ISSN 1070-4280, Russian Journal of Organic Chemistry, 2012, Vol. 48, No. 4, pp. 494–504. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © V.A. Vasin, P.S. Petrov, S.G. Kostryukov, V.V. Razin, 2012, published in Zhurnal Organicheskoi Khimii, 2012, Vol. 48, No. 4, pp. 496–506.

Adducts of Tricyclo[4.1.0.0^{2,7}]heptane Hydrocarbons with Methane- and Halomethanesulfonyl Thiocyanates and Their Transformations in the Presence of Bases (Nucleophiles)

V. A. Vasin[a], P. S. Petrov[a], S. G. Kostryukov[a], and V. V. Razin[b]

[a] *Ogarev Mordovian State University, ul. Bol'shevistskaya 68, Saransk, 430005 Russia*
e-mail: vasin@mrsu.ru

[b] *St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia*

Received June 22, 2011

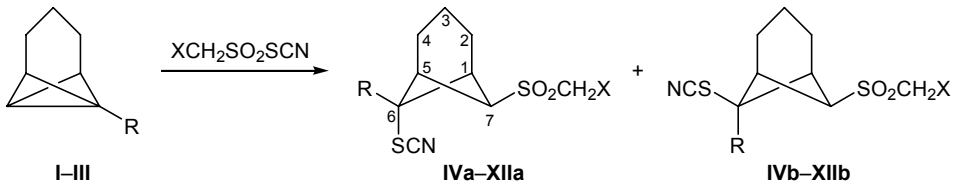
Abstract—1-R-Tricyclo[4.1.0.0^{2,7}]heptanes (R = H, Me, Ph) take up methane- and halomethanesulfonyl thiocyanates XCH_2SO_2SCN (X = H, Cl, Br) at the central C^1–C^7 bond in benzene at 20°C with high *anti*-selectivity to give bicyclo[3.1.1]heptane derivatives with the 7-*endo*-oriented sulfonyl group and the thiocyanato group in the geminal position with respect to the R substituent. The *syn*-adducts lose HSCN molecule by the action of potassium *tert*-butoxide in THF at 0°C or on heating in boiling aqueous dioxane containing NaOH with formation of 1-(X-methylsulfonyl)tricyclo[4.1.0.0^{2,7}]heptanes. Under analogous conditions the *anti*-adducts (X = Me) are converted into 1,2-bis(7-*syn*-methylsulfonyl-6-*endo*-R-bicyclo[3.1.1]hept-6-*exo*-yl)disulfanes. The *anti*-adduct derived from unsubstituted tricyclo[4.1.0.0^{2,7}]heptane and $MeSO_2SCN$ reacted with methyllithium or phenylmagnesium bromide to produce 7-*anti*-methyl(phenyl)sulfanyl-6-*endo*-methylsulfonylbicyclo[3.1.1]heptanes which were also obtained by photochemical addition of $MeSO_2SMe$(or Ph) to tricyclo[4.1.0.0^{2,7}]heptane. Geometric parameters of radical intermediates in the sulfonylation of 1-R-tricyclo[4.1.0.0^{2,7}]heptanes were optimized *ab initio* using 6-31G basis set.

DOI: 10.1134/S1070428012040057

We previously reported [1–6] on the addition of arene- and methanesulfonyl halides at the central bicyclobutane bond in tricyclo[4.1.0.0^{2,7}]heptanes **I**–**III**. In keeping with the proposed radical mechanism, the addition is initiated by strict *endo* attack by sulfonyl radical on the unsubstituted position at the C^1–C^7 bond to produce a mixture of *syn*- and *anti*-adducts having norpinane structure, the *anti*-adduct prevailing. We also showed [7] that sulfur-containing derivatives of arenesulfonic acids, such as $ArSO_2SPh$ and $ArSO_2SCN$, react with tricycloheptane **I** in a similar way with moderate *anti*-stereoselectivity. In continuation of our studies on regio- and stereoselectivity of radical sulfonylation of tricycloheptane derivatives, in the present work we examined reactions of compounds **I**–**III** with methane-, chloromethane-, and bromomethanesulfonyl thiocyanates. The expected products, i.e., norpinane derivatives having sulfonyl and thiocyanato groups, attract interest as subjects for subsequent transformations in reactions with bases (nucleophiles), and some results of such transformations are reported here. The radical addition of methanesulfonyl thiocyanate at multiple carbon–carbon bonds was described in [8], whereas there are no published data on analogous reactions with chloro- and bromomethanesulfonyl thiocyanates.

The initial sulfonyl thiocyanates were synthesized from methane- and halomethanesulfonyl halides which were reduced to the corresponding methanesulfinates with Na_2SO_3 in the presence of $NaHCO_3$ in aqueous medium at 20°C. Methanesulfinates thus obtained were converted into sulfonyl thiocyanates by treatment of their aqueous solutions with a solution of dirhodan in benzene according to the procedure described in [9]. As a result, we obtained a solution of the corresponding sulfonyl thiocyanate in benzene which was subjected to further transformations without isolation or purification. The reactions were performed with equimolar amounts of compounds **I**–**III** in benzene at 20°C (reaction time 6−14 h; TLC monitoring) without resorting to special initiation (Table 1, Scheme 1). From unsubstituted tricycloheptane **I** we obtained in

Scheme 1.



I, **IV**–**VI**, R = H; **II**, **VII**–**IX**, R = Me; **III**, **X**–**XII**, R = Ph; **IV**, **VII**, **X**, X = H; **V**, **VIII**, **XI**, X = Cl; **VI**, **IX**, **XII**, X = Br.

each case a mixture of norpinane *anti*- and *syn*-adducts **IVa**/**IVb**, **Va**/**Vb**, or **VIa**/**VIb**) ("**a**"–"**b**" ratio 2.5 : 1, 1.8 : 1, and 1.5 : 1, respectively, according to the GLC and ^{1}H NMR data). We succeeded in isolating compounds **IVa**–**VIa** and **IVb** as individual substances by column chromatography on silica gel and/or crystallization. Compounds **Vb** and **VIb** were not isolated and were characterized as mixtures with isomers **Va** and **VIa** by ^{1}H and ^{13}C NMR spectroscopy. Among the addition products formed from hydrocarbons **II** and **III**, only major *anti*-adducts **VIIa**–**XIIa** were isolated. However, their ^{1}H NMR spectra contained weak signals some of which could be assigned to *syn*-adducts **VIIb**–**XIIb**.

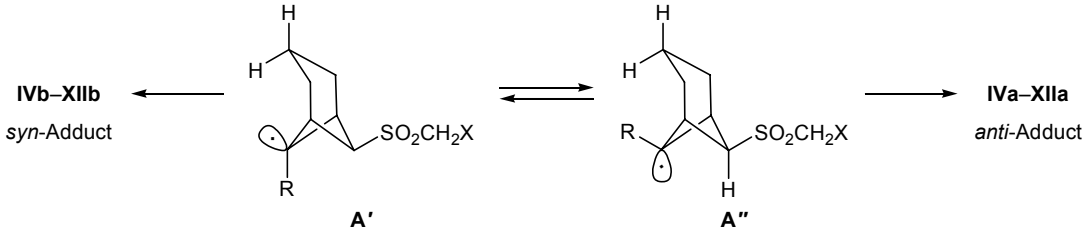
The structure of compounds **IV**–**XII** was determined on the basis of spectral data. Their IR spectra contained strong absorption bands at ~1150 and 1300 cm^{-1}, which are typical of symmetric and antisymmetric stretching vibrations of sulfonyl group. The thiocyanato group in **IV**–**XII** gave rise to a medium-intensity IR band at ~2150 cm^{-1}, and the carbon atom therein resonated in the ^{13}C NMR spectrum at about δ_C 110 ppm. The norpinane structure of the adducts follows from the presence in their ^{13}C NMR spectra of five signals belonging to the carbon skeleton, whose intensity and position were typical of structurally related compounds. Likewise, the position of signals from carbon atoms in the methyl- and halomethylsulfonyl groups was typical of such groups in model compounds [2, 5, 6]. The configuration of C^6 and C^7 was assigned by analysis of multiplicity and position of the 6-H and 7-H proton signals in the ^{1}H NMR spectrum with account taken of Wiberg's data [10]. The triplet signal of 7-H indicates its *anti* orientation. Likewise, singlet or triplet signal from 6-H corresponds to its *endo* or *exo* orientation in isomers **IVa**–**VIa** and **IVb**–**VIb**, respectively. The *exo* orientation of the SCN group in **VIIa**–**IXa** was assigned on the basis of similarity of the chemical shifts of *anti*-7-H and analogous proton in **IVa**–**VIa**, δ 4.25–4.49 and 4.07–4.27 ppm, respectively. In the case of different configuration of C^6, the *anti*-7-H proton would appear counterposed to CH_3; due to weaker deshielding effect of the latter as compared to SCN (cf. [7, 11]) the 7-H signal would be displaced upfield. In fact, the ^{1}H NMR spectra of the reaction mixtures obtained from compound **II** contained weak triplets at δ 3.70, 3.93, and 3.86 ppm, which are likely to belong to *anti*-7-H in the corresponding *syn*-adducts **VIIb**–**IXb**. Finally, the configuration at C^6 in **Xa**–**XIIa** is confirmed by the presence of an upfield one-proton multiplet signal from *endo*-3-H which is shielded by the *endo*-phenyl substituent (cf. [2, 4]).

Thus analysis of the regio- and stereoselectivity of the addition of sulfonyl thiocyanates to tricycloheptanes **I**–**III** led us to conclude that these reactions

Table 1. Reactions of tricycloheptanes **I**–**III** with methane- and halomethanesulfonyl thiocyanates

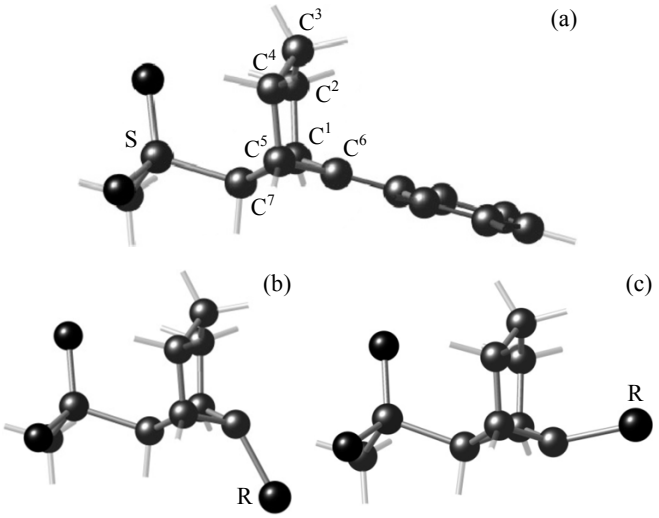
Tricycloheptane no.	Reagent	Reaction time, h	Product	Yield, %	Fraction of the *anti*-adduct, %
I	$MeSO_2SCN$	12	**IVa**, **IVb**	71	71
I	$ClCH_2SO_2SCN$	10	**Va**, **Vb**	49	64
I	$BrCH_2SO_2SCN$	14	**VIa**, **VIb**	30	60
II	$MeSO_2SCN$	11	**VIIa**	64	>93
II	$ClCH_2SO_2SCN$	10	**VIIIa**	44	>95
II	$BrCH_2SO_2SCN$	15	**IXa**	17	>95
III	$MeSO_2SCN$	6	**Xa**	73	>98
III	$ClCH_2SO_2SCN$	6	**XIa**	44	>98
III	$BrCH_2SO_2SCN$	8	**XIIa**	41	>98

Scheme 2.



follow the same pattern as in the addition of other sulfonic acid derivatives. The reactions take radical path involving intermediate norpinan-6-yl radical **A** generated by attack of methylsulfonyl radical on the less substituted bridgehead carbon atom (C^7) with complete inversion of its configuration. The subsequent thiocyanato group transfer to the radical center occurs mainly with retention of configuration, which eventually determines *anti*-stereoselectivity of the addition of sulfonyl thiocyanates at the central C^1–C^7 bond in **I**–**III**.

We previously [12] examined the stereoselectivity in the addition of sulfonyl halides to tricycloheptane compounds with different substituents in a bridgehead position and presumed pyramidal structure of radical intermediate like **A** which initially has conformation **A′** and is capable of undergoing reversible inversion to conformer **A″** (Scheme 2). We believed that the stereoselectivity should be determined by the relative rates of the inversion and transfer processes. The rate of the latter depends not only on the reactivity of reagent as radical species but also on spatial accessibility of the reaction center. We also presumed that high *anti*-selectivity in the sulfonylation of **I**–**III** is determined mainly by steric factors, namely by considerable shielding of the reaction center in **A′** by the trimethylene bridge. Fast and reversible transformation of **A′** into conformer **A″** where the trimethylene bridge exerts no such effect favors predominant formation of *anti*-adducts.



Calculated structures of 6-R-7-*endo*-methylsulfonylnorpinan-6-yl radicals **A**: (a) R = Ph, (b) R = H, Me, invertomer **A′**, and (c) R = H, Me, invertomer **A″**.

Additional information on the steric and electronic structure of intermediate radicals **A** (X = H) was obtained by optimization of their geometric parameters *ab initio* using 6-31G basis set (PC GAMESS 7.1 [13]). The results of calculations showed that the reaction center in the radical with R = Ph is planar and is similar to benzyl radical and that unsubstituted (R = H) and methyl-substituted analogs (R = Me) give rise to two invertomers **A′** and **A″** with different angles α between the C^6–R bond and $C^1C^6C^5$. These invertomers are also characterized by different total energies and energies of the singly occupied molecular orbitals (SOMO) (see figure; Table 2).*

In all cases the C^3H_2 fragment deviates from the $C^1C^2C^4C^5$ plane toward C^6, as follows from the dihedral angles β between the $C^1C^2C^4C^5$ and $C^2C^3C^4$ planes (Table 2). Comparison of the interatomic distances *anti*-7-H···C^6 (l_1) and *endo*-3-H···C^6 (l_2) in structures **A′** and **A″** showed that that steric shielding of the reaction center by the trimethylene bridge is not as significant as it may seem at first glance. Nevertheless, its effect cannot be ruled out completely, especially taking into account participation in the chain transfer process of such bulky reagents as sulfonic acid derivatives (which should approach the reaction center at a definite angle) and differences in the interplanar angles γ ($C^1C^2C^4C^5/C^1C^6C^5$) and δ ($C^1C^6C^5/C^1C^7C^5$) in the intermediates. Presumably, the stereoselectivity of the addition in the examined reactions (assuming high rate of invertomer interconversion) is determined by

* The calculations revealed energy-degenerate mirror isomers for each invertomer **A′** and **A″**, which differed by orientation of the methyl group in the methylsulfonyl fragment with respect to the $C^3C^6C^7$ plane.

Table 2. Calculated geometric parameters, relative energies ΔE (kcal/mol), and energies of singly occupied molecular orbitals E_{SOMO} (eV) of methylsulfonyl-substituted norpinanyl radicals **A**

R in **A**	Conformer	Angle, deg		Interatomic distance, Å		ΔE, kcal/mol	E_{SOMO}, eV
		α	β	l_1	l_2		
H	**A′**	149.7	151.2	2.490	2.815	0.78	–0.3575
	A″	–157.3	152.5	2.485	2.848	0.00	–0.3683
Me	**A′**	149.3	151.7	2.491	2.829	1.08	–0.3384
	A″	–159.8	157.4	2.486	2.962	0.00	–0.3435
Ph	**A′** = **A″**	179.4	152.1	2.485	2.838	–	–0.3110

conformational factor: axial approach of reagent to the *boat*-like conformation of the six-membered $C^1C^2C^3C^4C^5C^6$ ring in phenyl-substituted radical **A** and invertomers **A′** is less favorable than equatorial approach to the same radical **A** and invertomers **A″** (cf. [14]). The smaller effective volume of hydrogen atom (compared to other substituents) at the radical center is responsible for somewhat lower selectivity in the reactions of tricycloheptane **I** compared to **II** and **III**.

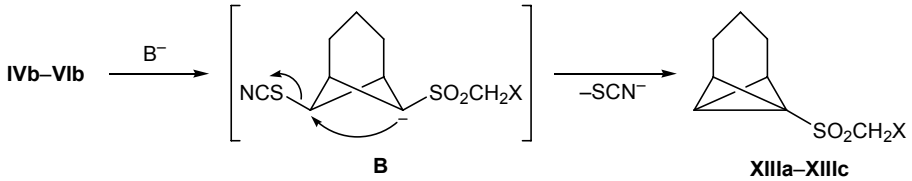
Apart from steric factors, the selectivity of the addition can also be affected by electronic factors, i.e., by different SOMO energies of the invertomers whose electrophilic nature is determined by the presence of an electron-withdrawing substituent in norpinanyl radicals **A**. The calculated (RHF/6-31G) energies of the frontier molecular orbitals of $MeSO_2SCN$ (E_{HOMO} = –0.4266, E_{LUMO} = –0.0227 eV) suggest preferential reaction with invertomers **A″** whose SOMO energy is closer to the HOMO energy of methanesulfonyl thiocyanate, as compared to **A′** [15]. Presumably, the relations revealed by quantum-chemical calculations are also inherent to intermediates in the reactions of **I**–**III** with halomethanesulfonyl thiocyanates.

Some stereoisomeric 7-sulfonylnorpinan-6-yl thiocyanates were subjected to the action of various bases (nucleophiles). Treatment of *syn*-adducts **IVb**–**VIb** with potassium *tert*-butoxide in THF at 0°C, as well as heating in a boiling solution of NaOH in aqueous dioxane, resulted in elimination of HSCN molecule with formation of known [5, 6] 1-methylsulfonyl-substituted tricycloheptanes **XIIIa**–**XIIIc**. The reaction is likely to involve intermediate formation of α-sulfonyl carbanion **B**, and intramolecular S_N2 substitution in the latter conforms to stereoelectronic requirements (rear attack) with the SCN group acting as pseudohalide ion (Scheme 3; cf. [3]).

Examples of formation of unsaturated sulfones via E_1cb elimination of HSCN from adducts derived from alkenes and arenesulfonyl thiocyanates were reported previously [8, 9, 16]. We have synthesized known [17, 18] methyl (*E*)-2-phenylethenyl sulfones **XVa**–**XVc** by dehydrothiocyanation of the styrene adducts with methane- and chloro- and bromomethanesulfonyl thiocyanates **XIVa**–**XIVc** prepared under UV initiation (Scheme 4).

1,3-Elimination of HSCN from norpinane *anti*-adducts **IVa**, **VIIa**, and **Xa** is forbidden for stereoelectronic reasons. Therefore, their reactions with hard nucleophiles, potassium *tert*-butoxide in THF at 0°C or NaOH in aqueous dioxane on heating, involved the *sp*-carbon atom in the SCN group and resulted in cleavage of the latter with formation of thiolate ion which was oxidized with atmospheric oxygen to produce disulfanes **XVI**–**XVIII** (Scheme 5; cf. [19]). Heating of *anti*-adduct **XIa** with sodium hydroxide in aqueous dioxane for a longer time afforded 42% of unsaturated disulfane **XIX**, which was formed from intermediate chlorine-containing disulfane analogous to **XVIII** via the Ramberg–Bäcklund reaction (cf. [2, 5]). We plan to optimize the conditions for the tandem process

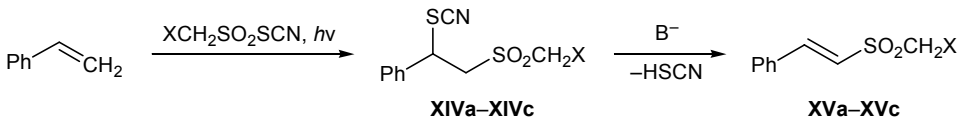
Scheme 3.



B **XIIIa–XIIIc**

X = H (**a**), Cl (**b**), Br (**c**).

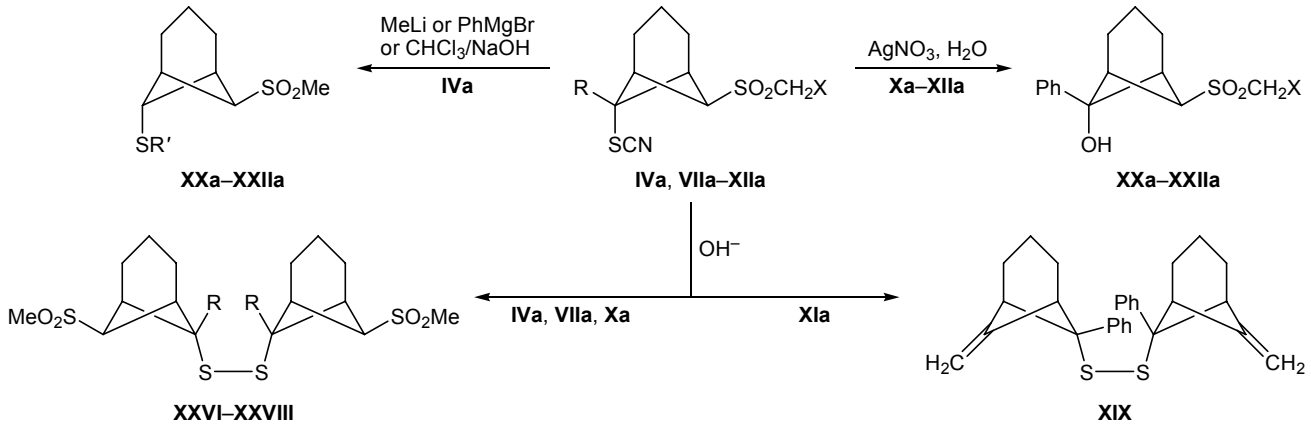
Scheme 4.



XIVa–XIVc **XVa–XVc**

X = H (**a**), Cl (**b**), Br (**c**).

Scheme 5.



XXa–XXIIa **IVa**, **VIIa–XIIa** **XXa–XXIIa**

XXVI–XXVIII **XIX**

IVa, **XVI**, R = H; **VIIa–IXa**, **XVII**, R = Me; **Xa–XIIa**, **XVIII**, R = Ph; **XXa**, R′ = Me; **XXIa**, R′ = Ph; **XXIIa**, R′ = CCl_3; **IVa**, **VIIa**, **Xa**, **XXIII**, X = H; **VIIIa**, **XIa**, **XXIV**, X = Cl; **IXa**, **XIIa**, **XXV**, X = Br.

ensuring the transformation of halogenated norpinanes **VIIIa**, **IXa**, **XIa**, and **XIIa** into unsaturated disulfanes like **XIX**.

Soft carbon-centered nucleophiles, such as methyllithium and phenylmagnesium bromide, also reacted with *anti*-adduct **IVa** at the SCN group, but the reaction center was the sulfur atom, and nucleophilic replacement of cyanide ion gave sulfides **XXa** and **XXIa**, respectively [19]. The structure of compounds **XXa** and **XXIa** was proved by their independent synthesis via photochemical reaction of tricycloheptane **I** with *S*-methyl and *S*-phenyl methanesulfonothioates (cf. [7]); these reactions were accompanied by formation of epimeric *syn*-adducts **XXb** and **XXIb**. Likewise, *anti*-adduct **IVa** reacted with chloroform in the presence of 40% aqueous NaOH and a phase-transfer catalyst to produce sulfide **XXIIa** (cf. [20]).

Finally, we have found that compounds **Xa–XIIa** are quantitatively converted into tertiary alcohols **XXIII–XXV** by the action of $AgNO_3$ in aqueous dioxane at 20°C. Here, the SCN group is replaced with retention of configuration. Presumably, the reaction follows the S_N1 mechanism, and high *exo*-selectivity of nucleophilic attack on the corresponding benzylic carbocation is its specific feature, as we noted in [2].

The described sulfonylation of tricycloheptane hydrocarbons may be regarded as a convenient synthetic route to substituted norpinane derivatives containing sulfonyl and thiocyanato groups; subsequent chemical modification of the latter could extend the series of preparatively accessible compounds of this type.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on a Bruker DPX-300 spectrometer at 300.13 and 75.47 MHz, respectively, using the residual proton and carbon signals of the solvent as reference. The IR spectra were measured in KBr on an InfraLYuM FT-02 spectrometer with Fourier transform (in all cases, frequencies of 10 most intense absorption bands are given). GLC analyses were performed on a KristallLyuks-4000 chromatograph equipped with a flame-ionization detector; carrier gas nitrogen, flow rate 30 ml/min; A: 1200×3-mm glass column packed with 3% of OV-225 on Inerton N-Super (0.125–0.160 mm), oven temperature 210°C, injector temperature 250°C; B: 1200×3-mm glass column packed with 3% of OV-17 on Inetron N-Super (0.125–0.160 mm), oven temperature 200°C, injector temperature 250°C. Components of reaction mixtures were quantitated by the internal normalization method (by peak area); the calibration factors for all components were assumed to be equal to unity. The chromatograms were processed using NetChrom 1.5 program.

Analytical thin-layer chromatography was performed on Silufol UV-254 plates using hexane–acetone (2:1; thiocyanates and disulfanes) and hexane–diethyl ether (1:1; sulfides) as eluents; spots were visualized by treatment with iodine vapor. Silicagel L (40–100 μm) and aluminum oxide of activity grade II were used for column chromatography; eluent petroleum ether–acetone (6:1). The elemental compositions were determined on an HP-185B CHN analyzer.

Tricycloheptanes **I** [21], **II** [22], and **III**** [23], bromomethanesulfonyl bromide [24], chloromethanesulfonyl chloride [25], *S*-methyl methanethiosulfonate [26], and *S*-phenyl methanethiosulfonate [27] were synthesized by known methods. Commercial methanesulfonyl chloride (Merck) contained more than 99% of the main substance.

Quantum-chemical calculations in terms of RHF approximation using 6-31G basis set with initial PM3 parameterization were performed using PC GAMESS 7.1 software [13].

Reaction of tricycloheptanes I–III with methanesulfonyl thiocyanates (*general procedure*). Sulfonyl halide $MeSO_2Cl$, $ClCH_2SO_2Cl$, or $BrCH_2SO_2Br$, 15.6 mmol, was added under vigorous stirring over a period of 10–20 min to a mixture of 1.96 g (15.6 mmol) of Na_2SO_3 and 2.62 g (31.2 mol) of $NaHCO_3$ in 64 ml of water. The mixture was stirred for 2 h at 20°C, and unreacted sulfonyl halide was removed by extraction with benzene (3 × 15 ml). A freshly prepared solution of dirhodan [obtained by treatment of a suspension of 4.52 g (14 mmol) of thoroughly dried $Pb(SCN)_2$ in 20 ml of anhydrous benzene with a solution of 0.65 ml (2.0 g, 12.5 mmol) of bromine in 20 ml of benzene] was added to the aqueous phase, and the mixture was vigorously shaken in a separatory funnel. The organic phase was separated, dried for 5 min by stirring with anhydrous $CaCl_2$, and immediately added (without additional purification) to a solution of 10 mmol of tricycloheptane **I–III** in 10 ml of anhydrous benzene. The mixture was kept for 6–14 h at 20°C in a tightly capped flask, the progress of the reaction being monitored by TLC. The solvent was removed under reduced pressure (water-jet pump), and the solid residue was analyzed by GLC, column A) and/or ^{1}H NMR and subjected to column chromatography on silica gel or crystallization.

7-*syn*-Methylsulfonylbicyclo[3.1.1]hept-6-*exo*-yl thiocyanate (IVa). mp 152–153°C (from acetone–hexane), R_f 0.29, R_t 12.3 min. IR spectrum, ν, cm^{-1}: 2967 w, 2160 m, 1335 m, 1300 m, 1289 s, 1258 m, 1134 v.s, 748 m, 556 m, 478 m. ^{1}H NMR spectrum, δ, ppm: 1.75–1.93 m (1H, *endo*-3-H), 1.95–2.13 m (3H, *exo*-3-H, *endo*-2-H, *endo*-4-H), 2.59–2.73 m (2H, *exo*-2-H, *exo*-4-H), 2.92 s (3H, Me), 2.98 br.d (2H, 1-H, 5-H), 3.77 s (1H, *endo*-6-H), 4.07 t (1H, *anti*-7-H, J = 5.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.4 (C^3), 24.0 (C^2, C^4), 41.9 (Me), 44.3 (C^1, C^5), 48.0 (C^6), 57.8 (C^7), 110.7 (SCN). Found, %: C 47.81; H 5.72; N 5.94. $C_9H_{13}NO_2S_2$. Calculated, %: C 46.73; H 5.66; N 6.05.

7-*syn*-Methylsulfonylbicyclo[3.1.1]hept-6-*endo*-yl thiocyanate (IVb). mp 71–72°C (from acetone–hexane), R_f 0.14, R_t 23.8 min. ^{1}H NMR spectrum, δ, ppm: 1.65–1.77 m and 2.05–2.14 m (1H each, 3-H), 1.90–2.05 m and 2.44–2.59 m (2H each, 2-H, 4-H), 2.91 s (3H, SO_2Me), 3.20 br.t (2H, 1-H, 5-H, J = 5.7 Hz), 3.43 t (1H, *exo*-6-H, J = 5.7 Hz), 3.97 t (1H, *anti*-7-H, J = 5.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.4 (C^3), 19.9 (C^2, C^4), 42.0 (SO_2Me), 43.2 (C^1, C^5), (Me), 47.6 (C^6), 57.1 (C^7), 111.1 (SCN). Found, %: C 46.84; H 5.73; N 6.11. $C_9H_{13}NO_2S_2$. Calculated, %: C 46.73; H 5.66; N 6.05.

7-*syn*-Chloromethylsulfonylbicyclo[3.1.1]hept-6-*endo*-yl thiocyanate (Va). mp 104–105°C (from $CHCl_3$–hexane), R_f 0.14, R_t 16.9 min. IR spectrum, ν, cm^{-1}: 2157 m, 1339 m, 1308 s, 1289 m, 1262 m, 1142 v.s, 1127 m, 606 s, 490 m. ^{1}H NMR spectrum, δ, ppm: 1.75–1.94 m (1H, *endo*-3-H), 1.95–2.13 m (3H, *exo*-3-H, *endo*-2-H, *endo*-4-H), 2.56–2.72 m (2H, *exo*-2-H, *exo*-4-H), 2.99 br.d (2H, 1-H, 5-H, J = 5.6 Hz), 3.74 s (1H, *endo*-6-H), 4.26 t (1H, *anti*-7-H, J = 5.8 Hz), 4.46 s (2H, CH_2Cl). ^{13}C NMR spectrum, δ_C, ppm: 13.4 (C^3), 24.4 (C^2, C^4), 45.2 (C^1, C^5), 48.9 (C^6), 55.6 (CH_2Cl), 57.4 (C^7), 110.5 (SCN). Found, %: C 40.52; H 4.59; N 5.32. $C_9H_{12}ClNO_2S_2$. Calculated, %: C 40.67; H 4.55; N 5.27.

7-*syn*-Chloromethylsulfonylbicyclo[3.1.1]hept-6-*endo*-yl thiocyanate (Vb) was isolated by fractional crystallization; stereochemical purity 80%, R_t 29.5 min. ^{1}H NMR spectrum, δ, ppm: 1.70–2.13 m (4H, 3-H, *endo*-2-H, *endo*-4-H; overlapped by the signal of **Va**), 2.42–2.56 m (2H, *exo*-2-H, *exo*-4-H), 3.19 br.t (2H, 1-H, 5-H, J = 5.4 Hz), 3.64 t (1H, *exo*-6-H, J = 5.4 Hz), 4.00 t (1H, *anti*-7-H, J = 5.4 Hz), 4.44 s (2H, CH_2Cl). ^{13}C NMR spectrum, δ_C, ppm: 12.5 (C^3), 20.2 (C^2, C^4), 44.2 (C^1, C^5), 47.9 (C^6), 54.7 (CH_2Cl), 57.4 (C^7), 110.9 (SCN). Found, %: C 40.77; H 4.52; N 5.7. $C_9H_{12}ClNO_2S_2$. Calculated, %: C 40.67; H 4.55; N 5.27.

7-*syn*-Bromomethylsulfonylbicyclo[3.1.1]hept-6-*exo*-yl thiocyanate (VIa). mp 91–92°C (from ace-

** Compound **II** contained ~8% of octane, and compound **III**, ~13% of 1-phenyltricyclo[4.1.0.0^{3,7}]heptane.

tone–hexane), R_f 0.60, R_t 5.5 min. IR spectrum, ν, cm^{-1}: 2951 m, 2944 m, 2157 s, 1335 m, 1308 s, 1289 m, 1138 v.s, 1100 m, 756 m, 536 s. ^1H NMR spectrum, δ, ppm: 1.80–1.94 m (1H, *syn*-3-H), 2.00–2.16 m (3H, *endo*-3-H, *endo*-2-H, *endo*-4-H), 2.61–2.74 m (2H, *exo*-2-H, *exo*-4-H), 3.04 br.s (2H, 1-H, 5-H), 3.77 s (1H, *endo*-6-H), 4.33 t (1H, *anti*-7-H, J = 5.5 Hz), 4.39 s (2H, CH_2Br). ^{13}C NMR spectrum, δ_C, ppm: 13.4 (C^3), 24.3 (C^2, C^4), 43.0 (CH_2Br), 45.4 (C^1, C^5), 48.8 (C^6), 55.9 (C^7), 110.6 (SCN). Found, %: C 34.94; H 4.02; N 4.45. $C_9H_{12}BrNO_2S_2$. Calculated, %: C 34.85; H 3.90; N 4.52.

7-*syn*-Bromomethylsulfonylbicyclo[3.1.1]hept-6-*endo*-yl thiocyanate (VIb) was isolated by fractional crystallization. Stereochemical purity 67%, R_f 0.35, R_t 9.3 min. ^1H NMR spectrum (a fragment), δ, ppm: 1.65–2.10 m (4H, 3-H, *endo*-2-H, *endo*-4-H; overlapped by the signal of **VIa**), 2.40–2.55 m (2H, *exo*-2-H, 4-H), 3.18 br.t (2H, 1-H, 5-H, J = 5.5 Hz), 3.60 t (1H, *exo*-6-H, J = 5.4 Hz), 3.97 t (1H, *anti*-7-H, J = 5.4 Hz), 4.34 s (2H, CH_2Br). ^{13}C NMR spectrum, δ_C, ppm: 12.7 (C^3), 20.3 (C^2, C^4), 42.0 (CH_2Br), 43.2 (C^1, C^5), 45.0 (C^6), 55.7 (C^7), 110.9 (SCN). Found, %: C 34.88; H 3.93; N 4.41. $C_9H_{12}BrNO_2S_2$. Calculated, %: C 34.85; H 3.90; N 4.52.

6-*endo*-Methyl-7-*syn*-methylsulfonylbicyclo[3.1.1]hept-6-*exo*-yl thiocyanate (VIIa). mp 119–120°C (from $CHCl_3$–hexane), R_f 0.40. IR spectrum, ν, cm^{-1}: 2150 s, 1291 s, 1283 s, 1267 m, 1208 w, 1140 v.s, 1094 w, 978 w, 750 w, 544 m. ^1H NMR spectrum, δ, ppm: 1.63–1.75 m (1H, *endo*-3-H), 1.77 s (3H, Me), 1.97–2.11 m (2H, *endo*-2-H, *endo*-4-H), 2.13–2.30 m (1H, *exo*-3-H), 2.45–2.59 m (2H, *exo*-2-H, *exo*-4-H), 2.92 br.d (2H, 1-H, 5-H, J = 5.5 Hz), 2.96 s (3H, $MeSO_2$), 4.25 t (1H, *anti*-7-H, J = 5.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.8 (C^3), 19.8 (Me), 22.0 (C^2, C^4), 42.6 ($MeSO_2$), 47.3 (C^1, C^5), 59.5 (C^7), 60.5 (C^6), 110.7 (SCN). Found, %: C 49.03; H 6.27; N 5.67. $C_{10}H_{15}NO_2S_2$. Calculated, %: C 48.95; H 6.16; N 5.71.

7-*syn*-Chloromethylsulfonyl-6-*endo*-methylbicyclo[3.1.1]hept-6-*exo*-yl thiocyanate (VIIIa). mp 126–127°C (from $CHCl_3$–hexane), R_f 0.44. IR spectrum, ν, cm^{-1}: 3002 w, 2936 m, 2145 m, 1335 m, 1304 s, 1154 s, 1119 v.s, 1092 m, 733 s, 532 s, 498 m. ^1H NMR spectrum, δ, ppm: 1.65–1.76 m (1H, *endo*-3-H), 1.77 s (3H, Me), 1.99–2.14 m (2H, *endo*-2-H, *endo*-4-H), 2.14–2.29 m (1H, *exo*-3-H), 2.47–2.62 m (2H, *exo*-2-H, *exo*-4-H), 2.96 br.d (2H, 1-H, 5-H, J = 5.7 Hz), 4.47 t (1H, *anti*-7-H, J = 5.7 Hz), 4.48 s (2H, CH_2Cl). ^{13}C NMR spectrum, δ_C, ppm: 12.6 (C^3), 19.7 (Me), 22.1 (C^2, C^4), 48.1 (C^1, C^5), 56.8 (CH_2Cl), 57.8 (C^7), 60.9 (C^6), 110.6 (SCN). Found, %: C 43.01; H 5.07; N 5.11. $C_{10}H_{14}ClNO_2S_2$. Calculated, %: C 42.93; H 5.04; N 5.01.

7-*syn*-Bromomethylsulfonyl-6-*endo*-methylbicyclo[3.1.1]hept-6-*exo*-yl thiocyanate (IXa). mp 114–115°C (from $CHCl_3$–hexane), R_f 0.42. IR spectrum, ν, cm^{-1}: 2970 w, 2149 s, 1331 m, 1316 s, 1142 v.s, 1096 m, 621 m, 575 m, 552 m, 478 m. ^1H NMR spectrum, δ, ppm: 1.62–1.75 m (1H, *endo*-3-H), 1.76 s (3H, Me), 1.97–2.12 m (2H, *exo*-2-H, *exo*-4-H), 2.13–2.27 m (1H, *exo*-3-H), 2.48–2.61 m (2H, *exo*-2-H, *exo*-4-H), 2.96 br.d (2H, 1-H, 5-H, J = 5.8 Hz), 4.38 s (2H, CH_2Br), 4.49 t (1H, *anti*-7-H, J = 5.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.7 (C^3), 19.7 (Me), 22.1 (C^2, C^4), 43.4 (CH_2Br), 48.5 (C^1, C^5), 57.3 (C^7), 110.5 (SCN). Found, %: C 36.90; H 4.42; N 4.21. $C_{10}H_{14}BrNO_2S_2$. Calculated, %: C 37.04; H 4.35; N 4.32.

7-*syn*-Methylsulfonyl-6-*endo*-phenylbicyclo[3.1.1]hept-6-*exo*-yl thiocyanate (Xa). mp 177–178°C (from $CHCl_3$–hexane). IR spectrum, ν, cm^{-1}: 2965 w, 2153 s, 1455 m, 1337 s, 1287 s, 1140 v.s, 946 w, 754 m, 737 m, 561 m, 530 m. ^1H NMR spectrum, δ, ppm: 0.60–0.79 m (1H, *endo*-3-H), 1.51–1.68 m (1H, *exo*-3-H), 2.09–2.22 m (2H, *endo*-2-H, *endo*-4-H), 2.57–2.71 m (2H, *exo*-2-H, *exo*-4-H), 2.99 s (3H, $MeSO_2$), 3.47 br.d (2H, 1-H, 5-H, J = 5.6 Hz), 4.38 t (1H, *anti*-7-H, J = 5.6 Hz), 7.27 d (2H, H_{arom}, J = 5.6 Hz), 7.37–7.51 (3H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 12.7 (C^3), 22.2 (C^2, C^4), 42.2 (Me), 46.9 (C^1, C^5), 58.0 (C^7), 63.7 (C^6), 110.4 (SCN); 125.3 (2C), 128.5, 129.0 (2C), 137.8 (C_{arom}). Found, %: C 58.57; H 5.66; N 4.46. $C_{15}H_{17}NO_2S_2$. Calculated, %: C 58.60; H 5.57; N 4.56.

7-*syn*-Chloromethylsulfonyl-6-*endo*-phenylbicyclo[3.1.1]hept-6-*exo*-yl thiocyanate (XIa). mp 181–182°C (from $CHCl_3$–hexane). IR spectrum, ν, cm^{-1}: 3011 m, 2149 m, 1456 w, 1337 m, 1304 m, 1156 s, 1115 v.s, 735 m, 704 w, 515 w. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.46–0.66 m (1H, *endo*-3-H), 1.36–1.55 m (1H, *exo*-3-H), 2.04–2.21 m (2H, *endo*-2-H, *endo*-4-H), 2.44–2.57 m (2H, *exo*-2-H, *exo*-4-H), 3.61 br.d (2H, 1-H, 5-H, J = 5.4 Hz), 4.77 t (1H, *anti*-7-H, J = 5.4 Hz), 5.36 s (2H, CH_2Cl), 7.41–7.61 m (5H, H_{arom}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 12.7 (C^3), 22.1 (C^2, C^4), 47.1 (C^1, C^5), 55.5 (CH_2Cl), 57.5 (C^7), 64.1 (C^6), 111.5 (SCN); 125.7 (2C), 128.3, 128.8 (2C), 138.5 (C_{arom}). Found, %: C 52.58; H 4.63; N 4.18. $C_{15}H_{16}ClNO_2S_2$. Calculated, %: C 52.70; H 4.72; N 4.10.

7-*syn*-Bromomethylsulfonyl-6-*endo*-phenylbicyclo[3.1.1]hept-6-*exo*-yl thiocyanate (XIIa). mp 189–

190°C (from $CHCl_3$–hexane). IR spectrum, ν, cm^{-1}: 3017 m, 2944 m, 2149 m, 1335 m, 1298 s, 1138 v.s, 1096 m, 737 m, 702 m, 675 m, 513 m. ^1H NMR spectrum, δ, ppm: 0.62–0.82 m (1H, *endo*-3-H), 1.53–1.71 m (1H, *exo*-3-H), 2.09–2.28 m (2H, *endo*-2-H, *endo*-4-H), 2.57–2.73 m (2H, *exo*-2-H, *exo*-4-H), 3.53 br.d (2H, 1-H, 5-H, J = 5.4 Hz), 4.41 s (2H, CH_2Br), 4.61 t (1H, *anti*-7-H, J 5.4 Hz), 7.26 d (2H, H_{arom}, J = 5.4 Hz), 7.38–7.53 m (3H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 12.6 (C^3), 22.3 (C^2, C^4), 43.2 (CH_2Br), 48.2 (C^1, C^5), 56.5 (C^7), 64.3 (C^6), 110.4 (SCN); 125.3 (2C), 128.5, 129.0 (2C), 137.8 (C_{arom}). Found, %: C 46.71; H 3.99; N 3.52. $C_{15}H_{16}BrNO_2S_2$. Calculated, %: C 46.64; H 4.17; N 3.63.

Reaction of styrene with methanesulfonyl thiocyanates (*general procedure*). A solution of the corresponding sulfonyl thiocyanate in benzene, prepared as described above from 15.6 mmol of $MeSO_2Cl$, $ClCH_2SO_2Cl$, or $BrCH_2SO_2Br$, was immediately mixed with a solution of 10 mmol of freshly distilled styrene in benzene. The mixture was kept for 48–72 h at 20°C, the solvent was removed under reduced pressure, and the solid residue was purified by crystallization to isolate compounds **XIVa**–**XIVc**.

2-Methylsulfonyl-1-phenylethyl thiocyanate (XIVa). Yield 32%, mp 83–84°C (from $CHCl_3$–hexane), R_f 0.18. IR spectrum, ν, cm^{-1}: 2157 m, 1420 s, 1412 m, 1323 s, 1312 s, 1285 v.s, 1146 s, 1138 s, 976 s, 810 m, 748 v.s, 706 s, 498 m, 448 m. ^1H NMR spectrum, δ, ppm: 2.60 s (3H, Me), 3.86 d.d (1H, CH_2, J = 5.1, 14.5 Hz), 3.94 d.d (1H, CH_2, J = 8.7, 14.5 Hz), 4.96 d.d (1H, CH, J = 5.1, 8.7 Hz), 7.48 br.s (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 42.5 (Me), 46.3 (CH_2), 59.4 (CH), 109.9 (SCN); 127.6 (2C), 129.7 (2C), 130.2, 135.2 (C_{arom}). Found, %: C 49.86; H 5.66; N 5.73. $C_{10}H_{11}NO_2S_2$. Calculated, %: C 49.77; H 4.59; N 5.80.

2-Chloromethylsulfonyl-1-phenylethyl thiocyanate (XIVb). Yield 21%, mp 87–88°C (from $CHCl_3$–hexane), R_f 0.23. IR spectrum, ν, cm^{-1}: 2149 m, 1319 v.s, 1308 m, 1277 m, 1239 m, 1150 v.s, 1119 s, 748 m, 698 m, 502 s. ^1H NMR spectrum, δ, ppm: 3.61 d (1H, J = 13.1 Hz), 4.21 d (1H, CH_2Cl, J = 13.1 Hz), 3.86 d.d (1H, CH_2, J = 5.1, 14.9 Hz), 4.27 d.d (1H, CH_2, J = 10.2, 14.9 Hz), 4.96 d.d (1H, CH, J = 5.1, 10.2 Hz), 7.49 br.s (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 46.1 (CH_2), 53.7 (CH_2Cl), 56.6 (CH), 109.6 (SCN); 127.6 (2C), 129.8 (2C), 130.5, 134.2 (C_{arom}). Found, %: C 43.44; H 3.69; N 5.16. $C_{10}H_{10}ClNO_2S_2$. Calculated, %: C 43.55; H 3.66; N 5.08.

2-Bromomethylsulfonyl-1-phenylethyl thiocyanate (XIVc). Yield 26%, mp 95–96°C (from $CHCl_3$–hexane), R_f 0.18. IR spectrum, ν, cm^{-1}: 2944 m, 2149 m, 1316 s, 1308 s, 1274 m, 1138 v.s, 1096 m, 849 m, 702 m, 502 m. ^1H NMR spectrum, δ, ppm: 3.53 d (1H, J = 12.3 Hz), 4.11 d (1H, CH_2Br, J = 12.3 Hz); 3.90 d.d (1H, CH_2, J = 4.8, 14.9 Hz), 4.33 d.d (1H, CH_2, J = 9.8, 14.9 Hz); 4.96 d.d (1H, CH, J = 4.8, 9.8 Hz), 7.50 br.s (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 42.3 (CH_2Br), 46.3 (CH_2), 54.1 (CH), 109.6 (SCN); 127.7 (2C), 129.8 (2C), 130.6, 134.2 (C_{arom}). Found, %: C 37.62; H 3.24; N 4.42. $C_{10}H_{10}BrNO_2S_2$. Calculated, %: C 37.51; H 3.15; N 4.37.

Elimination of HSCN from *syn*-adducts IVb–VIb (*general procedure*). *a*. A mixture of 0.72 g (18 mmol) of NaOH, 20 ml of aqueous dioxane (1:1), and 3 mmol of adduct **IVb**, **Vb**, or **VIb** (compounds **Vb** and **VIb** contained, respectively, 10 and 15% of isomer **Va** or **VIa**) was heated for 3 h under reflux. The mixture was cooled, diluted with five volumes of water, and extracted with CH_2Cl_2 (3×10 ml). The combined extracts were washed with water until neutral reaction, dried over $MgSO_4$, and evaporated, and the residue was purified by flash chromatography on silica gel and crystallization. The yield of tricycloheptanes **XVa**–**XVc** was 69, 52, and 44%, respectively, calculated on the initial *syn*-adduct **IVb**–**VIb**; the properties of the products were consistent with the data of [5, 6].

b. A solution of 0.23 g (1 mmol) of *syn*-adduct **IVb** in 10 ml of anhydrous THF was cooled to 0°C, 0.225 g (2 mmol) of powdered potassium *tert*-butoxide was added under stirring in a stream of argon, the mixture was stirred for 2 h at 0°C and filtered through a 1-cm layer of Al_2O_3, and the precipitate was washed on a filter with 10 ml of anhydrous diethyl ether. The solvent was evaporated, and the residue was recrystallized from $CHCl_3$–hexane (1:3). Yield of tricycloheptane **XVa** 0.126 g (73%).

Elimination of HSCN from adducts XIVa–XIVc (*general procedure*). A solution of 2 mmol of **XIVa**–**XIVc** in 20 ml of THF was treated with 0.3 g (2.7 mmol) of powdered *t*-BuOK as described above in *b* to isolate (*E*)-[(2-methylsulfonyl)-, (*E*)-[(2-chloromethylsulfonyl)-, and (*E*)-[(2-bromomethylsulfonyl)-vinyl]benzenes **XVa**–**XVc** in 67, 54, and 51% yield, respectively. The physical constants and spectral parameters of sulfones **XVa**–**XVc** coincided with those reported in [17, 18].

6-*anti*-Methylsulfanyl-7-*endo*-methylsulfonylbicyclo[3.1.1]heptane (XXa). A solution of 0.23 g

(1 mmol) of compound **IVa** in 15 ml of anhydrous diethyl ether was cooled to –20°C, 3 ml of a 1 M solution of methyllithium in diethyl ether was slowly added under vigorous stirring in an argon atmosphere, and the mixture was stirred for 30 min at –20°C and for 5 h at 20°C, cooled with an ice bath, treated with 10 ml of water, and extracted with diethyl ether (3× 10 ml). The extract was dried over $MgSO_4$, the solvent was removed under reduced pressure, the oily residue was subjected to column chromatography on Al_2O_3, and the eluate was distilled under reduced pressure. Yield 0.19 g (86%), bp 109–110°C (1 mm), R_t 3.6 min (column B), R_f 0.20. IR spectrum, ν, cm^{-1}: 2957 w, 2927 w, 2971 w, 2855 v.w, 1292 m, 1135 m, 730 m, 570 m, 479 w. ^{1}H NMR spectrum, δ, ppm: 1.73–2.01 m (4H, 3-H, *endo*-2-H, *endo*-4-H), 2.10 s (3H, SMe), 2.42–2.62 m (2H, *exo*-2-H, *exo*-4-H), 2.75 br.d (2H, 1-H, 5-H, J = 5.7 Hz), 2.84 s (3H, SO_2Me), 3.07 s (1H, 7-H), 4.07 t (1H, 6-H, J = 5.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.8 (C^3), 14.8 (SMe), 24.1 (C^2, C^4), 41.7 (SO_2Me), 43.4 (C^1, C^5), 47.8 (C^7), 59.3 (C^6). Found, %: C 48.97; H 7.21. $C_9H_{16}O_2S_2$. Calculated, %: C 49.06; H 7.32.

6-*endo*-Methylsulfonyl-7-*anti*-phenylsulfanylbicyclo[3.1.1]heptane (XXIa) was synthesized in a similar way from 0.23 g (1 mmol) of **IVa** in 15 ml of diethyl ether and 4 ml of a 0.8 M solution of PhMgBr in diethyl ether. Crystallization of the crude product from diethyl ether–hexane (1:4) gave 0.25 g (89%) of **XXIa**, mp 136–137°C, R_t 8.0 min (column B), R_f 0.26. IR spectrum, ν, cm^{-1}: 2924 w, 2867 w, 1586 m, 1485 m, 1285 m, 1258 m, 1134 m, 965 w, 745 m, 559 m. ^{1}H NMR spectrum, δ, ppm: 1.80–2.17 m (4H, 3-H, *endo*-2-H, *endo*-4-H), 2.70 br.d (2H, 1-H, 5-H, J = 5.7 Hz), 2.72 s (3H, SO_2Me), 3.58 s (1H, 7-H), 4.16 t (1H, 6-H, J = 5.7 Hz), 7.13–7.37 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 13.6 (C^3), 23.8 (C^2, C^4), 41.6 (SO_2Me), 43.3 (C^1, C^5), 46.8 (C^7), 58.7 (C^6); 126.0, 128.4 (2C), 128.8 (2C), 135.2 (C_{arom}). Found, %: C 59.62; H 6.55. $C_{14}H_{18}O_2S_2$. Calculated, %: C 59.54; H 6.42.

6-*endo*-Methylsulfonyl-7-*anti*-trichloromethylsulfanylbicyclo[3.1.1]heptane (XXIIa). A 1 M solution of sodium hydroxide, 2 ml, was added dropwise under vigorous stirring to a mixture of 0.23 g (1 mmol) of **IVa**, 3 ml of $CHCl_3$, 3 ml of dioxane, and 60 mg of benzyltriethylammonium chloride. The mixture was stirred for 1 h, following disappearance of **IVa** by TLC. The product was extracted into diethyl ether (3×5 ml), the extract was washed with water and dried over $MgSO_4$, the solvent was removed under reduced pressure, and the residue was recrystallized from $CHCl_3$–hexane (1:3). Yield 0.20 g (62%), mp 176–177°C (from $CHCl_3$–hexane). IR spectrum, ν, cm^{-1}: 2955 w, 2936 w, 2870 w, 1285 m (SO_2), 1142 m (SO_2), 864 m, 756 m, 559 m. ^{1}H NMR spectrum, δ, ppm: 1.87–2.17 m (3H, *endo*-3-H, *endo*-2-H, *endo*-4-H), 2.58–2.71 m (2H, *exo*-2-H, *exo*-4-H), 2.88 s (3H, SO_2Me), 3.16 br.d (2H, 1-H, 5-H, J 5.8 Hz), 3.74 s (1H, 7-H), 3.86 t (1H, 6-H, J = 5.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.7 (C^3), 23.9 (C^2, C^4), 41.9 (Me), 44.1 (C^1, C^5), 51.5 (C^7), 59.7 (C^6), 96.2 (CCl_3). Found, %: C 33.44; H 4.19. $C_9H_{13}Cl_3O_2S_2$. Calculated, %: C 33.40; H 4.05.

Reaction of tricycloheptane I with *S*-methyl methanesulfonothioate. A quartz test tube was charged with a solution of 0.94 g (10 mmol) of compound **I** and 1.26 g (10 mmol) of $MeSO_2SMe$ in 8 ml of anhydrous CH_2Cl_2. The test tube was tightly capped, and the mixture was irradiated over a period of 14 h at 20°C with a DRT-400 high-pressure mercury discharge lamp at a distance of ~20 cm. The progress of the reaction was monitored by TLC and GLC. By column chromatography on Al_2O_3 we isolated 1.32 g (60%) of **XXa** and 0.26 g (12%) of **XXb**.

6-*syn*-Methylsulfanyl-7-*endo*-methylsulfonylbicyclo[3.1.1]heptane (XXb). bp 105–108°C (1 mm), R_t 4.5 min (column B), R_f 0.09. ^{1}H NMR spectrum, δ, ppm: 1.72–2.03 m (4H, 3-H, *endo*-2-H, *endo*-4-H), 2.07 s (3H, SMe), 2.09–2.37 m (2H, *exo*-2-H, *exo*-4-H), 2.83 s (3H, SO_2Me), 2.96 br.t (2H, 1-H, 5-H, J = 5.7 Hz), 3.14 t (1H, *anti*-7-H, J = 5.7 Hz), 3.36 t (1H, *exo*-6-H, J = 5.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.3 (C^3), 15.1 (SMe), 20.1 (C^2, C^4), 41.8 (SO_2Me), 42.6 (C^1, C^5), 47.7 (C^7), 58.9 (C^6). Found, %: C 49.15; H 6.99. $C_9H_{16}O_2S_2$. Calculated, %: C 49.06; H 7.32.

Reaction of tricycloheptane I with *S*-phenyl methanesulfonothioate. As described above, irradiation of a solution of 0.94 g (10 mmol) of **I** and 1.88 g (10 mmol) of $MeSO_2SPh$ in 10 ml of anhydrous CH_2Cl_2 over a period of 12 h gave a mixture of sulfones **XXIa** and **XXIb** at a ratio of 65:35 (column B, oven temperature 240°C, R_t 8.0 and 13.5 min, respectively). By column chromatography on Al_2O_3 we isolated 1.69 g (60%) of **XXIa** and 0.42 g (15%) of **XXIb**.

6-*endo*-Methylsulfonyl-7-*syn*-phenylsulfanylbicyclo[3.1.1]heptane (XXIb). Viscous oily substance, R_f 0.09. ^{1}H NMR spectrum, δ, ppm: 1.75–2.23 m (4H, 3-H, *endo*-2-H, *endo*-4-H), 2.41–2.59 m (2H, *exo*-2-H, *exo*-4-H), 2.70 s (3H, SO_2Me), 2.92 br.s (2H, 1-H,

5-H), 3.36 t (1H, *anti*-7-H, J = 5.8 Hz), 3.55 t (1H, *exo*-6-H, J = 5.8 Hz), 7.12–7.25 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 13.3 (C^3), 20.2 (C^2, C^4), 41.8 (SO_2Me), 43.5 (C^1, C^5), 48.1 (C^7), 59.8 (C^6); 126.3, 128.8 (2C), 129.8 (2C), 136.0 (C_{arom}). Found, %: C 59.71; H 6.29. $C_{14}H_{18}O_2S_2$. Calculated, %: C 59.54; H 6.42.

1,2-Bis(7-*syn*-methylsulfonylbicyclo[3.1.1]hept-6-*exo*-yl)disulfane (XVI). *a*. Powdered potassium *tert*-butoxide, 2 mmol, was quickly added under stirring in an argon atmosphere to a solution of 1 mmol of *anti*-adduct **IVa** in 15 ml of anhydrous THF, and the mixture was stirred for 2 h at 0°C under argon, the progress of the reaction being monitored by TLC. The mixture was then filtered through a 1-cm layer of Al_2O_3, the filtrate was evaporated to dryness under reduced pressure (water-jet pump), and the residue was analyzed by ^1H NMR and purified by crystallization. Yield 72%, mp 189–190°C (from $CHCl_3$–hexane), R_f 0.28. IR spectrum, ν, cm^{-1}: 2951 s, 1321 s, 1306 s, 1281 s, 1256 s, 1136 v.s, 965 s, 754 s, 559 s, 478 s. ^1H NMR spectrum, δ, ppm: 1.73–1.88 m (2H, *endo*-3-H), 1.90–2.05 m (6H, *exo*-3-H, *endo*-2-H, *endo*-4-H), 2.53–2.68 m (4H, *exo*-2-H, *exo*-4-H), 2.83 br.d (4H, 1-H, 5-H, J = 5.7 Hz), 2.87 s (6H, $MeSO_2$), 3.30 s (2H, *endo*-6-H), 4.03 t (2H, *anti*-7-H, J = 5.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.9 (C^3), 24.2 (C^2, C^4), 41.9 ($MeSO_2$), 43.8 (C^1, C^5), 50.4 (C^6), 58.5 (C^7). Found, %: C 46.89; H 6.44. $C_{16}H_{26}O_4S_4$. Calculated, %: C 46.80; H 6.38.

b. *anti*-Adduct **IVa**, **VIIa**, or **Xa**, 2 mmol, was dissolved in 10 ml of dioxane, 10 ml of a 1.2 M solution of NaOH was added under argon, and the mixture was heated for 3.5 h under reflux, cooled to room temperature, and diluted with 100 ml of water. The precipitate of **XVI**–**XVIII** was filtered off, dried in air, and purified by recrystallization. Yield of **XVI** 65%.

1,2-Bis(6-*endo*-methyl-7-*syn*-methylsulfonylbicyclo[3.1.1]hept-6-*exo*-yl)disulfane (XVII). Yield 80%, mp 122–123°C (from $CHCl_3$–hexane), R_f 0.34. IR spectrum, ν, cm^{-1}: 2967 m, 2924 m, 1296 v.s, 1285 v.s, 1246 m, 1091 m, 927 m, 752 m, 544 s. ^1H NMR spectrum, δ, ppm: 1.45 s (6H, CH_3), 1.54–1.67 m (2H, *endo*-3-H), 1.86–1.98 m (4H, *endo*-2-H, *endo*-4-H), 2.04–2.18 m (2H, *exo*-3-H), 2.34–2.45 m (4H, *exo*-2-H, *exo*-4-H), 2.78 br.d (4H, 1-H, 5-H, J = 5.5 Hz), 2.87 s (6H, $MeSO_2$), 4.25 t (2H, 7-H, J = 5.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.1 (C^3), 19.0 (CH_3), 21.8 (C^2, C^4), 42.1 ($MeSO_2$), 46.8 (C^1, C^5), 56.4 (C^6), 59.2 (C^7). Found, %: C 49.09; H 6.74. $C_{18}H_{30}O_4S_4$. Calculated, %: C 49.28; H 6.89.

1,2-Bis(7-*syn*-methylsulfonyl-6-*endo*-phenylbicyclo[3.1.1]hept-6-*exo*-yl)disulfane (XVIII). Yield 62%, mp 210°C (decomp., from $CHCl_3$–hexane), R_f 0.32. IR spectrum, ν, cm^{-1}: 3067 w, 2926 s, 1456 w, 1318 s, 1287 v.s, 1140 v.s, 754 s, 704 s, 563 s. ^1H NMR spectrum, δ, ppm: 0.47–0.63 m (2H, *endo*-3-H), 1.37–1.51 m (2H, *exo*-3-H), 1.85–1.98 m (4H, *endo*-2-H, *endo*-4-H), 2.31–2.48 m (4H, *exo*-2-H, *exo*-4-H), 2.82 br.d (4H, 1-H, 5-H, J = 5.6 Hz), 2.87 s (6H, $MeSO_2$), 4.29 t (2H, *anti*-7-H, J = 5.6 Hz), 7.01 d (4H, H_{arom}, J = 7.6 Hz), 7.24–7.49 m (6H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 13.2 (C^3), 22.1 (C^2, C^4), 42.1 ($MeSO_2$), 47.2 (C^1, C^5), 57.9 (C^7), 61.6 (C^6); 126.5 (4C), 127.2 (2C), 128.3 (4C), 139.1 (2C) (C_{arom}). Found, %: C 59.62; H 5.97. $C_{28}H_{34}O_4S_4$. Calculated, %: C 59.75; H 6.09.

1,2-Bis(7-methylidene-6-*endo*-phenylbicyclo[3.1.1]hept-6-*exo*-yl)disulfane (XIX). *anti*-Adduct **XIa**, 342 mg, was added to a solution of 0.4 g of NaOH in 5 ml of aqueous dioxane (1:1). The mixture was heated for 5 h under reflux, cooled, and extracted with diethyl ether (5×5 ml). The extract was washed with water, dried over $MgSO_4$, and evaporated, and the residue was purified by recrystallization. Yield 91 mg (42%), mp 153–154°C (from $CHCl_3$–hexane). IR spectrum, ν, cm^{-1}: 2948 w, 1628 s, 1314 v.s, 1159 s, 1127 s, 1032 m, 721 m, 696 m, 527 m, 507 w. ^1H NMR spectrum, δ, ppm: 1.41–1.53 m (2H), 1.62–1.78 m (2H, 3-H), 1.98–2.17 m (4H), 2.29–2.45 m (4H, 2-H, 4-H), 3.83 br.s (4H, 1-H, 5-H), 5.28 s (4H, CH_2=), 7.21–7.30 m (4H) and 7.38–7.54 (6H) (H_{arom}). Found, %: C 78.11; H 7.19. $C_{28}H_{30}S_2$. Calculated, %: C 78.09; H 7.02.

Disulfane **XIX** was synthesized in a similar way from compound **XIIa**; yield 53%.

Reaction of *anti*-adducts Xa–XIIa with $AgNO_3$ in aqueous dioxane (*general procedure*). A flask protected from light was charged with 1 mmol of sulfone **Xa**–**XIIa** and 15 ml of dioxane, a solution of 0.255 g (1.5 mmol) of $AgNO_3$ in 15 ml of water was added, and the mixture was stirred for 5–10 h at 20°C. The resulting colorless suspension was treated with 8 ml of a 0.2 M solution of KCl, the precipitate was filtered off and washed with 10 ml of chloroform on a filter, and the filtrate was extracted with chloroform (3×10 ml). The combined extracts were dried over $MgSO_4$ and evaporated under reduced pressure, and the solid residue was analyzed by NMR. Alcohols **XXIII**–**XXV** were purified by recrystallization.

7-*syn*-Methylsulfonyl-6-*endo*-phenylbicyclo[3.1.1]heptan-6-*exo*-ol (XXIII). Yield 91%, mp 185–

186°C (from acetone–CH_2Cl_2). IR spectrum, ν, cm^{-1}: 556 m, 706 s, 760 m, 1084 m, 1134 s (ν_sSO_2), 1238 s, 1289 v.s ($\nu_{as}SO_2$), 2951 m, 3441 s (OH). ^1H NMR spectrum, δ, ppm: 0.62–0.92 m (1H, *endo*-3-H), 1.39–1.65 m (1H, *exo*-3-H), 1.70 br.s (1H, OH), 1.87–2.09 m (2H, *endo*-2-H, *endo*-4-H), 2.43–2.65 m (2H, *exo*-2-H, *exo*-4-H), 2.92 s (3H, SO_2Me), 3.29 br.d (2H, 1-H, 5-H, J = 5.7 Hz), 4.31 t (1H, *anti*-7-H, J = 5.7 Hz), 7.27 d (2H, H_{arom}, J = 7.5 Hz), 7.37–7.49 m (3H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 12.9 (C^3), 22.5 (C^2, C^4), 42.1 (SO_2Me), 48.0 (C^1, C^5), 57.5 (C^7), 79.6 (C^6); 125.3 (2C), 128.2, 129.0 (2C), 139.6 (C_{arom}). Found, %: C 63.01; H 6.97. $C_{14}H_{18}O_3S$. Calculated, %: C 63.13; H 6.81.

7-*syn*-Chloromethylsulfonyl-6-*endo*-phenylbicyclo[3.1.1]heptan-6-*exo*-ol (XXIV). Yield 88%, mp 176–177°C (from $CHCl_3$). IR spectrum, ν, cm^{-1}: 3511 m (OH), 3010 m, 2940 m, 1339 m, 1304 s ($\nu_{as}SO_2$), 1157 s (ν_sSO_2), 1115 s, 737 s, 540 w. ^1H NMR spectrum, δ, ppm: 0.70–0.92 m (1H, *endo*-3-H), 1.47–1.63 m (1H, *exo*-3-H), 1.93 br.s (1H, OH), 1.95–2.10 m (2H, *endo*-2-H, *endo*-4-H), 2.49–2.67 m (2H, *exo*-2-H, *exo*-4-H), 3.35 br.d (2H, 1-H, 5-H), 4.45 s (2H, CH_2Cl), 4.50 t (1H, 7-H, J = 5.5 Hz); 7.27–7.32 m (2H) and 7.40–7.49 m (3H) (H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 12.8 (C^3), 22.7 (C^2, C^4), 49.0 (C^1, C^5), 55.5 (CH_2Cl); 57.5 (C^7), 80.2 (C^6); 125.1 (2C), 128.0, 128.8 (2C), 139.4. Found, %: C 55.81; H 5.67. $C_{14}H_{17}ClO_3S$. Calculated, %: C 55.90; H 5.70.

7-s*yn*-Bromomethylsulfonyl-6-*endo*-phenylbicyclo[3.1.1]heptan-6-*exo*-ol (XXV). Yield 79% [2].

REFERENCES

1. Vasin, V.A., Bolusheva, I.Yu., Chernyaeva, L.V., Tanaseichuk, B.S., Surmina, L.S., and Zefirov, N.S., *Zh. Org. Khim*., 1990, vol. 26, p. 1509.
2. Vasin, V.A., Romanova, E.V., Kostryukov, S.G., and Razin, V.V., *Russ. J. Org. Chem*., 1999, vol. 35, p. 1161.
3. Vasin, V.A., Kostryukov, S.G., Razin, V.V., Bolusheva, I.Yu., and Zefirov, N.S., *Zh. Org. Khim*., 1994, vol. 30, p. 1351.
4. Vasin, V.A., Kostryukov, S.G., and Razin, V.V., *Russ. J. Org. Chem*., 1996, vol. 32, p. 49.
5. Vasin, V.A., Kostryukov, S.G., Romanova, E.V., Bolusheva, I.Yu., and Razin, V.V., *Russ. J. Org. Chem*., 1996, vol. 32, p. 1649.
6. Vasin, V.A., Romanova, E.V., Kostryukov, S.G., and Razin, V.V., *Russ. J. Org. Chem*., 1999, vol. 35, p. 1146.
7. Vasin, V.A., Kostryukov, S.G., Razin, V.V., and Zefirov, N.S., *Zh. Org. Khim*., 1994, vol. 30, p. 680.
8. Wolf, G.C., *J. Org. Chem*., 1974, vol. 39, p. 3454.
9. Tanaskov, M.M., Starodub, P.E., Stadnichuk, M.D., and Tanaskova, E.A., *Zh. Org. Khim*., 1981, vol. 17, p. 1800.
10. Wiberg, K.B. and Hess, B.A., *J. Org. Chem*., 1966, vol. 31, p. 2250.
11. Razin, V.V., Vasin, V.A., and Blinkov, I.E., *Zh. Org. Khim*., 1993, vol. 29, p. 916.
12. Vasin, V.A., Kostryukov, S.G., and Razin, V.V., *Russ. J. Org. Chem*., 1998, vol. 34, p. 1136.
13. Schmidt, M.W., Baldridge, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.J., Koseki, S., Matsunaga, N., Nguyen, K.A., Su, S., Windus, T.L., Dupuis, M., and Montgomery, J.A., *J. Comput. Chem*., 1993, vol. 14, p. 1347; Granovsky, A.A., *PC GAMESS/Firefly version 7.1.F*; *http://classic.chem.msu.su/gran/gamess/index.html*
14. Nicolaou, K.C. and Smith, A.L., *Acc. Chem. Res*., 1992, vol. 25, p. 497.
15. Tedder, J.M. and Nechvatal, A., *Pictorial Orbital Theory*, London: Pitman, 1985. Translated under the title *Orbital'naya teoriya v konturnykh diagrammakh*, Moscow: Mir, 1988, p. 41; Fleming, I., *Frontier Orbitals and Chemical Reactions*, Chichester: Wiley, 1976, chap. 5.
16. Olsen, S.C. and Christophersen, C., *Acta Chem. Scand., Ser. B*, 1975, vol. 29, p. 891.
17. Vasin, V.A., Bolusheva, I.Yu., and Razin, V.V., *Sulfur Lett*., 2003, vol. 26, p. 101.
18. Vasin, V.A., Bolusheva, I.Yu., and Razin, V.V., *J. Sulfur Chem*., 2005, vol. 26, p. 139.
19. Hogg, D.R., *Comprehensive Organic Chemistry*, Barton, D. and Ollis, W.D., Eds., Oxford: Pergamon, 1979, vol. 3. Translated under the title *Obshchaya organicheskaya khimiya*, Moscow: Khimiya, 1983, vol. 5, p. 418.
20. Makosza, M. and Fedorrynski, M., *Synthesis*, 1974, p. 274.
21. Razin, V.V., Eremenko, M.V., and Ogloblin, K.A., *Zh. Org. Khim*., 1978, vol. 14, p. 973.
22. Closs, G.L. and Closs, L.E., *J. Am. Chem. Soc*., 1963, vol. 85, p. 2022; Gassman, P.G. and Atkins, T.J., *J. Am. Chem. Soc*., 1972, vol. 94, p. 7748.
23. Razin, V.V., Zadonskaya, N.Yu., Alekseev, A.G., and Makarychev, Yu.A., *Zh. Org. Khim*., 1992, vol. 28, p. 972.
24. Block, E., Aslam, M., Eswarakrishnan, V., Gebreyes, K., Hutchinson, J., Jyer, R., Laffite, J.-A., and Wall, A., *J. Am. Chem. Soc*., 1986, vol. 108, p. 4568.
25. El-Hewehim, Z., *J. Prakt. Chem*., 1964, vol. 23, p. 38.
26. Chemla, F., *Synlett*, 1998, p. 894.
27. Boldyrev, B.G. and Trofimov, B.A., *Zh. Obshch. Khim*., 1958, vol. 28, p. 1940.