Russian Journal of Organic Chemistry, Vol. 40, No. 5, 2004, pp. 653–658. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 5, 2004, pp. 684–690.

Conjugate Iodination of 1-Methyltricyclo[4.1.0.0^{2,7}]heptane

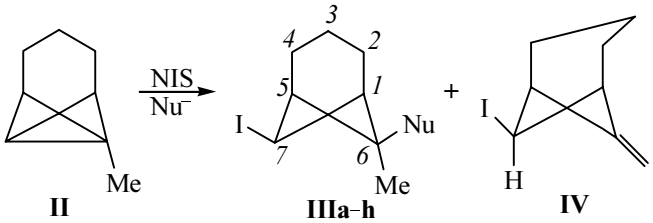
V.A. Vasin[1], A.V. Semenov[1], and V.V. Razin[2]

[1]*Ogarev Mordovian State University, Saransk, Russia*
[2]*St. Petersburg State University, St. Petersburg, 198504 Russia*

Received June 10, 2003

Abstract—Reactions of 1-methyltricyclo[4.1.0.0^{2,7}]heptane with *N*-iodosuccinimide in the presence of external nucleophiles result in products of conjugate *endo,syn*-addition across the central C^1–C^7 bond of the norpinane structure. Regio- and stereoselectivity of reactions is discussed.

As we have previously established [1], the conjugate iodination of tricyclo[4.1.0.0^{2,7}]heptane (**I**) occurred exclusively at the central bicyclobutane bond C^1–C^7 and entirely *endo,syn*-stereoselectively. Aiming at elucidating the effect of a substituent in the nodal position of the substrate on the direction and stereochemistry of iodination we investigated the reaction of 1-methyltricyclo[4.1.0.0^{2,7}]heptane (**II**) with N-iodosuccinimide (NIS) in the presence of methanol, acetic and benzoic acids, dimethylformamide, potassium thiocyanate and iodide, lithium bromide and chloride as sources of external nucleophiles (reactions *1–8*, Table 1). Besides for the sake of comparison we carried out reactions of compound **II** with iodine monochloridein the presence of lithium chloride (reaction *9*) and with elemental iodine in the presence of potassium thiocyanate καλθя (reaction *10*) and also in a nonnucleophilic solvent CCl_4 in the absence of external nucleophile (reaction *11*).



II **IIIa–h** **IV**

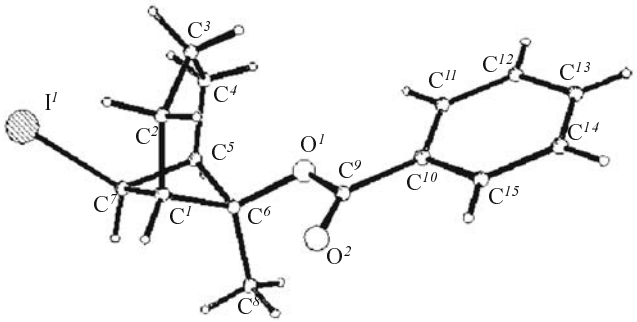
Nu = OMe (**a**), OAc (**b**), OCOPh (**c**), OCHO (**d**), SCN (**e**), I (**f**), Br (**g**), Cl (**h**). Hlg = Cl (**a**), I (**b**).

In all instances except for reactions *6* and *11* products obtained **IIIa-e, g, h** had norpinane structure corresponding to the conjugate iodination at the central C^1–C^7 bond occurring in strict regioselectivity in keeping with Markownikoff rule and in the *endo,syn*-stereochemistry. As admixture to compound **III** was detected by GLC also 6-methylenenorpinane (**IV**) that was the prevailing product in reactions *6* and *11*. In both latter cases we attribute the observed result to the extreme instability of the intermediately formed diiodide **IIIf** (in contrast to 6,7-diiodonorpinane [1]) suffering autocatalytic dehydroiodination. It is presumable that also in reactions *1–5* and *7–10* the admixture of compound **IV** originated from a side reaction providing diiodide **IIIf** at the use of NIS and ICl even in the absence of the external source of iodide ion [1]. The comparison of products yield in reactions *5* and *10*, and also *8* and *9* (Table 1) indicates that the application as iodinating reagents of elemental iodine or iodine monochloride instead of NIS has no advantages.

Table 1. Conditions of reaction of hydrocarbon **II** with iodinating agents, and yields of reaction products **III** and **IV**

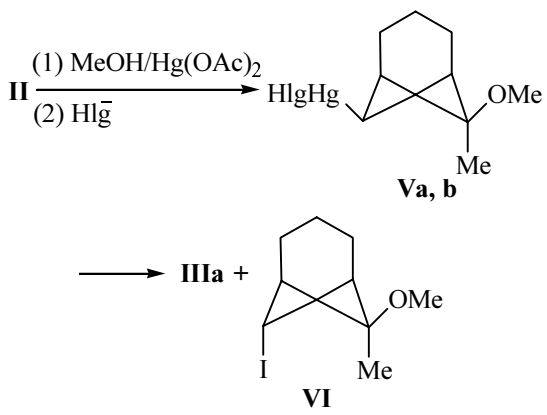
Reaction no.	Reagents	Solvent	I^+ / Nu^- (mol)	Yield of compd. **III** (**IV**), %
1	NIS + MeOH	MeOH	1:84	55 (1.7)
2	NIS + AcOH[a]	CH_2Cl_2	1:5	52 (2.2)
3	NIS + PhCOOH[a]	CH_2Cl_2	1:5	51 (3.8)
4	NIS + DMF	DMF	1:39	48 (2.5)
5	NIS + KSCN	CH_3CN	1:10	44 (3.8)
6	NIS + KI	THF	1:5	0 (12)
7	NIS + KBr	DMF	1:10	39 (2.0)
8	NIS + LiCl	CH_3CN	1:10	32 (0.7)
9	ICl + LiCl	DMF	1:10	30 (1.9)
10	I_2 + KSCN	DMF	1:10	37 (6.5)
11	I_2	CCl_4	–	0 (7)

[a] With addition of equimolar amount of triethylamine.



Structure of the molecule of *syn*-6-benzoxy-*anti*-6-methyl-*endo*-7-iodobicyclo[3.1.1]heptane (**IIIc**) from the data of X-ray diffraction analysis.

Compounds **IIIa-e, g, h** were isolated in individual state by flash-chromatography on silica gel and were purified by crystallization or distillation in a vacuum. The structure of compounds **III** was reliably proved by ^{1}H and ^{13}C NMR spectra that were in expected agreement (taking into account the effect of CH_3 group on the chemical shifts of atoms C^6 and H^7) with the spectral characteristics with their respective analogs lacking the methyl group [1]. *exo*-Orientation of atom H^7 unambiguously follows from the appearance of the corresponding triplet signal (J ~6.0 Hz) in the ^{1}H NMR spectra (cf. [2]), and the *anti*-orientation of the methyl group is testified by the chemical shift of the opposite thereto atom H^7. This value changes in a narrow range (4.5–4.8 ppm) in the compounds series under consideration, and it is only by ~0.3 ppm greater than that in the analog without methyl group [1]. Note that at the opposite *syn*-orientation of the CH_3 group the signal of the *exo*-H^7 should be significantly shifted downfield, for instance, in the spectra of diastereomers of compounds **IIIa-d** it should appear in the region ~5.5 ppm [3]. The lack of signals in this region of the ^{1}H NMR spectra of the reaction mixtures under consideration proves that in the products of conjugate iodination of compound **II** are no *endo,anti*-adducts.



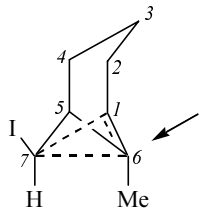
The above reasoning concerning the configuration of the substituents at C^7 atom of compounds **III** is consistent with the current concept [4] on exclusively *endo*-directed electrophilic attack on the bicyclobutane system. Unlike that, the *anti*-orientation of the methyl group attached to C^6 atom in these compounds is not necessarily expected, and its justification requires additional information. To this end we applied the method of chemical correlation of configuration by an example of one among norpinanes, compound **IIIa**. For this purpose we performed the known [5] methoxymercuration reaction of hydrocarbon **II** that always occurred strictly *endo,syn*-stereoselectively. Thus we obtained both a known mercurochloride **Va** and its iodine-substituted analog **Vb** where the methyl group had *anti*-orientation. Compound **Vb** was subjected to iododemercuration (cf. [6]). As a result was obtained a reaction products containing two components in 1:1.4 ratio. The minor component was identified by the ^{1}H NMR spectrum of the mixture as compound **IIIa**. Thus was proved the configuration at C^6 atom of the compound. The second component was tentatively assigned structure **VI** basing on the attributed thereto signals in the ^{1}H NMR spectrum of the mixture. Compound **VI** is regarded as epimer of compound **IIIa** with respect to C^7 atom. In agreement with this assumption a singlet signal is observed from H^6 atom (cf. [2]), and the singlet from the methyl group is shifted downfield by 0.4 ppm as compered with its position in the spectrum of epimer **IIIa** [3]. Formation of two stereoisomeric iodides **IIIa** and **VI** from compound **V** is not unexpected for the halodemercuration can occur nonstereoselectively [6].

Finally, an absolute proof of the structure of one among compounds synthesized, ester **IIIc**, was obtained by means of X-ray diffraction analysis (see figure and Table 2).

In the unit cell of the crystal of compound **IIIc** are present two independent conformationally different molecular structures that are atropoisomers. They differ from each other by the angle of benzoyl group rotation with respect to the plane through atoms $O^1C^6C^7$. The geometry parameters of the norpinane skeleton of the molecules are very similar. The trimethylene bridge $C^2C^3C^4$ therein is strongly flattened (cf. with the *endo,syn*-6,7-diiodonorpinane [7]).

For the sake of comparison and identification we specially prepared methylenenorpinane **IV** by 1,2-elimination of HBr at heating dihalide **IIIa** with potassium *tert*-butylate in THF. The structure of this compound was confirmed by NMR spectra as compared to those of model substances [8].

In treating the results of reactions studied we assumed that the conjugate iodination of hydrocarbon **II** occurred by a ionic mechanism. We believe that the reaction is initiated by the *endo*-directed attack of the electrophilic iodine on the unsubstituted position *7* of the substrate in keeping with the directing effect of the methyl substituent, and the completion occurs as a *syn*-stereodirected transfer of a nucleophile to the reaction center of the carbocationic intermediate. We ascribe to the intermediate a structure of a bicyclobutonium ion A (one of its enantiomers is represented on the scheme) analogously to the situation



A

with the *endo-syn*-iodination of hydrocarbon **I**, cf. [1].

The electron-donor methyl group stabilizes the cationic center yet apparently cannot sufficiently change its structure towards the classic one with charge localization on C^{6} atom where the strictly sterespecific interaction with a nucleophile was hardly probable

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on spectrometer Bruker DPX-300 (at 300.13 and 75.468 MHz respectively) from solutions of compounds in $CDCl_3$. IR spectra were measured on a Fourier Spectrometer InfraLum FT-02. The GLC analyses were performed on a chromatograph Kristallyuks-4000 equipped with a flame-ionization detector, glass column 3000×3 mm, stationary phase 3% OV-17 on Inerton N-Super (0.125–0.160 mm), carrier gas nitrogen, flow rate 65 ml/min, temperature of the detector, vaporizer, and oven 250, 220, and 130°C respectively. TLC analyses were carried out under the following conditions: adsorbent Silufol UV-254, eluent hexane–ether, 2 : 1, development with iodine vapor. Flash-chromatography was performed using silica gel L 40/100 μ, eluent light petroleum ether–ethyl ether, 3:1. Tricycloheptane **II** [9] and NIS [10] were prepared along published procedures.

Reaction of tricycloheptane (II) with NIS in methanol. To a solution of 1.08 g of tricycloheptane **II** in 20 ml of anhydrous methanol under nitrogen atmosphere at cooling to 0°C was added by portions within 30 min while stirring 2.25 g of NIS. The mixture was stirred for 30 min at cooling and then for 4 h at 20°C, then was diluted with 30 ml of water. The reaction products were extracted into ether (3×20 ml), the combined extract was washed with water and dried on $MgSO_4$, the solvent was evaporated in a vacuum. Using flash-chromatography we

Table 2. Coordinates (×10^{4}) and equivalent isotropic thermal parameters (Å^{2}×10^{3}) of atoms in the molecule of compound **IIIc**[a]

AtOM	*x*	*y*	*z*	U_{eq}
C^{1}	550(3)	3224(4)	–105(2)	52(1)
C^{2}	1547(4)	3721(4)	187(3)	61(1)
C^{3}	2513(4)	3029(5)	7(3)	70(1)
C^{4}	2291(4)	1876(4)	–378(3)	69(1)
C^{5}	1163(4)	1701(4)	–556(2)	61(1)
C^{6}	643(3)	2829(4)	–840(2)	55(1)
C^{7}	482(4)	1903(4)	44(2)	60(1)
C^{8}	–366(5)	2660(6)	–1257(3)	93(2)
C^{9}	1193(3)	4578(4)	–1396(2)	55(1)
C^{10}	1932(4)	5006(4)	–1893(2)	54(1)
C^{11}	2748(4)	4314(5)	–2115(3)	72(1)
C^{12}	3407(5)	4727(6)	–2587(3)	88(2)
C^{13}	3268(5)	5823(5)	–2855(3)	79(2)
C^{14}	2479(4)	6526(5)	–2635(3)	73(1)
C^{15}	1806(4)	6114(4)	–2155(3)	64(1)
O^{1}	1377(2)	3452(3)	–1245(2)	56(1)
O^{2}	533(3)	5161(3)	–1159(2)	73(1)
I^{1}	949(1)	1198(1)	1008(1)	82(1)
C$^{1'}$	4599(3)	8029(3)	–219(2)	53(1)
C$^{2'}$	3835(4)	8839(4)	112(3)	57(1)
C$^{3'}$	2719(4)	8367(4)	97(3)	70(1)
C$^{4'}$	2562(4)	7126(4)	–211(3)	67(1)
C$^{5'}$	3570(4)	6633(4)	–473(2)	58(1)
C$^{6'}$	4138(3)	7539(4)	–887(2)	53(1)
C$^{7'}$	4481(4)	6751(4)	31(2)	57(1)
C$^{8'}$	4904(4)	7055(5)	–1369(3)	76(1)
C$^{9'}$	3753(4)	9287(4)	–1509(2)	53(1)
C$^{10'}$	2915(3)	9869(4)	–1934(2)	51(1)
C$^{11'}$	1879(4)	9528(4)	–1948(2)	59(1)
C$^{12'}$	1149(4)	10084(5)	–2356(2)	69(1)
C$^{13'}$	1455(5)	10979(5)	–2765(3)	74(1)
C$^{14'}$	2455(5)	11334(5)	–2765(3)	79(2)
C$^{15'}$	3203(4)	10798(5)	–2352(3)	68(1)
O$^{1'}$	3404(2)	8278(3)	–1263(2)	54(1)
O$^{2'}$	4610(3)	9671(3)	–1406(2)	73(1)
I$^{1'}$	4307(1)	6375(1)	1072(1)	102(1)

[a] Equivalent isotropic thermal parameter U_{eq} was determined as one third of the orthogonalized U_{ij} of tenzor.

isolated ***endo*-7-iodo-*anti*-6-methyl-*syn*-6-methoxybicyclo[3.1.1]heptane (IIIa),*** a colorless oily substance turning dark on storage, R_f 0.55, R_t 1.45 min (130°C). IR spectrum (thin film), cm^{-1}: 2931 v.s, 2858 m, 2823 w, 1459 m, 1446 m, 1207 m, 1180 C, 1062 C, 815 w, 713 w. ^1H NMR spectrum, δ, ppm: 4.50 t (1H, H^7, *J* 6.0 Hz), 3.27 c (3H, OMe), 2.45 br.d (2H, $H^{1,5}$, *J* 6.0 Hz), 2.31–2.12 M (2H, $H^{2,4}$), 1.93–1.78 M (2H, $H^{2,4}$), 1.63–1.55 M (2H, H^3), 1.45 c (3H, Me). ^{13}C NMR spectrum, δ, ppm: 12.6 (C^3), 20.2 (Me), 26.9 ($C^{2,4}$), 32.4 (C^7), 49.1 ($C^{1,5}$), 50.9 (OMe), 74.6 (C^6). Found, %: C 40.88; H 5.73. $C_9H_{15}IO$. Calculated, %: C 40.62; H 5.68.

Reactions of hydrocarbon II with NIS in the presence of carboxylic acids. In 20 ml of anhydrous CH_2Cl_2 was dissolved 0.05 mol of acetic or benzoic acid and 7.0 ml of triethylamine. To the solution obtained having a weakly alkaline reaction a solution of 1.08 g of hydrocarbon **II** in 10 ml of the same solvent was added. At cooling to 0°C under nitrogen atmosphere was added by small portions while stirring 2.25 g of NIS. The mixture was stirred for 30 min at cooling and 4 h more at 20°C, then was diluted with 30 ml of water. The reaction products were extracted into CH_2Cl_2 (3×30 ml), the extracts were dried on $MgSO_4$, and the solvent was evaporated in a vacuum. By means of flash-chromatography esters **IIIb** and **IIIc** were isolated from the residue.

***endo*-7-Iodo-*anti*-6-methylbicyclo[3.1.1]hept-*syn*-6-yl acetate (IIIb)**. mp 60–61°C (from ether), R_f 0.65, R_t 5.62 min (150°C). IR spectrum (KBr), ν, cm^{-1}: 2947 m, 1728 s, 1714 s, 1367 m, 1255 v.s, 1244 v.s, 1143 m, 1130 m, 866 m, 711 m. ^1H NMR spectrum, δ, ppm: 4.52 t (1H, H^7, *J* 5.8 Hz), 2.67 br.d. (2H, $H^{1,5}$, *J* 5.8 Hz), 2.06 s (3H, COMe), 2.21–2.02 m (2H, $H^{2,4}$), 2.00–1.85 m (2H, $H^{2,4}$), 1.66 s (3H, Me), 1.72–1.54 m (1H, H^3), 1.52–1.34 m (1H, H^3). ^{13}C NMR spectrum, δ, ppm: 12.2 (C^3), 21.6 (Me), 27.1 ($C^{2,4}$), 30.8 (C^7), 49.9 ($C^{1,5}$), 76.6 (C^6), 21.3, 169.4 (OCOMe). Found, %: C 40.91; H 5.28. $C_{10}H_{15}IO_2$. Calculated, %: C 40.84; H 5.14.

***endo*-7-Iodo-*anti*-6-methylbicyclo[3.1.1]hept-*syn*-6-yl benzoate (IIIc)**. mp 54–55°C (from ether), R_f 0.57, R_t 26.35 min (180°C). IR spectrum (KBr), ν, cm^{-1}: 2953 m, 1716 v.s, 1450 m, 1313 s, 1290 s, 1273 v.s, 1151 s, 1109 s, 1066 m, 1024 m, 706 s. ^1H NMR spectrum, δ, ppm: 8.06 d (2H, Ph, *J* 7.4 Hz), 7.61 t (1H, Ph, *J* 7.4 Hz), 7.48 t (2H, Ph, *J* 7.4 Hz), 4.61 t (1H, H^7, *J* 5.9 Hz), 2.84 br.d (2H, $H^{1,5}$, *J* 5.9 Hz), 2.35–2.20 m (2H, $H^{2,4}$), 2.09–1.93 m (2H, $H^{2,4}$), 1.81 s (3H, Me), 1.71–1.57 m (1H, H^3), 1.55–1.38 m (1H, H^3). ^{13}C NMR spectrum, δ, ppm: 12,3 (C^3), 21.8 (Me), 27.3 ($C^{2,4}$), 30.6 (C^7), 50.2 ($C^{1,5}$), 77.3(C^6), 128.3, 129.4, 130.5, 132.9 (Ph), 164.8 (C=O). Found, %: C 50.47; H 4.66. $C_{15}H_{17}IO_2$. Calculated, %: C 50.58; H 4.81.

X-ray diffraction study of compound IIIc. The measurements were performed on colorless transparent crystals in plate form, crystal habit 0.3×0.2×0.2 mm, on automatic four-circle diffractometer CAD4 Enraf-Nonius (graphite monochromator, MoK_α-radiation, λ 0.71073 E, θ-5/3θ scanning, $2\theta_{max}$ 50.02°) at room temperature. Monoclinic crystals, space group $P2_1/C$, *a* 12.798(3), *b* 11.441(2), *c* 19.942(4) E, α 90, β 92.35(3), γ 90°, *V* 2917.5(10) E^3, *Z* 8, calculated density 1.622 g cm^{-3}. The structure was solved and refined using intensities of 5162 reflections (4929 independent reflections, R_{int} 0.0123). The correction for extination (μ 21.88 cm^{-1}) was not introduced. The structures were solved by the direct method and by successive syntheses of the electron density. The nonhydrogen atoms were refined in full-matrix least-squares procedure along F^2 in anisotropic approximation. The hydrogen atoms were placed into positions calculated from geometry considerations and were accounted for in the *rider* model at U(H) = 1.2 U(C), where U(C) is the equivalent thermal factor of the carbon linked to the corresponding hydrogen. The final divergence factors were: R1 0.0495 [calculated from F_{hkl} for 3353 reflections with I>2σ(I)] and wR2 0.1458 (calculated from F^2_{hkl} for all 4929 reflections taken into account in the final refinement), number of parameters refined 325, GOOF 1.030. All calculations were carried out using software package SHELXTL ver.5.1 [11]. In a unit cell are located two independent molecular structures of different conformation. The coordinates of nonhydrogen atoms and their equivalent isotropic thermal parameters are presented in Table 2. The coordinates and equivalent isotropic thermal parameters of hydrogens and also the values of anisotropic thermal parameters of nonhydrogen atoms are available from authors.

Reaction of tricycloheptane II with NIS in DMF. To a solution of 1.08 g of tricycloheptane **II** in 20 ml of anhydrous DMF cooled to 0°C was added dropwise under nitrogen while stirring within 30 min a solution of 2.25 g of NIS in 10 ml of the same solvent. The mixture was stirred for 30 min at cooling and then for 48 h at 20°C, and then it was worked up as described above. By means of flash-chromatography ***endo*-7-iodo-*anti*-6-**

* In order to apply the same names both for designation of the stereodirection of the electrophile reagent approach to the tricycloheptane substrate and for stereochemical nomenclature of the obtained bicyclo[3.1.1]heptane derivatives we used the terms *endo*- and *exo*- for substituents at C^7, and *syn*- and *anti*- for substituents at C^6.

methylbicyclo[3.1.1]hept-*syn*-6-yl formate (IIId) was isolated, oily fluid, R_f 0.59, R_t 4.74 min (150°C). IR spectrum (thin film), ν, cm^{-1}: 2955 m, 2872 w, 1722 v.s, 1716 s 1448 w, 1176 s, 1143 s, 868 w, 823 w, 717 w. ^{1}H NMR spectrum, δ, ppm: 8.09 s (1H, HCO), 4.51 t H, H^7, *J* 5.7 Hz), 2.71 br.d (2H, H^{1,5}, *J* 5.7 Hz), 2.23–2.08 m (2H, H^{2,4}), 2.04–1.89 m (2H, H^{2,4}), 1.70 s (3H, Me), 1.74–1.56 (1H, H^3), 1.55–1.38 m (1H, H^3). ^{13}C NMR spectrum, δ, ppm: 12.0 (C^3), 21.8 (Me), 27.1 (C^{2,4}), 29.8 (C^7), 50.0 (C^{1,5}), 77.7 (C^6), 159.5 (C=O). Found, %: C 38.71; H 4.77. $C_9H_{13}IO_2$. Calculated, %: C 38.59; H 4.68.

Reaction of hydrocarbon II with NIS in the presence of anionic nucleophiles. To a mixture of 0.1 mol of anhydrous KSCN (KI, LiBr, LiCl) and 1.08 g of hydrocarbon **II** in 30 ml of anhydrous acetonitrile or DMF (Table 1) at cooling to 0°C under nitrogen was added by small portions while stirring 2.25 g of NIS. The mixture was stirred for 30 min at cooling and 4 h more at 20°C, then it was diluted with 30 ml of water. The reaction products were extracted with ether (3×20 ml), the extracts were washed with a 5% solution of Na_2SO_3 till the washings were no more colored with iodine, dried on $MgSO_4$, and the solvent was evaporated in a vacuum. The residues were subjected to chromatography to isolate the products of conjugate addition **IIIe, g, h**.

***endo*-7-Iodo-*anti*-6-methylbicyclo[3.1.1]hept-*syn*-6-yl thiocyanate (IIIe).** mp 30–31°C (from ether), R_f 0.53, R_t 23.93 min (150°C). IR spectrum (KBr), ν, cm^{-1}: 2920 m, 2150 v.s, 1444 s, 1196 m, 1128 m, 1101 m, 870 w, 817 m, 715 m, 569 w. ^{1}H NMR spectrum, δ, ppm: 4.85 t (1H, H^7, *J* 5.5 Hz), 2.61 br.d (2H, H^{1,5}, *J* 5.5 Hz), 2.32–2.17 m (2H, H^{2,4}), 2.17–2.03 m (2H, H^{2,4}), 1.95 s (3H, Me), 1.95–1.80 m (1H, H^3), 1.68–1.52 m (1H, H^3). ^{13}C NMR spectrum, δ, ppm: 10.9 (C^3), 25.7 (Me), 27.6 (C^7), 27.9 (C^{2,4}), 49.3 (C^{1,5}), 54.7 (C^6), 110.8 (SCN). Found, %: C 36.93; H 4.24. $C_9H_{12}INS$. Calculated, %: C 36.87; H 4.13.

***syn*-6-Bromo-*endo*-7-iodo-*anti*-6-methylbicyclo-[3.1.1]heptane (IIIg).** mp 35–36°C (from ether–pentane), R_f 0.77, R_t 5.15 min (150°C). IR spectrum (KBr), ν, cm^{-1} : 2926 m, 1439 s, 1385 m, 1194 s, 1128 m, 1093 s, 1066 m, 796 s, 715 m, 559 w, 470 w. ^{1}H NMR spectrum, δ, ppm: 4.67 t (1H, H^7, *J* 5.5 Hz), 2.62 br.d (2H, H^{1,5}, *J* 5.5 Hz), 2.50–2.35 m (2H) and 2.23–2.09 m (2H, H^{2,4}), 2.13 s (3H, Me), 1.82–1.57 m (2H, H^3). ^{13}C NMR spectrum, δ, ppm: 10.8 (C^3), 25.3 (Me), 30.6 (C^7), 30.8 (C^{2,4}), 52.6 (C^{1,5}), 63.4 (C^6). Found, %: C 30.65; H 3.73. $C_8H_{12}BrI$. Calculated, %: C 30.50;H 3.84.

***endo*-7-Iodo-*anti*-6-methyl-*syn*-6-chlorobicyclo-[3.1.1]heptane (IIIh)**. Oily fluid, R_f 0.71, R_t 3.50 min (150°C). IR spectrum (thin film), ν, cm^{-1}: 2943 v.s, 2860 w, 1440 s, 1195 s, 1132 m, 1103 s, 815 s, 719 w, 570 w, 501 w. ^{1}H NMR spectrum, δ, ppm: 4.61 t (1H, H^7, *J* 5.6 Hz), 2.60 br.d (2H, H^{1,5}, *J* 5.6 Hz), 2.46–2.30 m (2H, H^{2,4}), 2.10–1.96 m (2H, H^{2,4}), 1.87 s (3H, Me), 1.82–1.55 m (2H, H^3). ^{13}C NMR spectrum, δ, ppm: 11.2 (C^3), 27.5 (Me), 28.5 (C^7), 28.7 (C^{2,4}), 51.9 (C^{1,5}), 66.8 (C^6). Found, %: C 35.73; H 4.53. $C_8H_{12}ClI$. Calculated, %: C 35.52; H 4.47.

The expected product of reaction 6 (NIS+KI), diiodide **IIIf**, was not detected. By vacuum distillation was instead isolated olefin **IV** containing an admixture of two unidentified compounds (~23% according to GLC).

Reaction of hydrocarbon II with elemental iodine in DMF in the presence of KSCN. To a solution of 7.76 g KSCN in 30 ml of anhydrous DMF was added 0.86 g of hydrocarbon **II**, and at cooling to 0°C was added dropwise while stirring under nitrogen within 30 min a solution of 2.00 g of I_2 in15 ml of the same solvent. The reaction mixture was stirred at cooling for 1.5 h and worked up as above. ***endo*-7-Iodo-*anti*-6-methyl-*syn*-6-thiocyanobicyclo[3.1.1]heptane (IIIe)** was isolated from the oily residue by flash chromatography.

Reaction of hydrocarbon II with ICl in DMF in the presence of LiCl. To a dispersion of 4.25 g of lithium chloride in 30 ml of anhydrous DMF was added 1.08 g of hydrocarbon **II**, and then under nitrogen at cooling to –5–0°C added dropwise while stirring within 30 min a solution of 1.63 g of iodine monochloride in 15 ml of the same solvent. The reaction mixture was stirred at cooling for 1.5 h and worked up as above. The solid residue was subjected to flash-chromatography to isolate ***endo*-7-iodo-*anti*-6-methyl-*syn*-6-chlorobicyclo-[3.1.1]heptane (IIIh)**.

Reaction of hydrocarbon II with elemental iodine in CCl_4. To a solution of 1.08 g of compound **II** in 15 ml of anhydrous CCl_4 at stirring under inert atmosphere and with external cooling by an ice bath was added dropwise within 30 min a solution of 2.55 g of I_2 in 15 ml of the same solvent. The mixture was stirred at 20°C for 1 h, washed with 10 ml of 5% Na_2SO_3, with water, and dried on $CaCl_2$. No signals originating from norpinane **IIIf** were revealed in the ^{1}H NMR spectrum of the crude reaction product. After evaporation of the solvent in 0.164 g (yield 7%) of volatile oily substance was isolated of bp 55–57°C (1 mm Hg.). According to GLC data the substance contained compound **IV** and two unidentified impurities in a ratio 82:13:5.

***endo*-7-Iodo-6-methylenebicyclo[3.1.1]heptane (IV).** To a solution of 1.00 g of bicycloheptane **IIIa** in 20 ml of anhydrous THF was added 1.34 g of potassium

tert-butylate powder. The mixture was heated under reflux in the argon atmosphere for 3 h, then cooled and filtered through a 1 cm bed of Al_2O_3. The precipitate on the filter was washed with 10 ml of THF, the solvent was removed under reduced pressure. Compound **IV** was isolated by vacuum distillation in amount of 0.63 g (yield 90%) as a transparent off-rosy oily substance, bp 56–58°C (1 mm Hg.), R_f 0.8, R_t 2.15 min (130°C). IR spectrum (thin film), ν, cm^{-1}: 3075 w, 2944 s, 2860 m, 1681 w, 1440 s, 1277 w, 1196 m, 1095 s, 881 m, 816 m, 798 s, 717 s. ^{1}H NMR spectrum, δ, ppm: 4.88 s (2H, CH_2=), 4.65 t (1H, H^7, *J* 6.0 Hz), 2.93 br.s (2H, $H^{1,5}$), 1.92–2.10 m (4H, $H^{2,4}$), 1.60–1.72 m (1H, *exo*-H^3) and 1.41–1.56 m (1H, *endo*-H^3). ^{13}C NMR spectrum, δ, ppm: 15.3 (C^3), 31.2 ($C^{2,4}$), 35.8 (C^7), 50.3 ($C^{1,5}$), 102.7 (CH_2=), 146.3 (C^6). Found, %: C 41.13; H 4.88. $C_8H_{11}I$. Calculated, %: C 41.05; H 4.74.

Methoxymercuration of tricycloheptane (II). To a mixture of 3.19 g of $Hg(OAc)_2$ and 15 ml of anhydrous methanol stirred under argon was added dropwise within 10 min a solution of 1.08 g of compound **II** in 5 ml of MeOH. The reaction mixture was stirred at 20°C for 0.5 h, then 5 ml of saturated NaCl solution was added, and the stirring was carried on for 1 h more. The most of solvent was removed under a slightly reduced pressure. The precipitate was filtered off, washed with water (2×10 ml), and dried in air. Crystallization from $CHCl_3$ afforded 2.81 g (yield 75%) of ***anti*-6-methyl-*syn*-6-methoxy-7-*endo*-chloromercurobicyclo[3.1.1]-heptane (Va)**, mp 105–106°C [publ.: mp 107°C (from methanol) [5]]. ^{1}H NMR spectrum, δ, ppm(m. [5]): 3.21 s (3H, OMe), 2.85 t (1H, H^7, *J* 5.5 Hz), 2.55–2.62 m (2H, $H^{1,5}$), 2.00–2.14 m (2H, $H^{2,4}$), 1.88–2.00 m (2H, $H^{2,4}$), 1.67–1.78 m (2H, H^3), 1.42 s (3H, Me).

A similar reaction at the use instead of NaCl solution a solution of KI afforded after crystallization from chloroform 3.15 g (yield 70%) of **7-*endo*-iodomercuro-*anti*-6-methyl-*syn*-6-methoxybicyclo[3.1.1]heptane (Vb)**, mp 114–115°C. ^{1}H NMR spectrum, δ, ppm: 3.22 s (3H, OMe), 2.95 t (1H, H^7, *J* 5.5 Hz), 2.59–2.63 m (2H, $H^{1,5}$), 2.09–2.13 m (2H, $H^{2,4}$), 1.85–2.09 m (2H, $H^{2,4}$), 1.72–1.80 m (2H, H^3), 1.41 s (3H, Me). Found, %: C 23.13; H 3.87. $C_9H_{15}HgIO$. Calculated, %: C 23.16; H 3.24.

Iododemercuration of compound (Vb). The organomercury compound **Vb** was dissolved in 30 ml of anhydrous ethyl ether, and thereto was added at stirring a solution of 1.78 g of I_2 in 10 ml of the same solvent. The reaction mixture was stirred at 20°C for 10 h. The precipitate of HgI_2 was filtered off, the filtrate was washed with 10 ml of 5% Na_2SO_3 solution and water, and dried on $MgSO_4$. On removing the ether at the slightly reduced pressure we obtained 1.6 g (yield 86%) of a mixture of compound **IIIa** and ***exo*-7-iodo-*anti*-6-methyl-*syn*-6-methoxybicyclo[3.1.1]-heptane (VI)**, R_t 4.37 min (130°C), in a ratio 42:58 as a colorless transparent oily substance, getting dark at storage. In the ^{1}H NMR spectrum of the mixture obtained were observed signals corresponding to compound **IIIa** [4.50 t (1H, H^7, *J* 6.0 Hz), 3.27 s (3H, OMe), 2.45m br.d (2H, $H^{1,5}$), 1.45 s (3H, Me)] and to compound **VI** [4.03 s (1H, H^7), 3.20 s (3H, OMe), 2.52 br.s (2H, $H^{1,5}$), 1.89 s (3H, Me)].

The study was carried out under financial support of the Ministry of Education of the Russian Federation (grants nos.E 00-5.0-30 and E 02-5.0-361).

REFERENCES

1. Vasin, V.A., Semenov, A.V., and Razin, V.V., *Zh. Org. Khim.,* 2002, vol. 38, p. 845.
2. Wiberg, K.B. and Hess, B.A., *J. Org. Chem.,* 1966, vol. 31, p. 2250.
3. Razin, V.V., Vasin, V.A., and Blinkov, I.E., *Zh. Org. Khim.,* 1993, vol. 29, p. 916.
4. Razin, V.V., *Sovr. Problemy Organ Khimii*, Izd. SPb. Univ., no. 11, 1996, p. 54; Christl, M., *Advances in Strain in Organic, Chemistry*, 1995, vol. 4, p. 163.
5. Müller, E., *Chem. Ber*., 1975, vol. 108, p. 1401.
6. Makarova, L.G. and Nesmeyanov, A.N., *Metody elementorganicheskoi khimii. Rtut'* (Methods of Organoelemental Chemistry. Mercury), Moscow: Nauka, 1965, p. 115; Larock, R. C., *Organomercury compounds in organic synthesis,* Heidelberg: Springer-Verlag, 1985, p. 158.
7. Mazur, S., Schruder, A.H., and Weiss, M.C., *Chem. Commun*., 1977, p. 262.
8. Vasin, V.A., Kostryukov, S.G., Romanova, E.V., Bolusheva, I.Yu., and Razin, V.V., *Zh. Org. Khim.,* 1996, vol. 32, p. 1701.
9. Closs, G.L. and Closs, L.E., *J. Am. Chem. Soc*., 1963, vol. 85, p. 2022; Razin, V.V, Eremenko, M.V, and Ogloblin, K.A., *Zh. Org. Khim.,* 1978, vol. 14, p. 973.
10. Chaikovskii, V.K., Skorokhodov, V.I., and Filimonov, V.D., *Zh. Org. Khim.,* 2001, vol. 37, p. 1572.
11. Sheldrick, G.M., *SHELXTL, v. 5.10, Structure Determination Software Suite*, Bruker AXS, Madison, Wisconsin, USA, 1998.