

Stereoselective Synthesis of Substituted Bicyclo[3.1.1]heptanes: II.* Synthesis of All Diastereoisomers of 7-Methyl- and 7-Phenylbicyclo[3.1.1]hept-6-yl Phenyl Sulfones from Tricyclo[4.1.0.0^{2,7}]heptane Precursors

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Received July 11, 2007

Abstract—All four possible diastereoisomers of 7-methyl- and 7-phenylbicyclo[3.1.1]hept-6-yl phenyl sulfones were intentionally synthesized from tricyclo[4.1.0.0^{2,7}]heptane and 1-phenyltricyclo[4.1.0.0^{2,7}]heptane, respectively. The key stage in the synthesis was regio- and stereoselective cleavage of the central bicyclobutane C¹–C⁷ bond in the tricycloheptane precursors by the action of radical, nucleophilic, and electrophilic reagents. The NMR spectra of the diastereoisomers were compared.

DOI: 10.1134/S1070428008030020

Tricyclo[4.1.0.0^{2,7}]heptane (**I**) is one of the most accessible bicyclo[1.1.0]butane derivatives. Compound **I** and its 1-phenyl-substituted derivative **II** are obtained according to Moore via dibromocyclopropanation–debromination of cyclohexene and 1-phenylcyclohexene, respectively [2, 3]. Due to relatively high CH acidity, hydrocarbons **I** and **II** can be converted into other tricycloheptane derivatives by preliminary metalation at the bridgehead position, followed by reaction with electrophiles. For example, the transformations of **I** into **III** [4] and of **II** into **IV** have been reported [5].

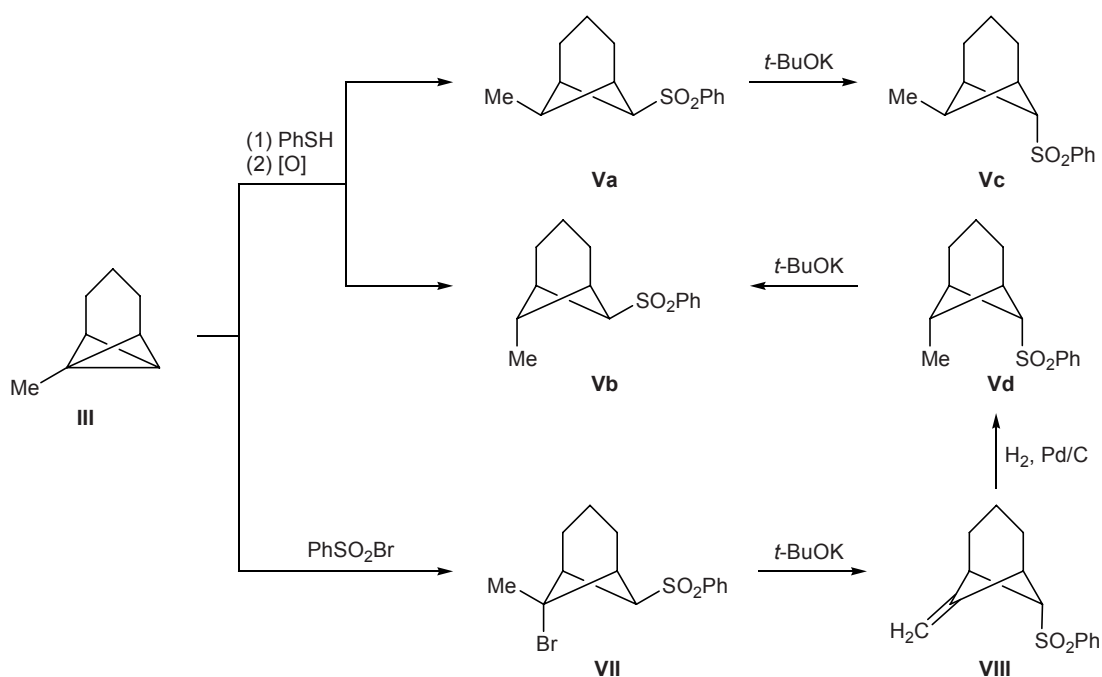
Specificity of the electronic structure predetermines the mode of cleavage of the tricycloheptane system by the action of radical [6] and in some cases nucleophilic and electrophilic reagents: rupture of the central bicyclobutane C¹–C⁷ bond leads to the formation of bicyclo[3.1.1]heptane derivatives [7]. For example, addition of benzenethiol to compound **I** and subsequent hydrodesulfurization gives unsubstituted norpinane (bicyclo[3.1.1]heptane) [8], and this reaction underlies the most efficient procedure for its preparation. Cleavage of the C¹–C⁷ bond by the action of a nucleophilic reagent is possible only when a strong electron-withdrawing substituent (such as phenylsulfonyl

group [9]) is present at the bridgehead position, while the presence of a donor group, e.g., phenyl ring [10], activates the above bond toward electrophiles. Finally, additions to tricycloheptane derivatives are characterized by strict *endo*-selectivity of the primary attack by any reagent (radical, electrophilic, or nucleophilic) on the C¹–C⁷ bond [6–10].

The above listed specific features of the chemical behavior of tricycloheptane derivatives allowed us to hope that 6- and 7-substituted norpinanes having a required configuration could be synthesized. It should be emphasized that purposeful synthesis of such compounds is a fairly difficult problem. In the present communication we describe the synthesis of all four possible diastereoisomers of two 6,7-disubstituted norpinane derivatives, phenyl sulfones **V** and **VI**, as a possible solution of this problem. Scheme 1 illustrates the syntheses of diastereoisomeric sulfones **Va**–**Vd**. Here, the tricycloheptane precursor was 1-methyltricyclo[4.1.0.0^{2,7}]heptane (**III**) which is available from tricycloheptane **I** via organolithium replacement [4].

In keeping with Scheme 1, tricycloheptane **III** was brought into known [8] reaction with benzenethiol, which afforded a mixture of two stereoisomeric norpinane sulfides. Their oxidation with NaIO₄–KMnO₄

Scheme 1.



in acetone at 20°C in the presence of MgSO₄ [11] gave the corresponding diastereoisomeric sulfones **Va** (*endo,syn* isomer) and **Vb** (*endo,anti* isomer). Each sulfone **Va** and **Vb** was isolated by column chromatography on aluminum oxide. The configuration of compounds **Va** and **Vb** is predetermined at the stage of addition of benzenethiol to tricycloheptane **III**: phenylsulfanyl radical attacks the C¹–C⁷ bond with strict *endo*-

selectivity and exclusively at the unsubstituted C¹ atom, while the subsequent hydrogen transfer is not stereoselective. Epimerization of sulfone **Va** by the action of potassium *tert*-butoxide in THF gave the third *exo,syn* isomer **Vc**. Finally, the fourth *exo,anti* isomer **Vd** was synthesized by a sequence of three reactions. In the first step, radical addition of benzenesulfonyl bromide to hydrocarbon **III** resulted in stereo-

Scheme 2.

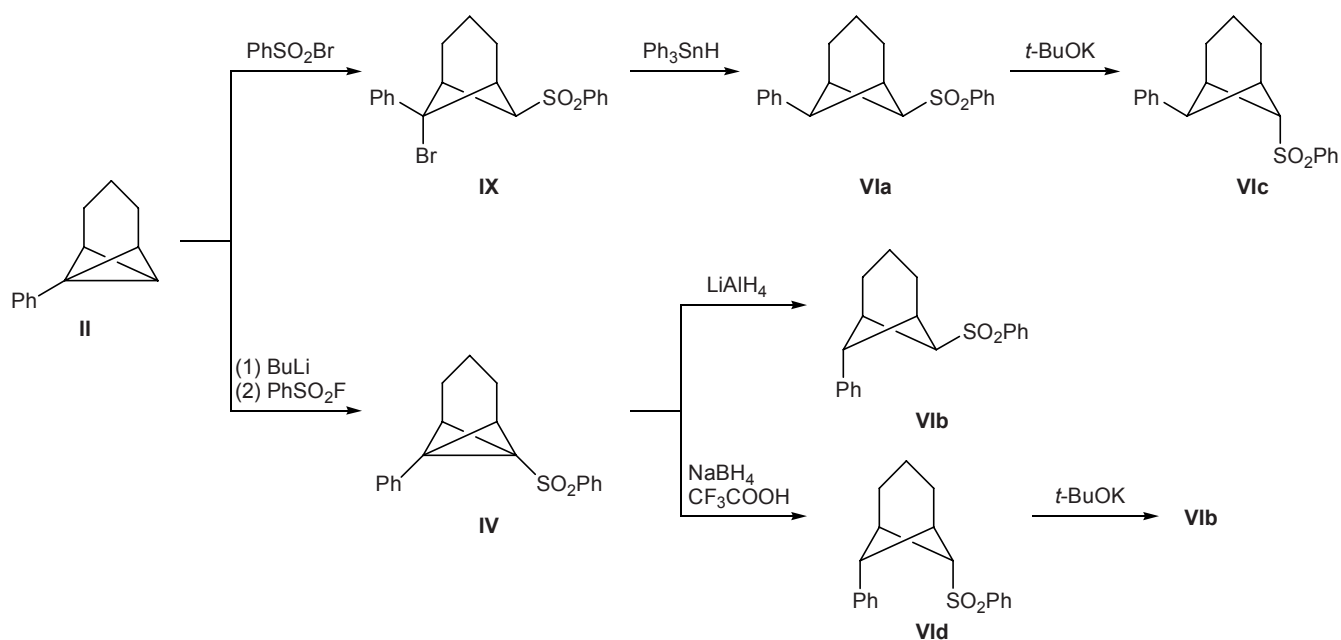


Table 1. ^1H NMR spectra of compounds **Va–Vd** and **Vla–VId**, δ , ppm (J , Hz)

Comp. no.	1-H, 5-H	<i>exo</i> -2-H, <i>exo</i> -4-H	<i>endo</i> -2-H, <i>endo</i> -4-H	<i>exo</i> -3-H	<i>endo</i> -3-H	7-H	6-H	Me	Ph
Va	2.60 br.s	2.32–2.46	1.79–1.91	2.11–2.27	1.62–1.77	2.06 sext ($J = 6.5$)	3.33 t ($J = 5.4$)	1.02 d ($J = 7.3$)	7.52–7.67 m (3H), 7.92 d (2H, $J = 7.3$)
Vb	2.57 br.s	2.35 br.s	1.71–2.15				3.62 t ($J = 5.8$)	1.10 d ($J = 7.3$)	7.48–7.68 m (3H), 7.87 d (2H, $J = 7.3$)
Vc	2.77 d ($J = 4.3$)	1.91–2.07	1.74–1.85	1.53–1.70		3.27 m	3.26 s	0.90 d ($J = 6.5$)	7.49–7.69 m (3H), 7.91 d (2H, $J = 7.3$)
Vd	2.62 br.s	2.01–2.14	1.85–1.98	1.72–1.84		1.59–1.71	3.10 d ($J = 2.9$)	1.50 d ($J = 7.3$)	7.50–7.69 m (3H), 7.90 d (2H, $J = 7.3$)
Vla	3.21–3.30 ^a	2.57–2.70	1.90–2.05	1.55–1.70	0.81–0.98	3.21–3.30 ^a	3.41 t ($J = 5.4$)	–	7.12 d (2H, $J = 7.7$), 7.20–7.40 m (3H), 7.57–7.72 m (3H), 7.96 d (2H, $J = 7.0$)
Vlb	3.00 br.d	2.73–2.87	2.09–2.24	2.06–2.20	1.90–2.06	3.22 s	3.58 t ($J = 5.9$)	–	7.21–7.38 m (5H), 7.50–7.68 m (3H), 7.85 d (2H, $J = 7.3$)
Vlc	3.35 br.d	2.15–2.27	1.70–1.85	1.25–1.39	0.90–1.08	4.47 t ($J = 6.1$)	3.05 s	–	7.05–7.39 m (5H), 7.55–7.75 m (3H), 8.00 d (2H, $J = 7.3$)
VId	3.30 br.s	2.24–2.39	2.10–2.23	1.91–2.07	1.76–1.91	3.06 d ($J = 3.1$)	3.23 d ($J = 3.1$)	–	7.22–7.43 m (5H), 7.43–7.65 m (3H), 7.70 d (2H, $J = 7.3$)

^a Signals from the 1-H, 5-H, and 6-H protons overlap each other, giving rise to unresolved multiplet.

selective formation of bromide **VII**. Compound **VII** was subjected to dehydrobromination to obtain methylenenorpinane **VIII**. Both these reactions were described by us previously [12]. It should be noted that the dehydrobromination process is accompanied by change of the orientation of the phenylsulfonyl group. In the final step, highly stereoselective catalytic hydrogenation of compound **VIII** over Pd/C gave isomer **Vd**. Here, the stereoselectivity is ensured by steric hindrances created by the PhSO_2 group to hydrogen approach from the *anti* side. Epimerization of sulfone **Vd** by the action of potassium *tert*-butoxide led to already available isomer **Vb**.

Diastereoisomeric sulfones **Vla–VId** were synthesized as shown in Scheme 2. Here, compound **II** and sulfone **IV** were used as tricycloheptane precursors. *endo,syn* Isomer **Vla** was obtained in two steps starting from hydrocarbon **II**. In the first step, addition of benzenesulfonyl bromide to **II** gave phenyl-substituted analog of bromide **VII**, compound **IX**, which was reduced with triphenylstannane in the second step. The reduction occurred with retention of configuration at the reaction center. An alternative procedure for the

synthesis of sulfone **Vla** was based on the oxidation of known [8] adduct of **II** with benzenethiol in a way similar to the preparation of sulfone **Va**. These transformations were described in [5]. Epimerization of sulfone **Vla** gave *exo,syn* isomer **Vlc** (cf. the above transformation of **Va** into **Vc**; Scheme 1). The two other diastereoisomers of sulfone **VI** were synthesized by hydrogenolysis of tricycloheptane **IV** in two different ways [13]. *exo,anti* Isomer **VId** was obtained by ionic hydrogenation of **IV** using the system $\text{NaBH}_4\text{--CF}_3\text{CO}_2\text{H}$ [14]. This transformation is an example of addition of electrophilic hydrogen atom, where NaBH_4 acts as hydride ion carrier. The stereoselectivity of this process is the same as in the addition of methanol to sulfone **IV**, catalyzed by a mineral acid [15]. Treatment of sulfone **VId** with potassium *tert*-butoxide in THF resulted in its complete epimerization into *endo,anti* isomer **Vlb** by analogy with the transformation of **Vd** into **Vb**. The same isomer (**Vlb**) was also synthesized by an alternative method, hydrogenation of sulfone **IV** with lithium tetrahydridoaluminate [9, 16]. These reactions may be regarded as examples of nucleophilic addition to the activated bicyclobutane

Table 2. ^{13}C NMR spectra of compounds **Va–Vd** and **VIa–VId**, δ_{C} , ppm

Compound no.	C^1, C^5	C^3	C^2, C^4	C^6	C^7	Me	Ph
Va	41.5	13.3	19.4	62.0	33.6	9.4	127.1, 129.0, 133.0, 140.8
Vb	43.5	15.8	24.4	60.6	35.5	14.1	127.3, 129.1, 133.1, 140.6
Vc	39.3	11.1	23.5	66.2	32.9	13.4	127.8, 129.1, 133.2, 139.6
Vd	41.1	15.9	33.0	70.5	38.6	14.1	127.2, 129.1, 133.0, 141.6
VIa	41.1	13.3	19.7	60.7	40.8	–	125.6, 125.7, 127.3, 128.1, 129.1, 133.1, 138.6, 140.5
VIb	43.1	14.6	24.6	60.0	44.8	–	126.4, 127.0, 127.4, 128.6, 129.2, 133.2, 140.2, 140.3
VIc	39.3	13.8	26.5	69.7	40.0	–	125.4, 125.5, 128.0, 128.3, 129.3, 133.5, 139.4, 141.1
VId	40.1	14.8	33.0	70.3	47.6	–	125.7, 126.9, 127.7, 127.9, 128.9, 133.0, 140.5

system. The reaction is initiated by attack by hydride ion, and it leads to the formation of more stable addition product, isomer **VIb**, rather than **VId**.

We believe that application of the epimerization method for the preparation of diastereoisomeric norpinane sulfones deserves special comments. Interestingly, epimerization at C^6 in isomers **Va** (**VIa**) and **Vd** (**VId**) occurs in different directions. This is explained by different orientations of the methyl (phenyl) substituents in their molecules. The methyl (phenyl) and phenylsulfonyl groups in molecules **Vd** and **VId** appear spatially close to each other, which is a destabilizing factor; therefore, their epimerization involves transition of the sulfonyl group to the *endo* position, i.e., to give isomers **Vb** and **VIb**. By contrast, epimerization of isomers **Va** and **VIa**, in which the methyl (phenyl) group is oriented *syn*, leads to isomers **Vc** and **VIc** with the phenylsulfonyl group located in the *exo* position, as was observed for 6-*endo*-norpinyl phenyl sulfone which was completely converted into 6-*exo*-norpinyl phenyl sulfone [9].

Now let us consider the ^1H and ^{13}C NMR spectra of diastereoisomers **Va–Vd** and **VIa–VId** (Tables 1, 2), in particular their structure-related specificity which was used to assign configuration of the isomers. Analysis of the ^1H NMR spectra of isomers **VIa–VId** is quite sufficient to determine their configuration. The 6-H signal in the spectra of **VIa** and **VIb** appear as a triplet with a coupling constant of about 5.5 Hz, which unambiguously indicates *exo* orientation of that proton; otherwise, the vicinal coupling constants with 1-H and 5-H would be much smaller [17]. Therefore, the phenylsulfonyl group in **VIa** and **VIb** is oriented *endo*. The *exo*-3-H proton in isomers **VIa** and **VIc** resonates

at $\delta \sim 1.0$ ppm, indicating *syn* orientation of the phenyl group on C^7 ; the signal is displaced upfield due to shielding by the benzene ring. However, the 6-H signal in the spectrum of **VIc** is a singlet, which means that the PhSO_2 group occupies *exo* position. The *syn* orientation of the phenyl group on C^7 in **VIc** is additionally confirmed by the multiplicity and downfield position of the 7-H signal (δ 4.47 ppm, t, $J = 6.1$ Hz); in this case, the phenylsulfonyl group located opposite exerts a deshielding effect. Thus the configuration of diastereoisomers **VIa** and **VIc** may be regarded as convincingly proved. The *anti* orientation of the phenyl substituent on C^7 in isomers **VIb** and **VId** was determined taking into account the absence of resonance signals at about δ 1 ppm. In keeping with the data of [17], the presence of a singlet from the 7-H proton and a triplet from the 6-H proton ($J = 5.8$ Hz) in the spectrum of **VIb** allowed us to assign its configuration. In the spectrum of **VId**, the 6-H and 7-H signals appear as doublets with a coupling constant of 3.1 Hz. These data unambiguously indicate *endo, syn* orientation of 6-H and 7-H: an appreciable long-range coupling between protons separated by four σ -bonds in norpinanes (*W*-coupling [18]) can be observed only for that configuration. Thus the configuration of diastereoisomer **VId** was also determined.

Comparison of the ^{13}C NMR spectra of diastereoisomers **VIa–VId** showed the following configuration-related differences. First, in the spectra of isomers **VIc** and **VId** with *exo* orientation of the PhSO_2 group, the chemical shift of C^6 is larger by ~ 10 ppm than that found for compounds **VIa** and **VIb** with *endo* orientation of the same group. Second, analogous difference is observed in the chemical shifts of C^7 : *anti* orienta-

tion of the phenyl group (**VIb**, **VIId**) is characterized by more downfield position of the C⁷ signal (by ~4–7 ppm) as compared to isomers **VIa** and **VIc** with *syn*-oriented phenyl group. Third, orientation of substituents on C⁶ and C⁷ affects the chemical shifts of C² and C⁴: *endo, syn* isomer **VIa** displays the C² and C⁴ signals in a stronger field (by ~13 ppm) than does *exo, anti* isomer **VIId**.

Configuration assignment of diastereoisomers **Va**–**Vd** required comparison of both ¹H and ¹³C NMR spectra with account taken of the above relations. The *endo* orientation of the PhSO₂ group in isomers **Va** and **Vb** follows both from the presence of a triplet signal from 6-H and from the similar chemical shifts of C⁶. The lowest chemical shift of C²/C⁴ in the ¹³C NMR spectrum of isomer **Va** eventually confirms its configuration and predetermines the configuration of **Vb**. The structure of isomer **Vd** is supported by the presence of a doublet signal from 6-H (*W*-coupling), maximal (in the examined series) chemical shift of C²/C⁴, and largest chemical shift of the methyl protons due to deshielding effect of the oppositely located phenylsulfonyl group. Then the remaining diastereoisomer has structure **Vc**.

EXPERIMENTAL

The elemental compositions were determined on an HP-185B CHN analyzer. The ¹H and ¹³C NMR spectra were measured from solutions in CDCl₃ on a Bruker DPX-300 spectrometer (300.130 and 75.468 MHz, respectively). Analytical thin-layer chromatography was performed on Silufol UV-254 plates using diethyl ether–hexane (1:1) as eluent; spots were detected by treatment with iodine vapor. Preparative separation of products and their purification were performed by column chromatography on silica gel L (40–100 μm) using light petroleum ether–ethyl acetate (3:1) as eluent. Tricycloheptanes **I** [2], **II** [3], **III** [4], and **IV** [5], and 7-methylidene-6-bicyclo[3.1.1]heptyl phenyl sulfone (**VIII**) [12] were synthesized by known methods.

Sulfones Va and Vb. *a.* A solution of 2.14 g (10 mmol) of NaIO₄ and 9.48 g (60 mmol) of KMnO₄ in 75 ml of distilled water was added over a period of 3 h to a solution of 10 mmol of a mixture of the *syn*- and *anti*-tricycloheptane **III**–benzenethiol adducts (obtained as described in [8]; isomer ratio 1:4, according to the ¹H NMR data) in 50 ml of acetone containing 6 g (50 mmol) of powdered anhydrous MgSO₄ under stirring at 20°C. The mixture was stirred for 10 h, excess KMnO₄ was reduced with Na₂SO₃, and the

precipitate of MnO₂ was filtered off and washed with chloroform (4×15 ml). The organic layer was separated and dried over MgSO₄, and the solvent was removed on a rotary evaporator. According to the ¹H NMR data, the residue contained compounds **Va** and **Vb** at a ratio of 77:23. Overall yield 87%. Individual isomers **Va** and **Vb** were isolated by column chromatography on aluminum oxide and were additionally purified by recrystallization.

b. A solution of 10 mmol of a mixture of the *syn*- and *anti*-tricycloheptane **III**–benzenethiol adducts in a mixture of 15 ml of acetic acid 20 ml of acetic anhydride was cooled to 0°C, 20 ml of 30% hydrogen peroxide was added, and the mixture was stirred for 1 h at 0°C and was then kept for 40 h at room temperature. The acetic acid was evaporated under reduced pressure, the residue was neutralized with a solution of Na₂CO₃, and the product was extracted into diethyl ether (3×20 ml). The subsequent procedure was the same as above in *a*. The ratio and overall yield of compounds **Va** and **Vb** were similar to those indicated above.

***syn*-7-Methylbicyclo[3.1.1]hept-endo-6-yl phenyl sulfone (Va).** mp 93–94°C (from chloroform–hexane, 1:1), *R*_f 0.52. Found, %: C 66.94; H 7.11. C₁₄H₁₈O₂S. Calculated, %: C 67.17; H 7.25.

***anti*-7-Methylbicyclo[3.1.1]hept-endo-6-yl phenyl sulfone (Vb).** mp 71–73°C, *R*_f 0.44. Found, %: C 67.14; H 7.41. C₁₄H₁₈O₂S. Calculated, %: C 67.17; H 7.25.

***anti*-7-Methylbicyclo[3.1.1]hept-exo-6-yl phenyl sulfone (Vd).** An apparatus for catalytic hydrogenation was charged with a solution of 0.5 g of compound **VIII** in 10 ml of methanol, 15 mg of 5% Pd/C was added, and hydrogenation was carried out at 20°C, following the absorption of hydrogen. The reaction was complete in 20 min (a theoretical amount of hydrogen was absorbed). The mixture was filtered, the filtrate was evaporated, and the residue was purified by recrystallization from hexane–diethyl ether. Yield 0.41 g (82%), mp 80–81°C, *R*_f 0.44. Found, %: C 67.22; H 7.31. C₁₄H₁₈O₂S. Calculated, %: C 67.17; H 7.25.

Phenyl *syn*-7-phenylbicyclo[3.1.1]hept-endo-6-yl sulfone (VIa) was synthesized according to the procedure described in [5]. mp 142–143°C, *R*_f 0.50.

Base-catalyzed epimerization of sulfones Va, Vd, VIa, and VIId (general procedure). A glass ampule was charged with a solution of 0.5 mmol of sulfone **Va**, **Vd**, **VIa**, or **VIId** in 5 ml of anhydrous THF, 50 mg of powdered *tert*-butoxide was added, and the ampule was sealed and heated for 6 h at 80°C. The ampule was cooled and opened, the mixture was diluted with 20 ml

of water, neutralized with 10% hydrochloric acid, and extracted with diethyl ether (3 × 20 ml).

syn-7-Methylbicyclo[3.1.1]hept-*exo*-6-yl phenyl sulfone (Vc) was obtained by epimerization of sulfone **Va**. Yield 81%, mp 97–98°C (from diethyl ether–hexane, 1 : 1), R_f 0.55. Found, %: C 66.90; H 7.17. $C_{14}H_{18}O_2S$. Calculated, %: C 67.17; H 7.25.

Sulfone Vb was obtained by epimerization of sulfone **Vd**. Yield 85%; the product contained about 10% of initial sulfone **Vd**. Compound **Vb** was identified by comparing its 1H NMR spectrum with that of a sample prepared as described above.

Phenyl syn-7-phenylbicyclo[3.1.1]hept-*exo*-6-yl sulfone (VIc) was obtained by epimerization of sulfone **VIa**. Yield 82%, mp 155–156°C (from chloroform–hexane), R_f 0.49. Found, %: C 72.89; H 6.34. $C_{19}H_{20}O_2S$. Calculated, %: C 73.04; H 6.45.

Phenyl anti-7-phenylbicyclo[3.1.1]hept-*endo*-6-yl sulfone (VIb) was obtained by epimerization of sulfone **VId**. Yield 92%, mp 127–128°C, R_f 0.61. The product was identified by comparing its 1H NMR spectrum with that of an authentic sample [5].

Phenyl anti-7-phenylbicyclo[3.1.1]hept-*exo*-6-yl sulfone (VId). A mixture of 0.59 g (1.9 mmol) of finely powdered sulfone **IV** and 0.72 g (19 mmol) of powdered $NaBH_4$ was carefully added in very small portions over a period of 20 min to 15 ml of trifluoroacetic acid on cooling with an ice bath and vigorous stirring in a strong stream of argon. The mixture was stirred for an additional 5 min, trifluoroacetic acid was removed under reduced pressure, and the residue was treated with 5 ml of ice water and 5 ml of a saturated solution of sodium chloride. The precipitate was filtered off, dried in air, and purified by chromatography using a short column charged with aluminum oxide. Yield 0.244 g (41%), mp 134–135°C, R_f 0.43. Found, %: C 72.87; H 6.37. $C_{19}H_{20}O_2S$. Calculated, %: C 73.04; H 6.45.

Synthesis of sulfone VIb by reduction of tricycloheptane IV with $LiAlH_4$. A solution of 0.93 g (3 mmol) of tricycloheptane **IV** in 10 ml of anhydrous THF was cooled to 0°C, and 0.57 g (15 mmol) of $LiAlH_4$ was added under stirring in an argon atmosphere. The mixture was stirred for 3 h at room temperature, 10 ml of a saturated solution of sodium sulfate and 20 ml of diethyl ether were carefully added, the organic phase was separated, and the aqueous phase was extracted with methylene chloride (2 × 10 ml). The extracts were dried over $MgSO_4$ and evaporated, and the solid residue was recrystallized from chloroform–hexane (2 : 1). Yield 0.74 g (80%),

mp 127–129°C. The product was identical to a sample obtained by epimerization of sulfone **VId** (see above).

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