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Products and Mechanism of Some Halogenation Reactions of 1-Sulfonyl-Substituted Tricyclo[4.1.0.0^{2,7}]heptanes

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Abstract—Reactions of 1-methylsulfonyl- and 1-phenylsulfonyltricyclo[4.1.0.0^{2,7}]heptanes with iodine, dioxane dibromide, and dichloro-λ^3-iodanylbenzene (under irradiation) gave products of stereoselective *syn* addition of halogen at the C^1–C^7 central bicyclobutane bond. 7-Methyl-1-phenylsulfonyltricyclo[4.1.0.0^{2,7}]-heptane reacted with dioxane dibromide in carbon tetrachloride to produce a mixture of 2-bromo- and 2,3-dibromo-1-methyl-*exo*-7-phenylsulfonylnorcaranes at a ratio of 1 : 4 as a result of cleavage of the C^1–C^2 bicyclobutane bond. 7-Bromo- and 7-methoxycarbonyl-1-phenylsulfonyltricyclo[4.1.0.0^{2,7}]heptanes take up bromine exclusively at the C^1–C^7 central bond with strict *syn* stereoselectively. The regio- and stereoselectivity of the addition and their relations with the halogen nature were interpreted with account taken of structural specificities of intermediate 6-sulfonyl-substituted 6-norpinanyl radicals determined by *ab initio* quantum-chemical calculations using 6-31G basis set.

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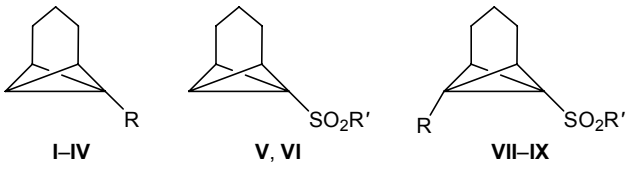
It is known that elemental halogens and halogen carriers (such as *N*-bromosuccinimide, dioxane dibromide, dichloro-λ^3-iodanylbenzene, etc.) are capable of acting as both electrophilic and radical reagents in the addition reactions with olefins. Bicyclo[1.1.0]-butane derivatives, in particular compounds of the tricyclo[4.1.0.0^{2,7}]heptane series, are formally saturated compounds; however, due to high π-character of bonds in the bicyclobutane fragment they react with many reagents as alkenes with rupture of these bonds. Electrophilic addition to tricyclo[4.1.0.0^{2,7}]heptanes can involve both central bicyclobutane C–C bond with formation of norpinane derivatives and side C–C bond to give norcarane derivatives [1, 2]; radical addition occurs exclusively at the central bond [3]. For instance, tricyclo[4.1.0.0^{2,7}]heptane (**I**) and its 1-methyl and 1-phenyl derivatives **II** and **III** undergo halomethoxylation at the C^1–C^7 bond according to the electrophilic addition mechanism [4–6]. Study on halomethoxylation of methyl tricyclo[4.1.0.0^{2,7}]heptane-1-carboxylate (**IV**) as substrate possessing reduced nucleophilicity showed that this reaction also follows electrophilic pattern [7]. However, the result of action of other halogenating agents, e.g., elemental iodine, on the same compound indicated competition between electrophilic and radical paths of halogenation at the C^1–C^7 bond.



I–IV **V**, **VI** **VII–IX**

I, R = H; **II**, **VII**, R = Me; **III**, R = Ph; **IV**, **IX**, R = MeOCO; **VIII**, R = Br; **V**, R′ = Me; **VI–IX**, R = Ph.

In the present work we studied reactions of some halogenating agents with 1-mono- and 1,7-disubstituted tricycloheptanes containing in the bridgehead position a sulfonyl group which is a stronger electron-withdrawing substituent than methoxycarbonyl group. Sulfones **V–IX** were expected to be largely deactivated toward electrophilic attack, so that their reactions with halogenating agents would follow mainly radical mechanism with formation of norpinane derivatives.

We initially found that none of sulfonyl-substituted tricycloheptanes **V–IX** reacted with *N*-halosuccinimides in methanol. Unlike sulfones **V–IX**, 7-phenyl-1-phenylsulfonyltricyclo[4.1.0.0^{2,7}]heptane was recently shown [8] to undergo, though slowly, electrophilic

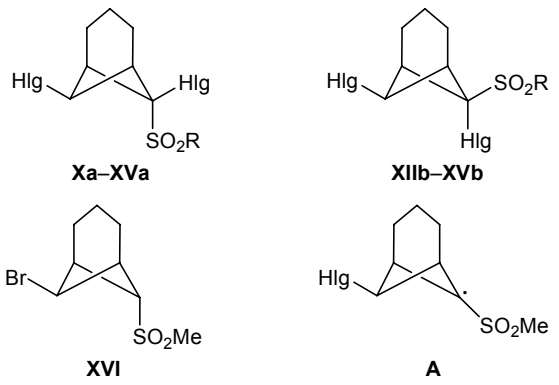
Table 1. Halogenation of tricycloheptanes **V** and **VI**

Tricycloheptane	Halogenating agent (solvent)	Products	Yield, %	Fraction of *syn*-adduct, %
V	I_2 (Et_2O)	**X**	60	~100
VI	I_2 (Et_2O)	**XI**	90	~100
V	Br_2·dioxane (CCl_4)	**XIIa**, **XIIb**	70	95
VI	Br_2·dioxane (CCl_4)	**XIIIa**, **XIIIb**	81	75 [9]
V	$PhICl_2$ (CCl_4)	**XIVa**, **XIVb**	<50	78
VI	$PhICl_2$ (CCl_4)	**XVa**, **XVb**	64	89 [11]

halomethoxylation at the central C^1–C^7 bond with exclusive formation of *syn*-addition product having norpinane structure. This was interpreted in terms of effect of donor substituent at the bridgehead carbon atom, which stabilizes intermediate benzyl-type carbocation.

We then examined reactions of monosubstituted tricycloheptanes **V** and **VI** with elemental iodine, dioxane dibromide, and dichloro-λ^3-iodanylbenzene (under irradiation). All these reactions occurred fairly readily at room temperature. The iodination gave norpinane derivative **Xa** or **XIa**, respectively, as the only product corresponding to rigorous s*yn* stereoselectivity of the addition. The bromination and chlorination followed analogous pattern, but in each case two diastereoisomeric 6,7-dihalo derivatives were formed (compounds **XIIa**–**XVa** and **XIIb**–**XVb**) with appreciable prevalence of the *syn*-adduct (Table 1; see also [9–11]). In addition, the bromination of tricycloheptane **V** gave monobromonorpinane **XVI** and dibromonorcarane **XVII** as by-products, whereas the chlorination of the same substrate was accompanied by formation of dichloronorcarane **XVIII**. Analogous norcarane dibromide **XIX** was formed as an impurity in the bromination of tricycloheptane **VI**.

syn-Adducts **Xa**–**XVa** were isolated as individual substances by column chromatography and crystallization. We failed to isolate pure minor *anti*-adducts **XIIb**–**XVb**, and they were characterized by spectral methods as mixtures with their major diastereoisomers.



Xa–XVa **XIIb–XVb** **XVI** **A**

X, **XII**, **XIV**, R = Me; **XI**, **XIII**, **XV**, R = Ph; **X**, **XI**, Hlg = I; **XII**, **XIII**, Hlg = Br; **XIV**, **XV**, Hlg = Cl.

The structure of compounds **XIIIa** and **XVa** was determined previously by X-ray analysis [9, 10]; proofs for the structure of dibromide **XIIIb** and dichloride **XVb** were given in [9, 11]. The structure of diiodides **X** and **XI**, dibromides **XIIa** and **XIIb**, and dichlorides **XIVa** and **XIVb** was confirmed using the ^1H and ^{13}C NMR spectra of structurally related compounds **XIIIa**, **XIIIb**, **XVa**, and **XVb**. *syn* Orientation of the halogen atom on C^7 follows from the presence of a triplet signal of *anti*-7-H ($J \approx 6$ Hz) in the ^1H NMR spectra [12]. The difference in the chemical shifts of *anti*-7-H between stereoisomeric dibromides **XIIa** and **XIIb** and dichlorides **XIVa** and **XIVb** allowed us to assign configuration of the C^6 atom with account taken of weaker long-range deshielding effect of the bromine or chlorine atom oriented opposite to *anti*-7-H, as compared to sulfonyl group (cf. [9, 11]). The configuration at C^6 in diiodides **Xa** and **XIa** was assumed to be the same as in dibromides **XIIa** and **XIIIa** and dichlorides **XIVa** and **XVa** on the basis of similarity of chemical shifts of *anti*-7-H in all three couples of compounds. The configuration at C^6 in dibromide **XIIa** was also confirmed chemically by stereospecific hydrodebromination with triphenyltin hydride, which afforded monobromide **XVI** (cf. [8, 13, 14]); we also identified compound **XVI** as one of minor products formed in the reaction of tricycloheptane **V** with dioxane dibromide. The configuration of C^6 and C^7 in compound **XVI** unambiguously followed from the presence of singlet and triplet signals belonging to *endo*-6-H and *anti*-7-H in the ^1H NMR spectrum (cf. [12]).

The formation of compounds **X**–**XV** was rationalized in terms of radical mechanism of halogenation of sulfones **V** and **VI**. Our interpretation was based on both regioselectivity of the addition (cleavage of the central rather than side C–C bond) and its stereo-

Table 2. Relative energies ΔH,[a] dihedral angles (α, β, γ, δ), and interatomic distances l_1 and l_2 in methylsulfonyl-substituted radicals **A**, according to quantum-chemical calculations with 6-31G basis set[b, c]

Radical	Invertomer	ΔH, kcal/mol	l_1, Å	l_2, Å	α, deg	β, deg	γ, deg	δ, deg
$\mathbf{A}_{Cl}$	**A′**	0.84	2.513	2.782	–153.7	152.5	125.6	139.5
	A″	0.00	2.485	2.886	140.0	155.0	110.3	137.6
$\mathbf{A}_{Br}$	**A′**	0.77	2.512	2.728	–153.7	151.0	108.7	139.6
	A″	0.00	2.471	2.825	141.0	153.8	110.7	137.9
$\mathbf{A}_{I}$	**A′**	1.19	2.483	2.679	–139.6	146.1	109.8	153.6
	A″	0.00	2.436	2.775	140.2	148.1	112.4	139.4

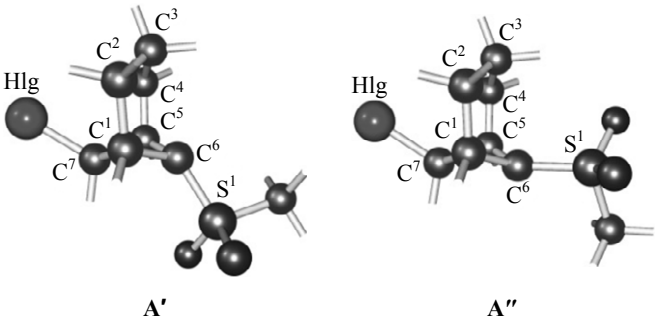
[a] Zero-point vibration energies (*ZPE*) of radicals were not estimated.

[b] Radicals $\mathbf{A}_I$ were calculated with the use of iodine functions from STO-6G basis set.

[c] Selected geometric parameters: l_1 stands for the 7-H$\cdots$C^6, l_2 stands for the 3-H$^3\cdots$C^6 distance, α is the dihedral angle between the C^{1}C^{6}C^5 plane and C^6–S bond, β is the dihedral angle between the C^{1}C^{2}C^{4}C^5 and C^{2}C^{3}C^4 planes, γ is the angle between the C^{1}C^{2}C^{4}C^5 and C^{1}C^{5}C^6 planes, and δ is the angle between the C^{1}C^{5}C^7 and C^{1}C^{5}C^6 planes.

selectivity: isomers "**b**" could be obtained only according to radical rather than ionic (with halogen as electrophile) reaction path. In all cases the addition is initiated by *endo* attack by halogen atom on C^7 with formation of 6-norpinanyl radical **A**, and the subsequent reagent transfer to the reaction center in **A** is characterized by *syn* stereoselectivity. The selectivity depends on the halogen nature and is the highest for iodine.

With a view to reveal factors responsible for stereoselectivity in the halogenation of sulfones **V** and **VI**, the electronic and steric structures of halogenated 6-methylsulfonyl-substituted 6-norpinanyl radicals **A** were estimated by *ab initio* quantum-chemical calculations with 6-31G basis set using PC GAMESS software [15]. According to the results of our previous calculations, analogous 6-methoxycarbonyl-substituted 6-norpinanyl radicals possess planar reaction center [7]. By contrast, the most stable radicals **A** had pyramidal reaction center and were represented by two invertomers **A′** and **A″** (see figure). The structures of mirror isomers with respect to the C^{3}C^{6}C^7 plane, which



A′ **A″**

Steric structure of invertomers **A′** and **A″** of methylsulfonyl-substituted radicals according to *ab initio* calculations.

are characterized by the same energy, were optimized for each invertomer **A′**. In these radicals, the 3-CH_2 fragment deviates toward the C^6 atom. Invertomers **A′** are initially formed via cleavage of the bicyclobutane system [16]. They are slightly less energetically favorable than invertomers **A″**, and reversible transformation **A′** ↔ **A″** is possible (Table 2). The reaction center in bromo- and chloro-substituted invertomers **A′** is more flattened as compared to analogous invertomers **A″** (cf. the angles α between the C^{1}C^{6}C^5 plane and the C^6–S bond). Obviously, adducts "**a**" should be derived from invertomers **A′**, and adducts "**b**," from **A″**.

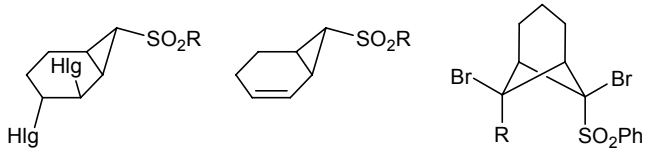
The "**a**/**b**" stereoisomer ratio can be determined by several factors, primarily by the relative rates of reagent transfer to the reaction center in norpinanyl radical and its inversion. We believe that, unlike analogous intermediates having a hydrogen atom or alkyl or phenyl substituent at the radical center (such intermediates are formed from tricycloheptane hydrocarbons **I**–**III**, e.g., in homolytic sulfonation [17] and sulfanylation [18] characterized by *anti* selectivity of the addition), in our case the rate of inversion of the radical center may be either lower than or comparable to the rate of reagent transfer due to *d*-orbital effect of the sulfonyl substituent. Then invertomer **A′** reacts mainly as it is generated (cf. [9]), which determines *syn* selectivity of the addition as a whole.

On the other hand, different selectivities in the halogenation of sulfone **V** may be related to differences in spatial accessibilities of the reaction centers in invertomers **A′** and **A″**. In all cases, the interatomic distance *anti*-7-H$\cdots$C^6 (l_1) in **A″** is shorter than the distance C^3–C^6 (l_2) in **A′**. Furthermore, the methyl group and atomic orbital bearing unpaired electron in

A″ are *synperiplanar* with respect to the C^6–S bond, which gives rise to additional shielding of the reaction center. The methyl group in **A′** is *synclinal* with respect to the unpaired electron orbital, and its shielding effect on the reaction center is weaker than in **A″**. Thus structure **A′** is more favorable for reagent approach to the reaction center, which also determined the observed *syn* stereoselectivity in the halogenation of tricycloheptane **V**. Taking into account considerable differences in steric volumes of iodine, bromine, and chlorine atoms (their van der Waals radii are 1.97, 1.86, and 1.73 Å, respectively [19]), it becomes clear why only one product is formed in the iodination reaction. Presumably, the above structural peculiarities of radicals **A** generated from tricycloheptane **V** are also inherent to radicals derived from tricycloheptane **VI**.

The formation of monobromonorpinane **XVI** in the reaction of tricycloheptane **V** with dioxane dibromide may be rationalized assuming that norpinanyl radical **A** is also involved in side process, abstraction of hydrogen from solvent molecules. Dihalonorcaranes **XVII**–**XIX** are likely to be formed as a result of partial isomerization of tricycloheptanes **V** and **VI** into norcarenes **XX** and **XXI** in the presence of traces of hydrogen halide and subsequent halogen addition at the C=C bond. This assumption was confirmed by special experiment: the reaction of bromine with preliminarily synthesized compounds **XX** and **XXI** [20] gave the same dibromonorcaranes **XVII** and **XIX**, respectively.

The structure of norcarane **XVII** was determined by ^1H and ^{13}C NMR spectroscopy. *exo* Orientation of the methylsulfonyl group on C^7 was assigned on the basis of the coupling constant for the α-H proton (5 Hz), which is typical of *trans* vicinal coupling in cyclopropanes [21]. We have no direct proofs for the assumed configuration of C^2 and C^3 in molecule **XVII**, and the assignment was made on the basis of general considerations on the formation of dibromide **XVII** in the bromination of norcarene **XX**. These included (1) *anti* addition at the double C=C bond, (2) *exo* approach of electrophilic bromine to the C=C bond of norcarene, and (3) asymmetric structure of the π-complex with a large positive charge on the C^2 atom due to stabilization by the three-membered carbocycle. Expected similarity of the NMR spectra of dihalo derivative **XVII**, on the one hand, and compounds **XVIII** and **XIX**, on the other, allowed us to assign analogous structure to the two latter.



XVII–XIX **XX**, **XXI** **XXII**, **XXIII**

XVII, **XVIII**, **XX**, R = Me; **XIX**, **XXI**, R = Ph; **XVII**, **XIX**, Hlg = Br; **XVIII**, Hlg = Cl; **XXII**, R = Br; **XXIII**, R = MeOCO.

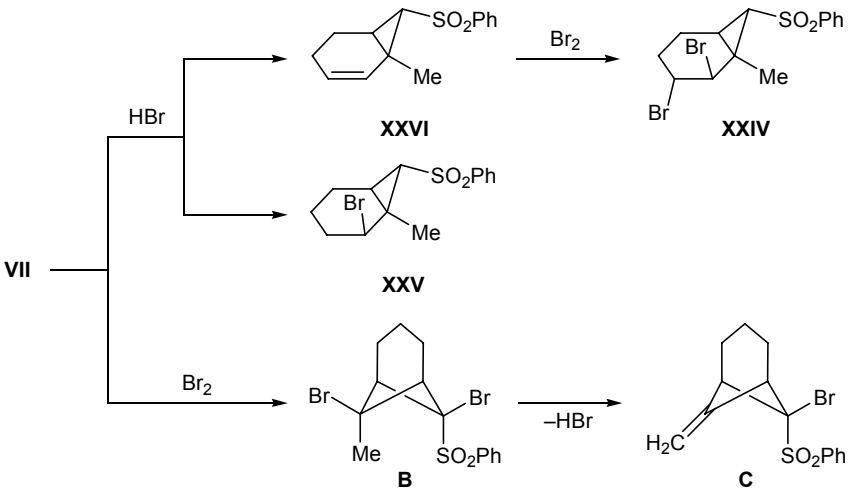
Disubstituted tricycloheptanes **VIII** and **IX** failed to react with dioxane dibromide and with iodine. Only prolonged reaction of **VIII** and **IX** with an equimolar amount of bromine in methylene chloride (7 days at 20°C) afforded compounds **XXII** and **XXIII**, the latter being the *syn*-addition product at the C^1–C^7 bond.

The structure of tetrasubstituted norpinanes **XXII** and **XXIII** was proved on the basis of their ^1H and ^{13}C NMR spectra, which were analogous to those of model compounds [8, 22]. Ester **XXIII** was characterized by nonequivalence of the 1-H and 5-H protons and C^1 and C^5 carbon nuclei due to staggered conformation of the ester group which is orthogonal to the $C^3C^6C^7$ plane (according to the X-ray diffraction data [23]). By contrast, the C^1H and C^5H fragments in the NMR spectra of tribromo sulfone **XXII** are equivalent.

We believe that sulfones **VIII** and **IX** react with bromine only according to radical mechanism because of their strong deactivation toward electrophiles. In fact, the reaction is accelerated under irradiation. Rigorous *syn* stereoselectivity in the bromination of **IX** may be rationalized by steric factors in intermediate norpinanyl radical where the methoxycarbonyl (or phenylsulfonyl) group hampers *anti* approach of the reagent to the reaction center.

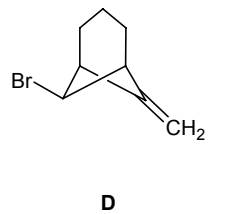
Disubstituted sulfone **VII** having an electron-donating group in the 7-position turned out to be more reactive than tricycloheptanes **VIII** and **IX**, and it readily reacted with dioxane dibromide at room temperature. However, instead of expected norpinane dibromide **B** we obtained two norcarane derivatives, dibromide **XXIV** and monobromide **XXV** at a ratio of 4:1. Compounds **XXIV** and **XXV** were identified in the reaction mixture by NMR and MALDI mass spectrometry. Bromonorcarane **XXV** was isolated as individual substance by column chromatography on silica gel. It was also synthesized independently by passing dry hydrogen bromide through a solution of compound **VII** in carbon tetrachloride. Dibromonorcarane **XXIV** was identified by comparing with a sample prepared by independent synthesis from norcarene **XXVI** [20] and bromine (Scheme 1).

Scheme 1.

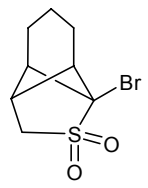


Presumably, the reaction of tricycloheptane **VII** with dioxane dibromide nevertheless involves initial formation of some amount of dibromonorpinane **B** as product of radical addition of bromine. However, unlike dibromides **XXII** and **XXIII**, intermediate **B** is unstable, and it undergoes spontaneous dehydrobromination [5] to give methylidenenorpinane **C**. The latter was not detected in the reaction mixture, probably because of its fast transformation into further bromination products. Liberated hydrogen bromide reacts with tricycloheptane **VII** along two pathways. One of these is stereoselective addition at the C^1–C^2 bond with formation of monobromide **XXV**, which is consistent with published data on regio- and stereoselectivity of cleavage of tricycloheptane system initiated by electrophilic hydrogen [1, 2, 20]. The second path is catalytic isomerization of tricycloheptane **VII** into norcarene **XXVI** which takes up bromine to produce dibromide **XXIV**, as in the above interpretation of the formation of dibromides **XVII** and **XIX** from tricycloheptanes **V** and **VI**.

Dihalo sulfones **XIIa** and **XIVa** seemed to be promising from the viewpoint of their further transformation either into 6-methylidenenorpinane derivative **D** via Ramberg–Bäcklund reaction [24] or into tricyclic sulfone **E** as a result of 1,5-dehydrohalogenation [25]. For this purpose we examined the behavior of dibromide **XIIa** under the action of bases with different strengths. However, compound **XIIa** remained unchanged on heating in a boiling solution of sodium hydroxide in aqueous dioxane or by the action of potassium *tert*-butoxide in THF at 0°C. Only heating of **XIIa** with excess potassium *tert*-butoxide in DMSO at 70°C (reaction time 2 h) resulted in its transformation into sulfone **V** (Scheme 2).

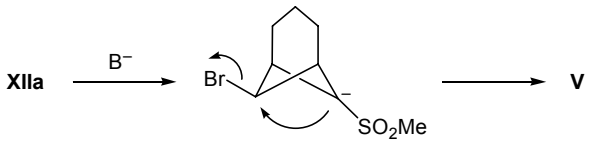


D



E

Scheme 2.



F

Thus dibromide **XIIa** undergoes 1,3-debromination rather than dehydrobromination in the reaction where dimethyl sulfoxide potassium salt acts as halophilic reagent capable of generating sulfonyl-substituted carbanion **F** [26]. Analogous transformation was reported previously [27] for *endo,syn*-6,7-diiodobicyclo-[3.1.1]heptane.

EXPERIMENTAL

The elemental compositions were determined on an HP-185B CHN analyzer. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer at 300.130 and 75.468 MHz, respectively, using $CDCl_3$ as solvent and tetramethylsilane as internal reference. The IR spectra were measured in KBr on an InfraLYuM FT-02 spectrometer with Fourier transform.

GLC analyses were performed on a Kristallyuks-4000 chromatograph equipped with a flame ionization

detector and a 1000×3-mm glass column packed with 3% of OV-17 on Inerton N-Super (0.125–0.160 mm); carrier gas nitrogen, flow rate 40 ml/min; oven temperature 200°C, injector temperature 240°C. The components were quantitated by the internal normalization method (by peak areas). The chromatograms were processed using NetChrom 1.5 program. The mass spectra (electron impact, 70 eV) were obtained on an Agilent 6890N chromatograph coupled with a mass-selective detector (Agilent 19091S-433 HP-5MS capillary column, 30 m×0.25 mm; oven temperature programming to 300°C; carrier gas helium, 1 ml/min).

The MALDI mass spectra were recorded on a Bruker Autoflex II instrument (FWHM resolution 18000) equipped with a nitrogen laser (λ 337 nm) and time-of-flight mass analyzer (reflector mode; accelerating voltage 20 kV); samples were applied onto a polished steel support; positive ions were detected. The resultant spectrum was a sum of 300 spectra recorded as different points of a sample. 2,5-Dihydroxybenzoic acid (99%, Acros Organics) and α-cyano-4-hydroxycinnamic acid (99%, Acros Organics) were used as matrices.

Analytical thin-layer chromatography was performed on Silufol UV-254 plates using hexane–diethyl ether (2:1) as eluent. Spots were detected by treatment with iodine vapor. Aluminum oxide of activity grade II and silica gel L (40–100 μm) were used for column chromatography; eluent light petroleum ether–diethyl ether, (2–3):1.

Quantum-chemical calculations were performed in terms of the unrestricted Hartree–Fock method (6-31G basis set supplemented by iodine functions from STO-6G basis set; initial PM3 parameterization) using PC GAMESS 7.1 [15].

Sulfone **VI** with a purity of no less than 97% was synthesized from tricycloheptane **I** by lithiation at the bridgehead position according to the procedure described in [28]. Sulfones **VII**–**IX** with the same purity were prepared as described in [17].

1-Methylsulfonyltricyclo[4.1.0.0^{2,7}]heptane (V). A mixture of 15.8 ml of acetonitrile, 4 g of potassium carbonate, and 14.0 g (0.1 mol) of 1-methylsulfanyltricyclo[4.1.0.0^{2,7}]heptane [29] was cooled to 0°C, and a mixture of 34 ml (0.3 mol) of 30% hydrogen peroxide and 30 ml of methanol was added dropwise under stirring. The progress of the reaction was monitored by TLC, following the disappearance of the initial sulfide. The solvent was removed under reduced pressure (water-jet pump), and the residue was washed with a 5% solution of sodium sulfite and water and dissolved in 20 ml of chloroform. The solution was dried over $MgSO_4$ and filtered, and the filtrate was evaporated under reduced pressure. Crystallization of the residue gave 15.7 g (90%) of sulfone **V** with mp 75–76°C (from petroleum ether–diethyl ether, 3:1), R_f 0.22. The ^{1}H and ^{13}C NMR spectra of the product coincided with the data reported in [25] for the same compound synthesized by us by a different method.

Reaction of sulfones V and VI with molecular iodine (*general procedure*). Sulfone **V** or **VI**, 1 mmol, was dissolved in 3 ml of anhydrous diethyl ether, a solution of 0.25 g (1 mmol) of iodine in 15 ml of diethyl ether was added, and the mixture was kept for 40 h at 20°C. The mixture was then washed with a 5% solution of sodium sulfite, dried over $MgSO_4$, and evaporated, and the solid residue was analyzed by ^{1}H NMR and purified by crystallization.

***endo*-6,*syn*-7-Diiodo-*exo*-6-methylsulfonylbicyclo[3.1.1]heptane (Xa).** Yield 58%, R_f 0.33, mp 157°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 1.63–1.78 m and 1.79–1.96 m (1H each, 3-H), 2.35–2.51 m and 2.55–2.71 m (2H each, 2-H, 4-H), 3.16 br.d (2H, 1-H, 5-H, J = 5.9 Hz), 3.34 s (3H, $MeSO_2$), 5.78 t (1H, 7-H, J = 5.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 10.4 (C^3), 18.8 (C^7), 35.2 (C^2, C^4), 39.1 ($MeSO_2$), 49.0 (C^1, C^5), 63.5 (C^6). Found, %: C 22.48; H 2.92. $C_8H_{12}I_2O_2S$. Calculated, %: C 22.55; H 2.84.

***endo*-6,*syn*-7-Diiodo-*exo*-6-phenylsulfonylbicyclo[3.1.1]heptane (XIa).** Yield 90%, mp 175–176°C (from hexane–acetone). ^{1}H NMR spectrum, δ, ppm: 1.53–1.71 m and 1.73–1.93 m (1H each, 3-H), 2.29–2.46 m and 2.58–2.67 m (2H each, 2-H, 4-H), 3.26 br.d (2H, 1-H, 5-H, J = 5.7 Hz), 5.94 t (1H, 7-H, J = 5.7 Hz), 7.59 t (2H, H_{arom}, J = 7.7 Hz), 7.70 t (1H, H_{arom}, J = 7.7 Hz), 8.03 d (2H, H_{arom}, J = 7.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 10.5 (C^3), 19.2 (C^7), 35.4 (C^2, C^4), 49.6 (C^1, C^5), 66.0 (C^6), 128.7 (2C), 130.7 (2C), 134.3, 136.7 (C_{arom}). Found, %: C 31.97; H 2.94. $C_{13}H_{14}I_2O_2S$. Calculated, %: C 31.99; H 2.89.

The reaction of sulfone V with dioxane dibromide was carried out according to the procedure described in [9] for the bromination of tricycloheptane **VI**. A solution of 2.15 g (8.7 mmol) of freshly prepared dioxane dibromide in 60 ml of carbon tetrachloride was added dropwise over a period of 1 h under stirring at 0°C to a mixture of 1.5 g (8.7 mmol) of sulfone **V**, 0.5 g of calcium carbonate, and 25 ml of anhydrous carbon tetrachloride. The mixture was stirred for 1 h more until complete decoloration, washed with 15 ml

of a 5% solution of sodium sulfite and with water, and dried over $CaCl_2$. According to the GLC and ^1H NMR data, the products were two diastereoisomeric norpinane dibromides **XIIa** and **XIIb** and norcarane dibromide **XVII** at a ratio of 8.3 : 1 : 2.5 with a small (~5%) impurity of monobromide **XVI**. Compounds **XIIa** and **XVII** were isolated by column chromatography on silica gel. Compound **XIIb** was identified by ^1H NMR in a 2 : 1 mixture with **XIIa**. Bromonorpinane **XVI** was detected by GC–MS and was identified by comparing with an authentic sample (see below).

***endo*-6,*syn*-7-Dibromo-*exo*-6-methylsulfonylbicyclo[3.1.1]heptane (XIIa).** Yield 57%, mp 117–118°C (from hexane–diethyl ether, 3:1), R_f 0.45, R_t 9.13 min. ^1H NMR spectrum, δ, ppm: 1.61–1.77 m and 1.77–1.92 m (1H each, 3-H), 2.30–2.44 m and 2.46–2.60 m (2H each, 2-H, 4-H), 3.20 s (3H, $MeSO_2$), 3.30 br.d (2H, 1-H, 5-H, J = 5.9 Hz), 5.49 t (1H, 7-H, J = 5.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.7 (C^3), 29.3 (C^2, C^4), 37.9 ($MeSO_2$), 45.5 (C^7), 48.8 (C^1, C^5), 81.7 (C^6). Mass spectrum, m/z (I_{rel}, %): 175 (14.4), 173 (15.7), 172 (12.4) [$M - Br_2$], 120 (16.4), 94 (12.2), 93 (100), 92 (9.9), 91 (45.2), 81 (41.9), 79 (25.1), 77 (42.5), 65 (17.0), 53 (12.3). Found, %: C 28.86; H 3.56. $C_8H_{12}Br_2O_2S$. Calculated, %: C 28.94; H 3.64.

***exo*-6,*syn*-7-Dibromo-*endo*-6-methylsulfonylbicyclo[3.1.1]heptane (XIIb).** R_f 0.30, R_t 7.35 min. ^1H NMR spectrum (**XIIa**/**XIIb**, 2:1), δ, ppm: 3.06 s (3H, $MeSO_2$), 3.20 br.s (2H, 1-H, 5-H), 5.24 t (1H, *anti*-7-H, J = 5.3 Hz).

Bromination of tricycloheptane **VI** according to the procedure described in [9] gave two diastereoisomeric norpinanes **XIIIa** and **XIIIb** and a small amount (~5%) of norcarane dibromide **XIX** which was identified by comparing with a sample obtained by independent synthesis (see below).

***endo*-2,*exo*-3-Dibromo-*exo*-7-methylsulfonylbicyclo[4.1.0]heptane (XVII).** Yield 20%, mp 155–156°C (from hexane–diethyl ether), R_f 0.38, R_t 6.51 min. ^1H NMR spectrum, δ, ppm: 1.86–2.01 m (2H), 2.09–2.25 m (2H), 2.31–2.50 m (2H), 2.60 t (1H, 7-H, J = 4.6 Hz), 3.02 s (3H, $MeSO_2$), 4.23–4.32 m (1H, 3-H), 4.94 d.d (1H, 2-H, J = 4.2, 7.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.4, 22.1, 24.8, 26.4, 41.5, 43.1, 50.9 and 51.1 (C^2, C^3). Found, %: C 28.88; H 3.55. $C_8H_{12}Br_2O_2S$. Calculated, %: C 28.94; H 3.64.

The reaction of sulfone V with dichloro(phenyl)-λ³-iodane was carried out as described in [11] for the chlorination of tricycloheptane **VI** [11]. A quartz ampule was charged with a mixture of 0.5 g (3 mmol) of tricycloheptane **V** and 0.82 g (3 mmol) of dichloro(phenyl)-λ³-iodane in 20 ml of anhydrous carbon tetrachloride, the ampule was tightly capped, and the mixture was irradiated with a KGL-500 lamp for 5 h at 20°C until it became homogeneous. The solvent was removed under slightly reduced pressure, and the residue was washed with 5 ml of diethyl ether to remove iodobenzene. We thus obtained 0.61 g of a product mixture containing stereoisomers **XIVa** and **XIVb** and norcarane **XVIII** at a ratio of 4.6 : 1.3 : 1. Compounds **XIVa** and **XVIII** were isolated by column chromatography, and compound **XIVb** was identified by spectral methods in a mixture with **XIVa**.

***endo*-6,*syn*-7-Dichloro-*exo*-6-methylsulfonylbicyclo[3.1.1]heptane (XIVa).** Yield 0.27 g (37%), mp 99–100°C (from hexane–diethyl ether, 4:1), R_f 0.71, R_t 8.23 min. ^1H NMR spectrum, δ, ppm: 1.60–1.74 m and 1.74–1.88 m (1H each, 3-H), 2.23–2.34 m and 2.37–2.47 m (2H each, 2-H, 4-H), 3.08 s (3H, $MeSO_2$), 3.30 d.t (2H, 1-H, 5-H, J = 1.3, 5.9 Hz), 5.27 t (1H, 7-H, J = 5.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.2 (C^3), 25.5 (C^2, C^4), 36.7 ($MeSO_2$), 48.5 (C^1, C^5), 54.0 (C^7), 86.6 (C^6). Found, %: C 39.39; H 4.88. $C_8H_{12}Cl_2O_2S$. Calculated, %: C 39.52; H 4.97.

***exo*-6,*syn*-7-Dichloro-*endo*-6-methylsulfonylbicyclo[3.1.1]heptane (XIVb)** was isolated with a stereochemical purity of 50%, R_f 0.45, R_t 6.40 min. ^1H NMR spectrum, δ, ppm: 1.70–1.90 m (1H), 2.12–2.35 m (3H, 3-H, *exo*-2-H, *exo*-4-H) (overlapped by signals of isomer **XIVa**); 2.55–2.66 m (2H, 2-H, 4-H), 3.06 s (3H, $MeSO_2$), 3.16–3.20 m (2H, 1-H, 5-H), 5.05 t (1H, 7-H, J = 5.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.9 (C^3), 24.2 (C^2, C^4), 39.1 ($MeSO_2$), 54.4 (C^1, C^5), 56.2 (C^7), 73.5 (C^6).

***endo*-2,*exo*-3-Dichloro-*exo*-7-methylsulfonylbicyclo[4.1.0]heptane (XVIII).** Yield 85 mg (12%), mp 131–132°C (from hexane–diethyl ether, 4:1), R_f 0.15, R_t 4.24 min. ^1H NMR spectrum, δ, ppm: 1.73–1.98 m (3H), 2.16–2.23 m (1H), 2.30–2.40 m (2H), 2.55 t (1H, 7-H, J = 4.8 Hz), 3.01 s (3H, $MeSO_2$), 3.93 d.d.d (1H, 3-H, J = 2.4, 5.4, 7.8 Hz), 4.61 d.d (1H, 2-H, J = 5.7, 7.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.2, 20.9, 24.9, 27.0 (C^1, C^4, C^5, C^6); 41.0 and 41.4 (Me, C^7); 58.9 and 59.2 (C^2, C^3). Found, %: C 39.47; H 5.05. $C_8H_{12}Cl_2O_2S$. Calculated, %: C 39.52; H 4.97.

***syn*-7-Bromo-*exo*-6-methylsulfonylbicyclo[3.1.1]heptane (XVI).** A mixture of 0.432 g (1.3 mmol) of dibromo sulfone **XIVa** and 0.567 g (2.0 mmol) of triphenyltin hydride in 15 ml of anhydrous benzene

containing 5 mg of azobis(isobutyronitrile) was heated for 4 h under reflux in a weak stream of nitrogen. The solvent was removed under reduced pressure (water-jet pump), and the solid residue was subjected to column chromatography to isolate 0.118 g (36%) of compound **XVI** with mp 105–106°C (from chloroform–hexane, 2:1). ^{1}H NMR spectrum, δ, ppm: 1.58–1.72 m and 1.72–1.88 m (1H each, 3-H), 2.02–2.17 m and 2.26–2.40 m (2H each, 2-H, 4-H), 2.90 s (3H, $MeSO_2$), 3.11–3.16 m (2H, 1-H, 5-H), 3.60 s (1H, 7-H), 5.42 t (1H, 6-H, J = 6.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.8 (C^3), 26.2 (C^2, C^4), 40.0 ($MeSO_2$), 42.4 (C^1, C^5), 52.2 (C^6), 62.6 (C^7). Mass spectrum, *m*/*z* (I_{rel}, %): 253/251 (24.8/18.2) $[M - 1]^+$, 173/171 (22.2/26.4), 93 (15.9), 92 (47.0), 91 (100), 81 (10.9), 79 (10.2), 77 (19.2), 65 (19.3), 63 (10.1). Found, %: C 38.03; H 5.06. $C_8H_{13}BrO_2S$. Calculated, %: C 37.96; H 5.18.

***exo*-7-Methylsulfonylbicyclo[4.1.0]hept-2-ene (XX).** Perchloric acid, 0.1 ml, was added to a solution of 1.38 g (8 mmol) of compound **V** in 50 ml of anhydrous benzene. The mixture was kept for 72 h at 20°C, washed with 5 ml of a 5% aqueous solution of $NaHCO_3$ and with water, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel to isolate 0.83 g (60%) of compound **XX** as a colorless viscous oily substance, R_f 0.52. ^{1}H NMR spectrum, δ, ppm: 1.66–1.81 m (2H), 2.01–2.22 m (4H, 1-H, 4-H, 5-H, 6-H), 2.59 t (1H, 7-H, J = 4.2 Hz), 2.94 s (3H, $MeSO_2$), 5.64–5.71 m (1H), 5.97–6.03 m (1H, 2-H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 16.5, 17.2, 20.1, 20.4, 40.5, 41.4 ($MeSO_2$), 123.4 and 126.8 (C^2, C^3). Found, %: C 55.53; H 7.06. $C_8H_{12}O_2S$. Calculated, %: C 55.78; H 7.02.

1-Methyl-*exo*-7-phenylsulfonylbicyclo[4.1.0]-hept-2-ene (XXVI) was synthesized according to the procedure described in [20]. Its ^{1}H NMR spectrum was identical to that given in [20]. ^{13}C NMR spectrum (DEPT), δ_C, ppm: 16.4 and 19.7 (C^4, C^5), 17.4 (CH_3), 24.8 (C^1), 27.7 (C^6), 46.4 (C^7), 125.4 and 133.0 (C^2, C^3); 127.0 (2C), 129.1 (2C), 130.9, 142.0 (C_{arom}).

Reactions of norcarenes XX, XXI, and XXVI with bromine (*general procedure*). Sulfone **XX**, **XXI** [20], or **XXVI**, 4 mmol, was dissolved in 5 ml of anhydrous methylene chloride, a solution of 0.2 ml (0.78 g, 4.9 mmol) of bromine in 5 ml of methylene chloride was added over a period of 10 min under stirring at 20°C, and the mixture was stirred for 24–30 h until it turned colorless. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel to isolate dibromonorcarane **XVII**, **XIX**, or **XXIV** in 78, 82, or 75% yield, respectively.

***endo*-2,*exo*-3-Dibromo-*exo*-7-phenylsulfonylbicyclo[4.1.0]heptane (XIX).** R_f 0.52, mp 149–150°C (from hexane–diethyl ether, 1:1). ^{1}H NMR spectrum, δ, ppm: 1.79–1.95 m (3H), 2.19–2.27 m (1H), 2.30–2.41 m (1H), 2.49–2.56 m (1H), 2.60 t (1H, 7-H, J = 4.9 Hz), 4.19–4.23 m (1H, 3-H), 4.78 d.d (1H, 2-H, J = 7.8, 4.0 Hz), 7.56 t (2H, H_{arom}, J = 7.6 Hz), 7.66 t (1H, H_{arom}, J = 7.3 Hz), 7.91 d (2H, H_{arom}, J = 7.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.2, 23.0, 24.7, 25.8, 44.8 (C^7), 49.8 and 51.3 (C^2, C^3); 127.9 (2C), 129.2 (2C), 133.6, 139.7 (C_{arom}). Found, %: C 39.83; H 3.61. $C_{13}H_{14}Br_2O_2S$. Calculated, %: C 39.62; H 3.58.

***endo*-2,*exo*-3-Dibromo-1-methyl-*exo*-7-phenylsulfonylbicyclo[4.1.0]heptane (XXIV).** mp 136–136.5°C (from hexane–diethyl ether). ^{1}H NMR spectrum, δ, ppm: 1.50 s (3H, Me), 1.75–1.85 m (1H), 1.86–1.96 m (2H), 2.31–2.41 m (1H), 2.45 t (1H, J = 6.4 Hz), 2.61 d (1H, 7-H, J = 6.1 Hz), 4.16 d.d.d (1H, 3-H, J = 2.3, 5.5, 8.3 Hz), 4.39 d (1H, 2-H, J = 6.2 Hz), 7.55 t (2H, H_{arom}, J = 7.7 Hz), 7.64 t (1H, H_{arom}, J = 7.2 Hz), 7.92 d (2H, H_{arom}, J = 7.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 19.2, 19.6, 26.7, 29.1, 31.6 (C^1), 49.3 (C^7), 52.2 (C^3), 59.3 (C^2); 127.4 (2C), 129.0 (2C), 133.4, 140.8 (C_{arom}). Mass spectrum (MALDI), *m*/*z* (I_{rel}, %): 428.65 (27.6), 430.54 (40.1), 432.87 (32.3) $[M + Na]^{+\cdot}$; 444.54 (19.4), 446.55 (56.3), 448.54 (24.3) $[M + K]^{+\cdot}$. Found, %: C 41.28; H 3.85. $C_{14}H_{16}Br_2O_2S$. Calculated, %: C 41.20; H 3.95.

Reaction of tricycloheptane VII with dioxane dibromide. A solution of 0.74 g (3 mmol) of sulfone **VII** in 15 ml of anhydrous carbon tetrachloride containing 0.1 g of $CaCO_3$ was cooled to –10°C, and a solution of 1.24 g (3 mmol) of freshly prepared dioxane dibromide in 35 ml of anhydrous carbon tetrachloride was added dropwise over a period of 1 h under stirring in a nitrogen atmosphere. The mixture was stirred for ~2 h at 0°C until it turned colorless and filtered, and the solvent was distilled off from the filtrate under reduced pressure. The MALDI mass spectrum of the crystalline residue contained peaks corresponding to the molecular ions of compounds **XXV** and **XXIV** (ratio 1:4 according to the ^{1}H NMR data). Norcarane **XXV** was isolated as individual substance by column chromatography on silica gel.

***endo*-2-Bromo-1-methyl-*exo*-7-phenylsulfonylbicyclo[4.1.0]heptane (XXV).** Yield 0.24 g (24%),

mp 113–114°C (from hexane–diethyl ether), R_f 0.45. ^{1}H NMR spectrum, δ, ppm: 1.15–1.28 m (1H), 1.40–1.56 (2H), 1.48 s (3H, Me), 1.59–1.73 m (1H), 2.00–2.09 m (1H), 2.09–2.19 m (1H), 2.38–2.45 m (1H, 6-H), 2.57 d (1H, 7-H, J = 6.1 Hz), 4.13 d.d (1H, 2-H, J = 5.8, 10.9 Hz), 7.52–7.68 m (3H, H_{arom}), 7.94 d (2H, H_{arom}, J = 7.1 Hz). ^{13}C NMR spectrum (DEPT), δ_C, ppm: 18.2 (Me); 21.7, 22.9, 32.4 (C^3, C^4, C^5); 30.8 (C^6), 49.6 (C^7), 56.8 (C^2); 127.5 (2C), 128.9 (2C), 133.3, 141.0 (C_{arom}). Mass spectrum (MALDI), m/z (I_{rel}, %): 351.04/353.01 (51.4/48.6) $[M + Na]^{+\cdot}$; 366.98/368.99 (46.7/53.3) $[M + K]^{+\cdot}$. Found, %: C 51.18; H 5.25. $C_{14}H_{17}BrO_2S$. Calculated, %: C 51.07; H 5.20.

Reaction of tricycloheptane VII with hydrogen bromide. A solution of 0.62 g (2.5 mmol) of compound **VII** in 15 ml of anhydrous carbon tetrachloride was cooled to 0°C, and a weak stream of dry hydrogen bromide was passed through the solution over a period of 1 h under stirring [30]. The mixture was then washed with a 2% solution of sodium carbonate and with water and dried over $MgSO_4$, the solvent was removed under reduced pressure, and crystallization of the residue gave 0.68 g (83%) of norcarane **XXV**.

Reactions of sulfones VIII and IX with bromine (*general procedure*). A solution of 1.5 mmol of tricycloheptane **VIII** or **IX** in 7 ml of anhydrous methylene chloride was mixed with a solution of 62 μl (1.5 mmol) of bromine in 3 ml of methylene chloride. The mixture was kept for 7 days at 20°C in a tightly capped vessel, washed with 5 ml of a 5% aqueous solution of Na_2SO_3 and with water, and dried over $MgSO_4$. The solvent was removed under reduced pressure (water-jet pump), and the solid residue was subjected to column chromatography on silica gel to isolate compound **XXII** or **XXIII** in 82 or 86% yield, respectively. The physical constants and spectral parameters of **XXIII** coincided with those given in [23].

6,6,7-Tribromo-*endo*-7-phenylsulfonylbicyclo-[3.1.1]heptane (XXII). Yield 82%, mp 172–173°C (from hexane–diethyl ether), R_f 0.73. ^{1}H NMR spectrum, δ, ppm: 1.56–1.67 m and 1.68–1.81 m (1H each, 3-H), 2.47–2.58 m and 2.78–2.89 m (2H each, 2-H, 4-H), 3.96 s (2H, 1-H, 5-H), 7.52 t (2H, H_{arom}, J = 7.7 Hz), 7.60 t (1H, H_{arom}, J = 7.3 Hz), 7.89 d (2H, H_{arom}, J = 7.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.2 (C^3), 37.0 (C^2, C^4), 57.8 (C^6), 61.4 (C^1, C^5), 84.9 (C^7), 128.4 (2C), 129.2 (2C), 133.6, 142.4 (C_{arom}). Found, %: C 32.98; H 2.72. $C_{13}H_{13}Br_3O_2S$. Calculated, %: C 33.01; H 2.77.

Reaction of dibromide XIIa with potassium *tert*-butoxide in DMSO. A solution of 3.32 g (10 mmol) of compound **XIIa** in 20 ml of anhydrous DMSO was added under stirring and cooling (with tap water) in a dry nitrogen atmosphere to a solution of 5.61 g (50 mmol) of potassium *tert*-butoxide in 20 ml of anhydrous DMSO. The mixture was stirred for 2 h at 70°C, cooled, diluted with 40 ml of water, and extracted with diethyl ether (5×20 ml). The extracts were dried over $MgSO_4$, the solvent was distilled off on a water bath, and the residue was subjected to column chromatography on Al_2O_3 to isolate 0.56 g (33%) of compound **V**.

REFERENCES

1. Christl, M., *Adv. Strain Org. Chem*., 1995, vol. 4, p. 163.
2. Razin, V.V., *Sovremennye problemy organicheskoi khimii. Mezhvuzovskii sbornik* (Current Problems of Organic Chemistry. An Interinstitution Collection), St. Petersburg: Sankt-Peterb. Gos. Univ., 1996, no. 11, p. 54.
3. Vasin, V.A., *Russ. J. Org. Chem*., 1995, vol. 31, p. 1258.
4. Vasin, V.A., Semenov, A.V., and Razin, V.V., *Russ. J. Org. Chem*., 2002, vol. 38, p. 803.
5. Vasin, V.A., Semenov, A.V., and Razin, V.V., *Russ. J. Org. Chem*., 2004, vol. 40, p. 653.
6. Vasin, V.A., Semenov, A.V., and Razin, V.V., *Russ. J. Org. Chem*., 2004, vol. 40, p. 1599.
7. Vasin, V.A., Semenov, A.V., Kostryukov, S.G., and Razin, V.V., *Russ. J. Org. Chem*., 2008, vol. 44, p. 1296.
8. Vasin, V.A., Petrov, P.S., Kostryukov, S.G., and Razin, V.V., *Russ. J. Org. Chem*., 2010, vol. 46, p. 186.
9. Vasin, V.A., Kostryukov, S.G., and Razin, V.V., *Russ. J. Org. Chem*., 1998, vol. 34, p. 1136.
10. Borbulevych, O.Ya., Semenov, A.V., Vasin, V.A., and Razin, V.V., *Acta Crystallogr., Sect. E*, 2002, vol. 58, p. 925.
11. Vasin, V.A., Kostryukov, S.G., Semenov, A.V., and Razin, V.V., *Russ. J. Org. Chem*., 2008, vol. 44, p. 528.
12. Wiberg, K.B. and Hess, B.A., *J. Org. Chem*., 1966, vol. 31, p. 2250.
13. Razin, V.V., Makarychev, Yu.A., and Zolotarev, R.N., *Russ. J. Org. Chem*., 1998, vol. 34, p. 1503.
14. Razin, V.V. and Makarychev, Yu.A., *Russ. J. Org. Chem*., 1996, vol. 32, p. 1640.
15. 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; Nemukhin, A.V., Grigorenko, B.L., and Granovsky, A.A., *Moscow Univ. Chem. Bull*., 2004, vol. 45, p. 75.

16. Hoz, S., *The Chemistry of the Cyclopropyl Group*, Rappoport, Z., Ed., New York: Wiley, 1987, chap. 19, p. 1121.
17. Vasin, V.A., Kostryukov, S.G., and Razin, V.V., *Russ. J. Org. Chem*., 1996, vol. 32, p. 49.
18. Szeimies, G., Schloβer, A., Philipp, F., Dietz, P., and Mickler, W., *Chem. Ber*., 1978, vol. 111, p. 1922.
19. Bott, G., Field, L.D., and Sternhell, S., *J. Am. Chem. Soc*., 1980, vol. 102, p. 5618.
20. Vasin, V.A., Petrov, P.S., Kalyazin, V.A., and Razin, V.V., *Russ. J. Org. Chem*., 2010, vol. 46, p. 812.
21. Solladie-Cavallo, A. and Isarno, T., *Tetrahedron Lett*., 1999, vol. 40, p. 1579.
22. Razin, V.V., Makarychev, Yu.A., Zolotarev, R.N., Vasin, V.A., Hennig, L., and Baldamus, J., *Russ. J. Org. Chem*., 2007, vol. 43, p. 817.
23. Vasin, V.A., Petrov, P.S., Genaev, A.M., Gindin, V.A., and Razin, V.V., *Zh. Strukt. Khim*., 2010, vol. 51, p. 982.
24. Philips, J.Ch. and Oku, M., *J. Am. Chem. Soc*., 1972, vol. 94, p. 1012.
25. 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.
26. Zefirov, N.S. and Makhon'kov, D.J., *Chem. Rev*., 1982, vol. 82, p. 615.
27. Mazur, S., Schröder, A.H., and Weiss, M.C., *J. Chem. Soc., Chem. Commun*., 1977, p. 262; Morf, J., *Dissertation Univ. München*, 1988.
28. 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.
29. Szeimies, G., Philipp, F., Baumgärtel, O., and Harnisch, I., *Tetrahedron Lett*., 1977, vol. 18, p. 2135.
30. Vasin, V.A., Belozerov, A.I., Tanaseichuk, B.S., Shishkin, V.N., Yagodin, A.I., and Davydova, R.G., USSR Inventor's Certificate no. 1206229, 1986; *Byull. Izobret*., 1986, no. 3.