sodium borohydride, and the multiple bonds underwent hydrogenation. Taking into account that alkyliodiodides are prone to generation of hydrocarbon radicals we used for cyclization iodides **IVa** and **Va**. To perform the reductive cyclization of iodide **IVa** we applied the widely known method with the use of tributyltin hydride [7] and obtained a single reduction product, ether **VIII**. Apparently in an intermediate stage forms radical **A** that further undergoes 6-*exo*-cyclization resulting in compound **VIII**. The structure of compound **VIII** was reliably confirmed by ^{1}H and ^{13}C NMR spectra. In the ^{1}H NMR spectrum alongside the multiplet of aromatic protons appeared two broadened singlets from non-equivalent olefin protons (5.33 and 5.45 ppm), and a singlet of protons of OCH_2 group (4.18 ppm), and also signals from the protons of norpinane fragment analogous to the corresponding signals in the spectra of norpinanes **IIa–VIIa**.

Yield and stereoselectivity (*anti:syn*) of conjugate halogenation of hydrocarbon **I**

Reaction product	Yield, %	*anti:syn* (**a:b**)
IIa, IIb	58	20:1
IIIa, IIIb	28	5:1
IVa, IVb	63	7:1
Va, Vb	32	3:1
VIIa, VIIb	59	7:1

The other route to building up the system of 3-oxatricyclo[4.4.0.0^{2,7}]decene that we succeeded to find was a radical isomerization of iodide **Va** initiated by benzoyl peroxide [8]. Apparently first formed radical **B** that further



suffered 6-*exo*-cyclization. The structure of iodide **IX** unambiguously follows from its ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectrum confirms magnetic nonequivalence of protons in each methylene group OCH_2 and CH_2I, and also of protons H^1 and H^7 and and methylene groups C^8 and C^{10} originating from the chirality of C^5 atom. Nonequivalence of C^1 and C^7 atoms is observed also in the ^{13}C NMR spectrum, but C^8 and C^{10} more remote from the chiral center appear as a unique signal.

The relation of framework structures **VIII** and **IX** as derivatives of 3-oxatricyclo-[4.4.0.0^{2,7}]decene was proved by conversion of iodide **IX** into methylene derivative **VIII** by dehydroiodination effected with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker AM-300 (300 MHz) from solutions in $CDCl_3$. IR spectra were recorded on a spectrophotometer UR-20 from solutions in CCl_4. Elemental analysis was carried out on a CHN-analyzer HP 185B. TLC was performed on Silufol UV-254 plates. Preparative column chromatography was done on silica gel L 40/100 (Chemapol). 1-Phenyltricyclo[4.1.0.0^{2,7}]heptane (**I**) was prepared by method [2]. Chloro(pyridin)bis-(dimethylglyoximato)cobalt(III) [cobaloxime(III)] was obtained by a known procedure [9]. Tributyltin hydride, diazabicyclo[5.4.0]undec-5-ene, and benzoyl peroxide were commercial reagents.

Bromides IIa, IIb, IIIa, IIIb, VIIa, and VIIb. To a suspension of 3.56 g (20 mmol) of N-bromosuccinimide in 10 ml of propargyl alcohol and 10 ml of dichloromethane was added dropwise within 45 min a solution of 2.55 g (15 mmol) of hydrocarbon **I** in 10 ml of dichloromethane. The mixture was stirred at room temperature for 12 h, then 20 ml of 1 N water solution of NaOH was added, and the products were extracted into dichloromethane (3×20 ml). The extract was washed with 1 N water solution of NaOH and dried with magnesium sulfate. The ratio of reaction products **IIa** and **IIb** in the reaction mixture was determined by means of ^{1}H NMR spectroscopy. The main amount of the major component of the mixture **IIa** was isolated by crystallization from methanol of the residue obtained on removing the solvent. The mother liquor was subjected to chromatography on a column charged with silica gel (eluent hexane–dichloromethane) to isolate the minor component **IIb** and additional portion of bromide **IIa**.

***syn*-7-Bromo-*exo*-6-propargyloxy-6-phenylbicyclo[3.1.1]heptane (IIa).** Yield 2.61 g (55%), mp 114–116°C (methanol), R_f 0.47 (eluent hexane–dichloromethane, 8:1). IR spectrum, cm^{-1}: 3320 s, 3040 m, 2950 s, 2875 m, 2120 w, 1950 w, 1870 w, 1810 w, 1760 w, 1070 s, 1050 s. ^{1}H NMR spectrum, δ, ppm: 0.45–0.90 m (1H) and 0.95–1.34 m (1H) – H^3; 1.70–2.40 m (4H, $H^{2,4}$), 2.95 d.t (2H, $H^{1,5}$, *J* 6.0 and 1.5 Hz), 2.14 t (1H, *J* 2.5 Hz) and 3.61 d (2H, *J* 2.5 Hz) – OCH_2Ca"CH; 5.22 t (1H, H^7, *J* 6.0 Hz), 7.24 br.s (5H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 12.3 (C^3), 25.2 (2C, $C^{2,4}$), 47.1 (2C, $C^{1,5}$), 55.3 (C^7), 51.6, 73.8 and 80.7 (OCH_2Ca"CH), 85.8 (C^6), 127.3 (2C), 128.3 (2C), 128.5 and 137.8 (C_6H_5). Found, %: C 62.87; H 5.63; Br 25.85. $C_{16}H_{17}BrO$. Calculated, %: C 62.96; H 5.62; Br 26.18.

***syn*-7-Bromo-*endo*-6-propargyloxy-6-phenylbicyclo[3.1.1]heptane (IIb)**. Yield 0.14 g (3%), mp 98–99°C (methanol), R_f 0.57 (eluent – hexane–dichloromethane, 8:1). IR spectrum, cm^{-1}: 3320 s, 3040 m, 2950 s, 2875 m, 2120 s, 1950 w, 1870 w, 1810 w, 1760 w, 1125 s, 1070 s, 1050 s. ^{1}H NMR spectrum, δ, ppm: 1.50–1.85 m (2H, H^3), 1.90–2.40 m (4H, $H^{2,4}$), 2.98 d.t (2H, $H^{1,5}$, *J* 6.0 and 1.4 Hz), 2.12 t (1H, *J* 2.5 Hz) and 3.55 d (2H, *J* 2.5 Hz) – OCH_2Ca"CH; 4.07 t (1H, H^7, *J* 6.0 Hz), 7.10–7.50 m (5H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 13.4 (C^3), 24.3 (2C, $C^{2,4}$), 48.3 (C^7), 48.8 (2C, $C^{1,5}$), 52.7, 73.7 and 79.9 ($OCH_2C{\equiv}CH$), 80.2 (C^6), 127.6 (2C), 128.2 (2C), 128.8 and 140.2 (C_6H_5). Found, %: C 62.89; H 5.68; Br 25.97. $C_{16}H_{17}BrO$. Calculated, %: C 62.96; H 5.62; Br 26.18.

By analogous procedure applying allyl alcohol and propanol we obtained the corresponding bromides **IIIa**, **IIIb** and **VIIa, VIIb**. The isolation of individual stereoisomers was performed by column chromatography on silica gel.

***exo*-6-Allyloxy-*syn*-7-bromo-6-phenylbicyclo-[3.1.1]heptane (IIIa)**. Yield 23%, mp 38–39°C, R_f 0.65 (eluent hexane–dichloromethane, 8:1). IR spectrum, cm^{-1}: 3090 m, 3070 m, 3035 m, 2950 s, 2875 s, 1950 w, 1880 w, 1850 w, 1820 w, 1760 w, 1650 m, 1540 m, 1450 s, 1205 s, 1070 s, 1050 s. ^{1}H NMR spectrum, δ, ppm: 0.40–0.85 m (1H) and 1.05–1.25 m (1H) – H^3, 1.70–2.40 m (4H, $H^{2,4}$), 3.01 d.t (2H, $H^{1,5}$, *J* 6.0 and 1.5 Hz), 3.52 d (1H, OCH_2, *J* 6.5 Hz), 4.82–5.12 m (2H) and 5.40–5.90 m (1H) – $CH{=}CH_2$; 5.16 t (1H, H^7, *J* 6.0 Hz), 7.25 br.s (5H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 12.3 (C^3), 25.0 (2C, $C^{2,4}$), 46.8 (2C, $C^{1,5}$), 55.6 (C^7), 64.2 (OCH_2), 84.5 (C^6), 115.9 and 135.0 ($CH{=}CH_2$), 127.1 (2C), 127.8 (2C), 128.1 and 138.5 (C_6H_5). Found, %:

C 62.63; H 6.27. $C_{16}H_{19}BrO$. Calculated, %: C 62.55; H 6.23.

***endo*-6-Allyloxy-*syn*-7-bromo-6-phenylbicyclo-[3.1.1]heptane (IIIb)**. Yield 4.5%, oily fluid, R_f 0.72 (eluent hexane–dichloromethane, 8:1). IR spectrum, cm^{-1}: 3070 m, 3050 m, 3015 m, 2920 s, 2875 s, 1950 w, 1880 w, 1850 w, 1820 w, 1760 w, 1650 m, 1540 m, 1450 s, 1205 s 1050 s, 950 s. ^{1}H NMR spectrum, δ, ppm: 1.45–1.75 m (2H, H^3), 1.80–2.35 m (4H, H^{2,4}), 2.96 d.t (2H, H^{1,5}, *J* 6.0 and 1.5 Hz), 3.47 d (1H, OCH_2, *J* 6.5 Hz), 4.08 t (1H, H^7, *J* 6.0 Hz), 4.78–5.06 m (2H) and 5.45–5.82 m (1H) – $CH=CH_2$; 7.05–7.40 m (5H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 13.2 (C^3), 24.5 (2C, C^{2,4}), 48.3 (2C, C^{1,5}), 48.4 (C^7), 65.1 (OCH_2), 80.0 (C^6), 115.7 and 134.2 ($CH=CH_2$), 126.3 (2C), 127.6 (2C), 128.5 and 141.6 (C_6H_5). Found, %: C 62.47; H 6.19. $C_{16}H_{19}BrO$. Calculated, %: C 62.55; H 6.23.

***syn*-7-Bromo-*exo*-6-propyloxy-6-phenylbicyclo-[3.1.1]heptane (VIIa)**. Yield 51%, oily yellowish fluid, R_f 0.76 (eluent hexane–dichloromethane, 8:1). IR spectrum, cm^{-1}: 3070 m, 3040 m, 2950 s, 2880 s, 1950 w, 1880 w, 1810 w, 1760 w, 1600 s, 1450 s, 1290 s, 1200 m, 1070 s, 1020 m. ^{1}H NMR spectrum, δ, ppm: 0.45–0.90 m (1H) and 0.95–1.35 m (1H) – H^3; 1.60–2.30 m (4H, H^{2,4}), 0.72 t (3H, *J* 7.5 Hz), 1.28 m (2H) and 2.91 t (2H, *J* 6.3 Hz) – $OCH_2CH_2CH_3$; 2.90 d.t (2H, H^{1,5}, *J* 6.0 and 1.5 Hz), 4.07 t (1H, H^7, *J* 6.0 Hz), 7.0–7.35 m (5H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 11.9 (C^3), 25.0 (2C, C^{2,4}), 14.5, 31.3 and 49.6 ($OCH_2CH_2CH_3$), 46.1 (2C, C^{1,5}), 55.9 (C^7), 84.1 (C^6), 126.1 (2C), 127.4 (2C), 127.4 and 137.1 (C_6H_5). Found, %: C 62.15; H 6.84. $C_{16}H_{21}BrO$. Calculated, %: C 62.13; H 6.84.

***syn*-7-Bromo-*endo*-6-propyloxy-6-phenylbicyclo-[3.1.1]heptane (VIIb)**. Yield 7%, oily yellowish fluid, R_f 0.82 (eluent hexane–dichloromethane, 8:1). IR spectrum, cm^{-1}: 3085 m, 3030 m, 2950 s, 2860 s, 1950 w, 1860 w, 1810 w, 1720 w, 1600 s, 1440 s, 1290 s, 1210 m, 1105 s, 1010 m. ^{1}H NMR spectrum, δ, ppm: 1.45–1.70 m (2H, H^3), 1.70–2.30 m (4H, H^{2,4}), 0.77 t (3H, *J* 7.5 Hz), 1.30 m (2H) and 2.80 t (2H, *J* 6.2 Hz) – $OCH_2CH_2CH_3$; 2.95 d.t (2H, H^{1,5}, *J* 6.0 and 1.5 Hz), 5.11 t (1H, H^7, *J* 6.0 Hz), 7.20 br.s (5H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 13.1 (C^3), 23.7 (2C, C^{2,4}), 15.1, 31.7 and 51.2 ($OCH_2CH_2CH_3$), 47.7 (2C, C^{1,5}), 48.7 (C^7), 78.9 (C^6), 127.2 (2C), 127.3 (2C), 128.2 and 140.5 (C_6H_5). Found, %: C 62.22; H 6.90. $C_{16}H_{21}BrO$. Calculated, %: C 62.13; H 6.84.

Iodides IVa, IVb and Va, Vb. To a suspension of 4.50 g (20 mmol) of *N*-iodosuccinimide in 10 ml of propargyl alcohol and 10 ml of dichloromethane was added within 25 min a solution of 1.70 g (10 mmol) of hydrocarbon **I** in 10 ml of dichloromethane. The mixture was stirred for 8 h at room temperature, then 20 ml of 10% solution of sodium carbonate was added, and the reaction products were extracted into dichloromethane (3×20 ml). The extract was washed in succession by 10% solution of sodium thiosulfate (2×10 ml), with water, and with saturated NaCl solution, and dried with sodium sulfate. The ratio of reaction products **IVa** and **IVb** in the reaction mixture was determined by means of ^{1}H NMR spectroscopy. The main amount of the major component of the mixture **IVa** was isolated by crystallization from methanol, and iodide **IVb** and additional portion of iodide **IVa** were obtained by subjecting the mother liquor to column chromatography on silica gel.

***syn*-7-Iodo-*exo*-6-propargyloxy-6-phenylbicyclo-[3.1.1]heptane (IVa).** Yield 1.97 g (56%), mp 123°C (methanol), R_f 0.57 (eluent hexane– dichloromethane, 2:1). ^{1}H NMR spectrum, δ, ppm: 0.42–0.78 m (1H) and 0.96–1.35 m (1H) – H^3; 1.81–2.25 m (4H, H^{2,4}), 3.10 d.t (2H, H^{1,5}, *J* 6.0 and 1.5 Hz), 2.32 t (1H, *J* 2.5 Hz) and 3.76 d (2H, *J* 2.5 Hz) – $OCH_2C{\equiv}CH$; 5.49 t (1H, H^7, *J* 6.0 Hz), 7.15–7.60 m (5H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 11.6 (C^3), 28.2 (2C, C^{2,4}), 38.9 (C^7), 46.5 (2C, C^{1,5}), 51.4, 73.5 and 80.3 ($OCH_2C{\equiv}CH$), 85.0 (C^6), 126.7 (2C), 128.0 (2C), 128.1 and 137.7 (C_6H_5). Found, %: C 54.52; H 4.85; I 35.97. $C_{16}H_{17}IO$. Calculated, %: C 54.56; H 4.86; I 36.03.

***syn*-7-Iodo-*endo*-6-propargyloxy-6-phenyl-bicyclo[3.1.1]heptane (IVb)**. Yield 0.25 g (7%), mp 102°C (methanol), R_f 0.65 (eluent hexane– dichloromethane, 2:1). ^{1}H NMR spectrum, δ, ppm: 1.55–1.85 m (2H, H^3), 1.90–2.40 m (4H, H^{2,4}), 3.03 d.t (2H, H^{1,5}, *J* 5.8 and 1.4 Hz), 2.33 t (1H, *J* 2.5 Hz) and 3.68 d (2H, *J* 2.5 Hz) – $OCH_2C{\equiv}CH$; 4.25 t (1H, H^7, *J* 5.5 Hz), 7.14–7.65 m (5H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 12.5 (C^3), 26.8 (2C, C^{2,4}), 28.8 (C^7), 48.5 (2C, C^{1,5}), 52.3, 73.5 and 79.9 ($OCH_2C{\equiv}CH$), 85.0 (C^6), 127.3 (2C), 128.0 (2C), 128.5 and 139.7 (C_6H_5). Found, %: C 54.51; H 4.84; I 35.94. $C_{16}H_{17}IO$. Calculated, %: C 54.56; H 4.86; I 36.03.

By analogous procedure using allyl alcohol we obtained iodides **Va** and **Vb**, and the separation of the mixture required application of column chromatography on silica gel.

***exo*-6-Allyloxy-*syn*-7-iodo-6-phenylbicyclo-[3.1.1]heptane (Va)**. Yield 24%, mp 41°C, R_f 0.68

(eluent hexane–ether, 10:1). ^{1}H NMR spectrum, δ, ppm: 0.49–0.72 m (1H) and 1.13–1.34 m (1H) – H^3; 2.0–2.24 m (4H, H^{2,4}), 3.07 d.t (2H, H^{1,5}, *J* 6.1 and 1.5 Hz), 3.66 d (2H, OCH_2, *J* 6.6 Hz), 5.02–5.23 m (2H) and 5.69–5.84 m (1H) – $CH=CH_2$; 5.47 t (1H, H^7, *J* 6.1 Hz), 7.21–7.45 m (5H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 11.7 (C^3), 28.1 (2C, C^{2,4}), 38.7 (C^7), 46.2 (2C, C^{1,5}), 64.1 (OCH_2), 84.1 (C^6), 116.2 and 135.5 ($CH=CH_2$), 126.8 (2C), 127.5 (2C), 127.9 and 138.1 (C_6H_5). Found, %: C 54.33; H 5.42. $C_{16}H_{19}IO$. Calculated, %: C 54.25; H 5.41.

***endo*-6-Allyloxy-*syn*-7-iodo-6-phenylbicyclo-[3.1.1]heptane (Vb).** Yield 8%, mp 32°C, R_f 0.75 (eluent – hexane–ether, 10:1). ^{1}H NMR spectrum, δ, ppm: 1.41–1.71 m (2H, H^3), 1.86–2.34 m (4H, H^{2,4}), 3.02 d.t (2H, H^{1,5}, *J* 6.0 and 1.5 Hz), 3.51 d (1H, OCH_2, *J* 6.5 Hz), 4.87–5.14 m (2H) and 5.73–5.89 m (1H) – $CH=CH_2$; 4.29 t (1H, H^7, *J* 6.0 Hz), 7.01–7.36 m (5H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 12.5 (C^3), 26.9 (2C, C^{2,4}), 29.0 (C^7), 48.1 (2C, C^{1,5}), 65.2 (OCH_2), 79.3 (C^6), 115.8 and 134.3 ($CH=CH_2$), 126.2 (2C), 127.5 (2C), 128.3 and 141.0 (C_6H_5). Found, %: C 54.31; H 5.43. $C_{16}H_{19}IO$. Calculated, %: C 54.25; H 5.41.

Treatment of bromides IIa and IIIa with the reagent cobaloxime(III)–sodium borohydride. To a solution of 31 mg (1 mmol) of bromide **IIa** in 15 ml of 95% ethanol was added 0.5 g (13 mmol) of sodium borohydride and 1 ml of 0.1 N alcoholic solution of sodium hydroxide. Then under an argon atmosphere while stirring at 50°C was added within 3 h by small portions 90 mg (0.22 mmol) of cobaloxime(III). On adding to the reaction mixture of each new portion of catalyst a gas evolution was observed, and the solvent got darker, but some time later it turned again colorless. Additionally 0.5 g of sodium borohydride and 40 mg of cobaloxime(III) was introduced, and stirring was continued for 2 h. Then the mixture was diluted with 10 ml of ether and 10 ml of water, the organic layer was separated, and the reaction products were extracted from the water layer into ether (3×10 ml). The extract was dried with magnesium sulfate. The residue after removal of ether was separated by column chromatography (eluent hexane–ether, 20:1). Yield of bromoether **IIIa** 86 mg (28%). Its ^{1}H and ^{13}C NMR spectra were identical to the spectra of the previously obtained sample of compound **IIIa**.

By similar procedure bromoether **IIIa** was treated with the reagent cobaloxime(III)–sodium borohydride (reaction time ~ 20 h). By chromatography on silica bromoether **VIIa** was isolated (yield 34%), whose ^{1}H NMR spectrum was identical to the spectrum of the previously obtained sample of compound **VIIa**.

Reductive cyclization of iodide IVa. 5-Methylene-3-oxa-2-phenyltricyclo[4.4.0.0^{2,7}]decene (VIII). To a solution of 0.352 g (1 mmol) of iodide **IVa** and 0.350 g (1.2 mmol) of tributyltin hydride in 50 ml of toluene under an argon atmosphere while stirring and heating (114°C) was added by portions 0.024 g (0.1 mmol) of benzoyl peroxide. The reaction progress was monitored by TLC (reaction time ~2 h). The solvent was evaporated in a vacuum, the residue was subjected to column chromatography on silica gel (eluent hexane–ether, 20:1). Yield of ether **VIII** 82 mg (36%). Colorless oily fluid, R_f 0.69 (eluent hexane– ether, 10:1). ^{1}H NMR spectrum, δ, ppm: 0.51–0.69 m (1H) and 1.04–1.21 m (1H) – H^9; 1.91–2.10 m (4H, H^{8,10}), 2.96 s (1H, H^6), 3.12 s (2H, H^{1,7}), 4.18 s (2H, OCH_2), 5.34 br.s (1H) and 5.46 br.s (1H) – $C=CH_2$; 7.24–7.43 m (5H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 11.6 (C^9), 29.2 (2C, C^{8,10}), 50.4 (2C, C^{1,7}), 57.6 (C^6), 70.2 (C^4), 83.9 (C^2), 124.1 (CH_2=), 133.3 (C^5), 125.8 (2C), 127.4 (2C), 128.6 and 138.7 (C_6H_5). Found, %: C 84.81; H 8.07. $C_{16}H_{18}O$. Calculated, %: C 84.91; H 8.02.

Izomerization of iodide Va. 5-Iodomethyl-3-oxa-2-phenyltricyclo[4.4.0.0^{2,7}]-decene (IX). To a solution of 0.354 g (1 mmol) of iodide **Va** in 50 ml of benzene under an argon atmosphere was added at heating (80°C) by portions 0.048 g (0.2 mmol) of benzoyl peroxide within 4 h, and the mixture was stirred till complete conversion of initial iodide **Va** (~ 4 h, TLC monitoring). The cooled reaction mixture was washed with 5% solution of sodium hydrogen carbonate (3×10 ml) and with water, and dried with sodium sulfate. On subjecting the product to column chromatography (eluent hexane– ether, 20:1) we obtained 113 mg (32%) of iodide **IX**. Colorless oily substance, R_f 0.79 (eluent hexane– ether, 10:1). ^{1}H NMR spectrum, δ, ppm: 0.51–0.69 m (1H) and 1.07–1.22 m (1H) – H^9; 2.02–2.20 m (2H) and 2.30–2.46 m (2H) – H^{8,10}; 2.55–2.66 m (1H, H^5), 2.92 br.s (1H, H^6), 3.04 d.d (1H, *J* 16 and 4.5 Hz) and 3.14 d.d (1H, *J* 16 and 6 Hz) – CH_2I; 3.22 br.s (1H) and 3.24 br.s (1H) – H^{1,7}; 4.01 d.d (1H, *J* 16.5 and 4.5 Hz) and 4.18 d.d (1H, *J* 16.5 and 10 Hz) – OCH_2; 7.28–7.43 m (5H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 6.6 (CH_2I), 11.8 (C^9), 28.5 (2C, C^{8,10}), 43.5 (C^5), 49.8 and 50.2 (2C, C^{1,7}), 55.7 (C^6), 64.8 (C^4), 86.8 (C^2), 125.0 (2C), 128.1, 128.3 (2C) and 141.2 (C_6H_5). Found, %: C 54.35; H 5.46. $C_{16}H_{19}IO$. Calculated, %: C 54.25; H 5.41.

Dehydrohalogenation of iodide IX. A mixture of 106 mg (0.3 mmol) of iodide **IX** and 76 mg (0.5 mmol) of diazabicyclo[5.4.0]undec-7-ene in 5 ml of 1,2-dimethoxyethane was heated for 1 h at 80°C. The reaction mixture was poured into 20 ml of 1 N hydrochloric acid cooled to 0°C, and it was stirred. From the solution obtained the reaction product was extracted into hexane (4×10 ml). The extract was washed in succession with 10 ml of 0.5 N hydrochloric acid, with water (3×5 ml), and with saturated NaCl solution, and dried with magnesium sulfate. On subjecting the product to column chromatography (eluent hexane–ether, 20:1) we obtained 52 mg (76%) of ether **VIII**, whose ^{1}H and ^{13}C NMR spectra were identical to the spectra of the sample previously prepared.

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