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Products of Reaction of Tricyclo[4.1.0.0^{2,7}]heptane and 1-Bromotricyclo[4.1.0.0^{2,7}]heptane with Hydrogen Sulfide, and Syntheses Based Thereon*

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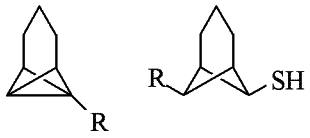
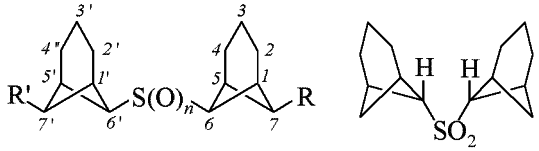
Abstract—By reactions of 1-R-tricyclo[4.1.0.0^{2,7}]heptanes (R = H, Br) with hydrogen sulfide initiated by UV irradiation *endo*-6-bicyclo[3.1.1]heptanethiols and bis(*endo*-6-bicyclo[3.1.1]heptyl) sulfides were synthesized. The sulfides were oxidized to the corresponding sulfoxides and sulfones. The results of HBr elimination from the bromine-substituted sulfoxides and sulfones effected by potassium *tert*-butylate are discussed. The latter reaction results in the recovery of the system of 1-substituted tricyclo[4.1.0.0^{2,7}]heptane.

It is known [1] that hydrogen sulfide adds to the terminal alkenes at UV irradiation in the anti-Markownikoff mode yielding thioethers, and the process is believed to be a free-radical reaction. Considering that the bicyclo[1.1.0]butane system is prone to radical addition reactions we were the first to investigate the hydrogen sulfide action on the tricyclic derivatives of the bicyclobutane, tricyclo[4.1.0.0^{2,7}]-heptane (**Ia**) and 1-bromotricyclo[4.1.0.0^{2,7}]heptane (**Ib**). The interest to this study originated from the possibility to obtain sulfides, sulfoxides, and sulfones of the bicyclo[3.1.1]heptane series, and therefrom also of the tricyclo[4.1.0.0^{2,7}]heptane series. These expectations were fulfilled as we report in the present article.



Ia, b **IIa, b**



IIIa–c, IVa, b, Va–c **Va'**

R = H (**a**), Br (**b, c**); R' = H (**a, c**), Br (**b**); *n* = 0 (**III**), 1 (**IV**), 2 (**V**).

The reactions of compounds **Ia, b** with H_2S were carried out in quartz glass vessels at 20°C in CH_2Cl_2 solution saturated with three-fold excess of the reagent. After 8 h of UV irradiation the reaction mixtures contained as the main products according to GLC and ^{1}H NMR data thiols **IIa, b** and sulfides **IIIa, b** in the ratio 1 : 2–3. To bind thiols **IIa, b** into sulfides **IIIa, b** to the reaction mixtures was added one equiv. of the corresponding tricycloheptane **Ia** or **Ib**, and the irradiation was continued for 8 h more. The same sulfides **IIIa, b** were obtained also at a direct reaction of thiols **IIa** and **IIb** with the respective tricycloheptanes **Ia** and **Ib** under UV irradiation. By reaction of equimolar amounts of compounds **Ia** and **IIb** or **Ib** and **IIa** was prepared also sulfide **IIIc**.

The results of reaction performed show that the hydrogen sulfide adds to tricycloheptanes **Ia** and **Ib** exclusively at the central bond C^1–C^7, and the opening of this bond in compound **Ib** occurs strictly regioselectively with thiyl attack on the unsubstituted position. A remarkable stereochemical result was obtained in reaction of bromide **Ib** with hydrogen sulfide and thiols **IIa** and **IIb**: the addition occurred with a high *trans*-stereoselectivity and *endo*-direction of the thiyl attack. It was indirectly detected (with respect to reaction of thiol **IIb** with bromide **Ib**) that some contribution of the *cis*-addition took place. The mentioned features of hydrogen sulfide addition to tricycloheptanes **Ia** and **Ib** are similar to those observed in reactions of bicyclobutane compounds with the other sulfur-centered radicals [2–6]. Therefore the reactions studied may be regarded as free-radical processes.

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Table 1. Constants and elemental analyses of sulfides **IIIa–c,** sulfoxides **IVa, b**, and sulfones **Va–c, VII–IX**

Compd. no.	Compound name	mp, °C (solvent)	R_f	Found, %		Formula	Calculated, %	
				C	H		C	H
IIIa	Bis(*endo*-6-bicyclo[3.1.1]heptyl) sulfide	79–80 (pentane)	0.87	75.88	10.02	$C_{14}H_{22}S$	75.61	9.97
IIIb	Bis(*syn*-7-bromo-*endo*-6-bicyclo[3.1.1]heptyl) sulfide	99–100 (hexane)	0.74	44.45	5.40	$C_{14}H_{20}Br_2S$	44.23	5.30
IIIc	*endo*-6'-Bicyclo[3.1.1]heptyl *syn*-7-bromo-*endo*-6-bicyclo[3.1.1]heptyl sulfide	51–52 (hexane)	0.84	55.53	6.89	$C_{14}H_{21}BrS$	55.81	7.03
IVa	Bis(*endo*-6-bicyclo[3.1.1]heptyl) sulfoxide	137–138 (CH_2Cl_2–hexane)	0.02	70.37	9.17	$C_{14}H_{22}OS$	70.54	9.30
IVb	Bis(*syn*-7-bromo-*endo*-6-bicyclo[3.1.1]heptyl) sulfoxide	190–191 ($CHCl_3$–hexane)	0.03, 0.13[a]	42.48	5.06	$C_{14}H_{20}Br_2OS$	42.44	5.09
Va	Bis(*endo*-6-bicyclo[3.1.1]heptyl) sulfone	155–156 ($CHCl_3$–hexane)	0.28	66.40	8.75	$C_{14}H_{22}O_2S$	66.10	8.72
Va'	Bis(*exo*-6-bicyclo[3.1.1]heptyl) sulfone	67–68 (ether–hexane)	0.30	66.01	8.42	$C_{14}H_{22}O_2S$	66.10	8.72
Vb	Bis(*syn*-7-bromo-*endo*-6-bicyclo[3.1.1]heptyl) sulfone	225–226 ($CHCl_3$)	0.20, 0.41[a]	40.96	5.04	$C_{14}H_{20}Br_2O_2S$	40.80	4.89
Vc	*endo*-6'-bicyclo[3.1.1]heptyl *syn*-7-bromo-*endo*-6-bicyclo[3.1.1]heptyl sulfone	145–146 ($CHCl_3$–hexane)	0.25	50.38	6.29	$C_{14}H_{21}BrO_2S$	50.45	6.35
VI	*anti*-7'-bromo-*endo*-6'-*syn*-bicyclo[3.1.1]heptyl 7-bromo-*endo*-6-bicyclo[3.1.1]heptyl sulfone	171–172 ($CHCl_3$)	0.33, 0.51[a]	40.90	4.78	$C_{14}H_{20}Br_2O_2S$	40.80	4.89
VII	*exo*-6-bicyclo[3.1.1]heptyl 1'-tricyclo[4.1.0.0^{2,7}]heptyl sulfone	83–84 (hexane)	0.29	66.67	7.93	$C_{14}H_{20}O_2S$	66.63	7.99
VIII	Bis(1-tricyclo[4.1.0.0^{2,7}]heptyl) sulfone	30–31 (hexane)	0.27	67.10	7.38	$C_{14}H_{18}O_2S$	67.17	7.25
IX	*endo*-6-*anti*-7-bromobicyclo[3.1.1]heptyl 1'-tricyclo[4.1.0.0^{2,7}]heptyl sulfone	55–57 ($CHCl_3$)	0.28	50.48	5.40	$C_{14}H_{19}BrO_2S$	50.76	5.78
X	Bis(1-tricyclo[4.1.0.0^{2,7}]heptyl) sulfoxide	Oily compound	0.07, 0.13[a]	71.40	7.65	$C_{14}H_{18}OS$	71.75	7.74

[a] Eluent hexane–ethyl acetate, 1 : 1.

Sulfides **IIIa–c** were transformed into the corresponding sulfones **Va–c** by treating with hydrogen peroxide in acetic acid in the presence of acetic anhydride. At the use of the crude sulfide **IIIb** prepared from bromide **Ib** and thiol **IIb** the oxidation afforded alongside sulfone **Vb** some sulfone **VI**. The latter might arise as a result of *cis*-addition of thiol **IIb** across the central C–C bond of tricycloheptane **Ib** giving a sulfide present in **IIIb** compound as irremovable impurity. The subsequent oxidation of the sulfide afforded sulfone **VI**. In two cases by treating sulfides **IIIa, b** with hydrogen peroxide in acetone we succeeded in stopping the oxidation at the stage of sulfoxides **IVa** and **IVb** respectively.

Compounds **IIIa–c, IVa, b, Va–c**, and **VI** are crystalline substances; their elemental analyses and constants are listed in Table 1. The norpinane carbon skeleton of these compounds is reliably proved by the ^{13}C NMR spectra (Table 2). The signals were assigned with the use of spectra of model compounds [3–6]. The orientation of substituents was established from

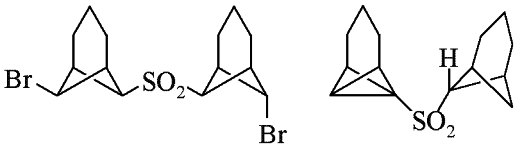
Table 2. ^{13}C NMR spectra of sulfides **IIIa**–**c**, sulfoxides **IVa, b**, and sulfones **Va**–**c, VI,** δ, ppm

Compd. no.	C^6 and $C^{6'}$	C^7 and $C^{7'}$	$C^{1,5}$ and $C^{1',5'}$	$C^{2,4}$ and $C^{2',4'}$	C^3 and $C^{3'}$
IIIa	48.7	27.2	38.1	23.6	14.3
IIIb	50.0	43.2	45.4	22.7	12.3
IIIc	49.7 and 50.4	27.2 and 42.2	38.2 and 45.4	22.8 and 23.6	12.3 and 14.3
IVa	63.1	29.2	36.9 and 37.5	24.5 and 25.8	14.8
IVb	59.1	50.0	43.1 and 43.6	22.4 and 23.5	12.9
Va	59.5	29.1	39.0	22.9	14.4
Va'	66.6	29.5	35.9	30.2	14.7
Vb	56.7	48.6	45.0	21.5	12.4
Vc	55.7 and 60.0	28.3 and 49.2	38.6 and 44.9	21.5 and 22.8	12.5 and 13.7
VI	56.4 and 57.9	48.9 and 51.3	45.0 and 48.5	21.5 and 24.8	12.3 and 13.4

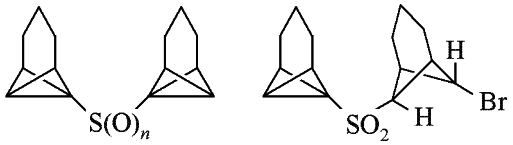
the multiplicity (triplet or singlet) of the methine proton signals of H^6 and H^7 in the ^1H NMR spectra according to the rules formulated before in [7]. The chirality of sulfoxides **IVa, b** is reflected in the ^1H and ^{13}C NMR spectra: the signals from atoms H^1 and H^5, C^1 and C^5, C^2 and C^4 reveal their chemical nonequivalence.

Bromosulfone **Vc** and dibromosulfones **Vb** and **VI** are interesting as convenient precursors of sulfones from the tricycloheptane series that are prepared by dehydrobromination. Actually, bromosulfone **Vb** treated with potassium tert-butylate in THF at 0°C is transformed into norpinanyl tricycloheptyl sulfone (**VII**), and dibromosulfone **Vb** transforms into bis-(tricycloheptyl) sulfone **VIII**. This process seems quite regular, for we have established before [5] that in this kind system 1,3-dehydrobromination proceeding along carbanion mechanism occurs only in keeping with a stereoelectronic requirement: the leaving group (bromide ion) should be located in the *syn*-position. The dehydrobromination of dibromosulfone **VI** goes in agreement with this requirement: the compound is subject to monodehydrobromination yielding sulfone **IX**, i.e. the *anti*-located bromine in compound **VI** cannot be eliminated. It is remarkable that dehydrobromination of compound **Vb** is accompanied by epimerization at C^6 atom whereas in an analogous reaction of compound **VI** the configuration at C^6 remains intact. We believe that this result is simply due to higher thermodynamical stability of 6-monosubstituted norpinane **VII** in an *exo*-configuration (cf. [8]), and of 6,7-disubstituted norpinane **IX** in an *endo,anti*-configuration (as compared to *exo,anti*-configuration). To the higher thermodynamical stability of *exo*-6-sulfosubstituted norpinane testified also epimerization of compound **Va** that we performed by treating it with butyllithium in ether–hexane solution to obtain sulfone **Va'**.

The orientation of substituents attached to the norpinane skeleton in compounds **VII** and **IX** was established from ^1H NMR spectra along the rules cited above. Note that the signal from *endo*-H^6 in compound **VII** appeared as a doublet due to remote coupling ($^4J_{6,7}$ 5.5 Hz) [7].



VI **VII**

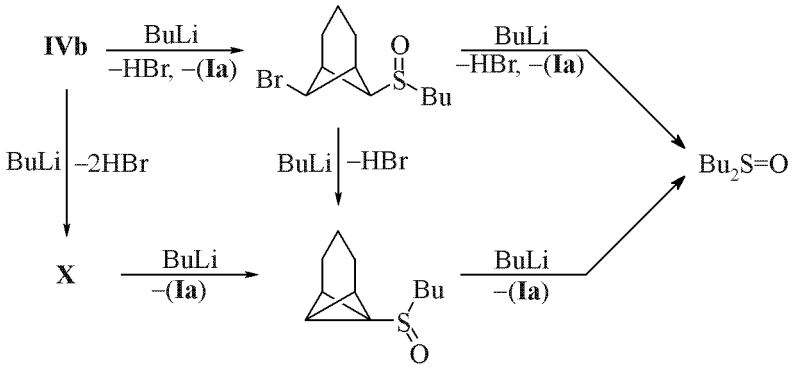


VIII, X **IX**

n = 1 (**X**), 2 (**VIII**).

Finally in this study we demonstrated for the first time that 1,3-elimination of hydrogen halide effected by a base similar to the above described for bromosulfones **V, VI** could be performed also in the related bromosulfoxides. Treating dibromosulfoxide **IVb** with potassium *tert*-butylate in THF solution furnished bistricycloheptane **X** in 81% yield. The attempt to eliminate HBr from sulfoxide **IVb** with butyllithium in ether resulted in formation of dibutyl sulfoxide as the main product. Apparently in this case a nucleophilic attack of the reagent occurred at the sulfoxide group (cf. [9]). This fact presumably means that the

Scheme.



potassium *tert*-butylate turned out to be less nucleophilic with respect to sulfoxide **IVb** than butyllithium. Therewith remained unclear whether the attack is directed on compound **IVa** or first still forms sulfoxide **X**. In any case the second reaction product is hydrocarbon **Ia** (see the scheme).

The tricycloheptane fragment in compounds **VII–X** is reliably proved by ^{1}H and ^{13}C NMR spectra considering the spectral data on phenyl(methyl)sulfonyltricycloheptanes [5, 6], The chirality of sulfoxide **X** is revealed in its NMR spectra as chemical nonequivalence of atoms H^2 and H^6 and also of C^2 and C^6. The dibutyl sulfoxide was identified by its characteristics similar to the published data and also by ^{1}H and ^{13}C NMR spectra [10].

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on spectrometer Bruker AM-300 (at 300.130 and 75.468 MHz respectively) from solutions of compounds in $CDCl_3$. The conditions of TLC analysis were as follows: adsorbent Silufol UV-254, eluent hexane–ether, 1 : 1, development in a iodine chamber. The column chromatography was carried out on Al_2O_3 of **II** grade activity. The constants and elemental analyses of compounds **III–X** are listed in Table 1, the ^{13}C NMR spectra in Table 2.

Tricycloheptanes **Ia** [11] and **Ib** [12] were prepared by published methods. The substances used in the study were pure according to GLC (30–70°C) to about 97%.

Thiols IIa and IIb. To 40 ml of CH_2Cl_2 saturated with hydrogen sulfide at –5°C in a tightly capped quartz vessel was added 43 mmol of compound **Ia** or **Ib**. The solution was irradiated with UV light (lamp DRSh-400) for 8 h at 20°C. The reaction mixture was filtered, the solvent was distilled off at reduced pressure (300 mm Hg) from a flask equipped with a Vigreux column. Thiols **IIa** and **IIb** were isolated from the residue by a vacuum distillation in 32 and 27% yield respectively.

***endo*-6-Bicyclo[3.1.1]heptanethiol (IIa).** bp 70–71°C (13 mm Hg). ^{1}H NMR spectrum, δ, ppm: 1.02 d (1H, SH, ^3J 6.5 Hz); 1.35–1.69 m (8H); 2.77–2.85 m (2H, $H^{1,5}$); 3.43 d.t (1H, H^6, ^3J 6.4 and 6.5 Hz). Found, %: C 65.77; H 9.18. $C_7H_{12}S$. Calculated, %: C 65.57; H 9.43.

***syn*-7-Bromo-*endo*-6-bicyclo[3.1.1]heptanethiol (IIb).** bp 74–76°C (2 mm Hg). ^{1}H NMR spectrum, δ, ppm: 1.05 d (1H, SH, ^3J 6.5 Hz); 1.54–1.70 m (8H); 3.47 m (2H, $H^{1,5}$); 3.67 d.t (1H, H^6, ^3J 6.4 and 6.5 Hz); 4.07 t (H^7, ^3J 6.4 Hz). Found, %: C 40.72; H 5.22. $C_7H_{11}BrS$. Calculated %: C 40.59; H 5.35.

Sulfides IIIa and IIIb. (a) To the reaction mixtures obtained as described above were added 43 mmol of the corresponding tricycloheptane **Ia** or **Ib**, and irradiation was continued for 8 h under the same conditions. After removing the solvent in a vacuum sulfides **IIIa** and **IIIb** were isolated from the solid residue by crystallization from hexane in the yield of 41 and 46% respectively.

(b) In a tightly capped quartz test tube was mixed under argon a solution of 0.49 g of tricycloheptane **Ia** in 5 ml of CH_2Cl_2 and 0.64 g of thiol **IIa**. The mixture was irradiated by the lamp DRSh-400 at 20°C for 7 h, then the content of the tube was washed with 5% NaOH solution and dried with $MgSO_4$. On removing the solvent the crystallization afforded 0.74 g (yield 67%) of sulfide **IIIa**. In a similar way from 0.58 g of tricycloheptane **Ib** and 0.69 g of thiol **IIb** was prepared 0.93 g (yield 73%) of sulfide **IIIb**.

Sulfide IIIa. ^{1}H NMR spectrum, δ, ppm: 3.28 t (2H, $H^{6,6'}$, ^3J 5.8 Hz); 2.38 narrow m (4H, $H^{1,1',5,5'}$); 1.88–2.10 m (4H, *endo*-$H^{2,2',4,4'}$); 1.53–1.88 m (12H).

Sulfide (IIIb). ^{1}H NMR spectrum, δ, ppm: 4.44 t (2H, $H^{7,7'}$, ^3J 5.6 Hz); 3.13 t (2H, $H^{6,6'}$, ^3J 5.6 Hz); 2.72 narrow m (4H, $H^{1,1',5,5'}$); 1.95–2.15 m (8H, $H^{2,2',4,4'}$); 1.62–1.79 m (4H, $H^{3,3'}$).

Sulfide IIIc. To a solution of 0.4 g of tricycloheptane **Ia** in 5 ml of dichloromethane was added 0.83 g of thiol **IIb**. The mixture was placed into a quartz test tube flushed with dry argon, it was tightly capped and subjected to irradiation for 9 h. Then the reaction mixture was washed with 5% NaOH solution and dried with $MgSO_4$. On removing the solvent the crystallization afforded 1.05 g (yield 76%) of sulfide **IIIc**. In a similar way from tricycloheptane **Ib** and thiol **IIa** sulfide **IIIc** was obtained in 60% yield. ^{1}H NMR spectrum, δ, ppm: 4.45 t (1H, H^7, ^3J 5.5 Hz); 3.32 t (1H, H^6, ^3J 5.6 Hz); 3.08 t (1H, $H^{6'}$, ^3J 5.6 Hz); 2.69 narrow m (2H, $H^{1,5}$); 2.42 narrow m (2H, $H^{1',5'}$); 1.90–2.05 m (6H); 1.55–1.90 m (8H).

Sulfoxides IVa, b. In a round-bottom flask a mixture of 10 mmol of sulfide **IIIa** or **IIIb** with 7 ml of acetone and 3 ml of 30% hydrogen peroxide was boiled for 65 h. Then the solution was cooled, and acetone was removed in a vacuum of a water-jet pump. To the residue 25 ml of water and 25 ml of ether was added. The organic phase was separated, and the water phase was extracted with ether (3 × 10 ml). The combined ether solutions were dried with $MgSO_4$. On evaporating the solvent the residue was subjected to column chromatography on Al_2O_3 (column *l* 40 cm, eluent light petroleum ether–ethyl acetate, 6–8 : 1). Sulfoxides **IVa** and **IVb** were obtained in 39.9 and 31% yield respectively. Sulfoxide (**IVa**). ^{1}H NMR spectrum, δ, ppm: 3.26 t (2H, *exo*-$H^{6,6'}$, ^3J 5.8 Hz); 2.89 narrow m (2H) and 2.54 narrow m (2H), $H^{1,5}$ and $H^{1',5'}$; 2.30–2.47 m (2H, *anti*-$H^{7,7'}$); 1.78–2.05 m (12H); 1.62 d (2H, *syn*-$H^{7,7'}$, ^2J 9 Hz). Sulfoxide (**IVb**). ^{1}H NMR spectrum, δ, ppm: 4.52 t (2H, $H^{7,7'}$, ^3J 5.5 Hz); 3.20 t (2H, $H^{6,6'}$, ^3J 5.5 Hz); 3.03 narrow m (2H) and 2.58 narrow m (2H), $H^{1,5}$ and $H^{1',5'}$; 2.26–2.49 m (2H); 2.0–2.49 m (4H); 1.69–2.0 m (6H).

Sulfones Va–c. To 10 mmol of sulfide **IIIa–c** at external cooling to –5°C was added a mixture containing 8 ml of glacial acetic acid, 8 ml of acetic anhydride, and 6 ml of 30% hydrogen peroxide. The reaction mixture was stirred for 6 h at 0°C, and then at room temperature for 48, 87, and 240 h for sulfide **IIIa, IIIb**, and **IIIc** respectively. The mixture was diluted with water (30 ml), and the separated precipitate was filtered off. The crystallization from chloroform furnished sulfones **Va** (yield 75%), **Vb** (yield 60%), and **Vc** (yield 70%). Sulfone (**Va**). ^{1}H NMR spectrum, δ, ppm: 3.17 t (2H, $H^{6,6'}$, ^3J 5.9 Hz); 2.77 br.t (4H, $H^{1,1',5,5'}$); 2.34–2.56 m (4H, *endo*-$H^{2,2',4,4'}$); 1.64–1.90 m (10H); 1.55 d (2H, *syn*-$H^{7,7'}$, ^2J 8.8 Hz). Sulfone (**Vb**). ^{1}H NMR spectrum, δ, ppm: 4.38 t (2H, $H^{7,7'}$, ^3J 6.0 Hz); 3.23 t (2H, $H^{6,6'}$, ^3J 6.0 Hz); 3.05 br.t (4H, $H^{1,1',5,5'}$); 2.33–2.53 m (4H); 1.95–2.12 m (4H); 1.72–1.95 m (4H). Sulfone (**Vc**). ^{1}H NMR spectrum, δ, ppm: 4.41 t (1H, H^7, ^3J 5.6 Hz); 3.28 t (1H, ^3J 5.6 Hz) and 3.17 t (1H, ^3J 5.6 Hz), H^6 and $H^{6'}$; 3.02 br.t (2H) and 2.85 br.t (2H), $H^{1,5}$ and $H^{1',5'}$; 2.55–2.38 m (4H); 2.16–1.75 m (10H); 1.65 d (1H, *endo*-$H^{7'}$, ^2J 9 Hz).

Sulfone VI. Treating along the above described procedure of 10 mmol of crude sulfide **IIIb** provided a solid product subjected to chromatography on a column packed with Al_2O_3 (eluent light petroleum ether–ethyl acetate, 3–4 : 1). Sulfoxide **IVb**, sulfone **Vb**, and sulfone **VI** were obtained in 9.8, 45, and 1% yield respectively. ^{1}H NMR spectrum, δ, ppm: 4.42 t (1H, *exo*-H^6, ^3J 6.3 Hz); 4.13 s (1H, *syn*-H^7); 4.10 t (1H, *anti*-$H^{7'}$, ^3J 6.3 Hz); 3.22 t (1H, *exo*-$H^{6'}$, ^3J 6.3 Hz); 3.07 narrow m and 2.97 narrow m (4H, $H^{1,5}$ and $H^{1',5'}$); 2.54–2.70 m and 2.36–2.54 m (4H, *endo*-$H^{2,2',4,4'}$); 1.70–2.16 m (8H).

Epimerization of sulfone Va. To a solution of 0.38 g of sulfone **Va** in 10 ml of anhydrous ether cooled to –15°C was added under argon 5 ml of 0.9 M butyllithium solution in hexane. The mixture was stirred at 0°C for 30 min, and then 3 ml of water were cautiously added. The organic layer was separated, the products were extracted from the water layer into ether (3 × 7 ml). The combined organic solution was dried with $MgSO_4$. On removing the solvent in a vacuum the obtained 0.32 g of solid was subjected to column chromatography on Al_2O_3 (eluent hexane–ether, 2 : 1). After subsequent crystallization sulfone **Va'** was obtained in amount of 0.22 g (yield 56.5%). ^{1}H NMR spectrum, δ, ppm: 2.96 d (2H, H^6, ^4J 5.1 Hz); 2.94–2.78 m (6H, $H^{1,5}$ and *anti*-H^7); 2.16–2.02 m (4H); 2.02–1.85 m (6H); 1.85–1.68 m (2H); 1.40 d.d (2H, *syn*-H^7, ^4J 5.1 Hz and ^2J 9.0 Hz).

Reaction of sulfoxide IVb with potassium *tert*-butylate. To a solution of 0.79 g of sulfoxide **IVb** in

20 ml of anhydrous THF cooled with an ice bath was added under dry argon at stirring 0.9 g of powdered potassium *tert*-butylate. The stirring at the same temperature continued for 4 h. Then the reaction mixture was filtered through a 1 cm bed of Al_2O_3 on a glass frit. The precipitate on the filter was washed with 5 ml of THF. The solvent was removed in a vacuum. The obtained 0.38 g (yield 81%) of oily substance contained individual sulfoxide **X** (according to TLC). ^{1}H NMR spectrum, δ, ppm: 1.28–1.65 m (12H); 2.10 br.s (2H, H^{7}); 3.12 narrow m (2H) and 3.18 narrow m (2H), H^{2,6} and H$^{2',6'}$. ^{13}C NMR spectrum, δ, ppm: 15.2 (C$^{7,7'}$), 20.0 (C$^{4,4'}$), 20.3 (C$^{3,3',5,5'}$), 30.3 (C$^{1,1'}$), 43.5 and 46.9 (C$^{2,2'}$ and C$^{6,6'}$).

Reaction of sulfoxide IVb with butyllithium. To a solution of 1.08 g (2.73 mmol) of sulfoxide **IVb** in 10 ml of anhydrous THF at external cooling to –10°C was added under dry argon at stirring 20 ml of 0.6 M butyllithium solution in hexane. The mixture was stirred for 30 min at 0°C, and then 15 ml of water was added. The organic layer was separated, from the water layer the reaction products were extracted into chloroform (3 × 15 ml). The combined organic solutions were washed with water and dried with $MgSO_4$. The solvent was removed in a vacuum of a water-jet pump, and the residue was subjected to column chromatography on Al_2O_3 (eluent hexane–ether, 2 : 1). We obtained 0.20 g (yield 45%) of dibutyl sulfoxide, mp 32–34°C (from hexane–ether). The constants and ^{1}H and ^{13}C NMR spectra are identic to published data [10].

Dehydrobromination of sulfone Vb. At 0°C were mixed 0.82 g of sulfone **Vb**, 30 ml of anhydrous THF, and 0.9 g of potassium *tert*-butylate powder. The reaction mixture was stirred at 20°C for 6 h and then worked up as described above. On crystallization 0.26 g (yield 52%) of tricycloheptane **VIII** was obtained. ^{1}H NMR spectrum, δ, ppm: 1.28–1.48 m (4H, H$^{4,4'}$); 1.48–1.65 m (8H, H$^{3,3',5,5'}$); 2.52 t (2H, H$^{7,7'}$, ^3J 3.3 Hz); 3.28 narrow m (4H, H$^{2,2',6,6'}$). ^{13}C NMR spectrum, δ, ppm: 19.8 (C$^{7,7'}$); 19.9 (C$^{3,3',5,5'}$); 20.1 (C$^{4,4'}$); 29.8 (C$^{1,1'}$); 47.2 (C$^{2,2',6,6'}$).

Dehydrobromination of sulfone VI. At 20°C a mixture of 0.117 g of sulfone **VI** and 0.127 g of potassium *tert*-butylate in 6 ml of anhydrous THF was stirred for 5 h. After working up the reaction mixture as above we obtained 41 mg (yield 43%) of tricycloheptane IX. ^{1}H NMR spectrum, δ, ppm: 4.48 t (1H, *exo*-H^{6}, ^3J 5.7 Hz); 4.21 s (1H, *syn*-H^{7}); 3.26 narrow m (2H) and 3.04 narrow m (2H), H$^{2',6'}$ and H^{1,5}; 2.70 br.t (1H, H$^{7'}$); 2.66–2.51 m (2H, *endo*-H^{2,4}); 2.16–2.02 m (2H, *exo*-H^{2,4}); 1.96–1.70 m (2H, H^{3}); 1.60–1.45 m (4H, H$^{3',5'}$); 1.45–1.30 m (2H, H$^{4'}$).

Dehydrobromination of sulfone Vc. At 20°C a solution of 0.67 g of sulfone **Vc** in 20 ml of anhydrous THF was stirred for 3 h in the presence of 0.90 g of potassium *tert*-butylate. After working up the reaction mixture as above we obtained 0.30 g (yield 59%) of tricycloheptane **VII**. ^{1}H NMR spectrum, δ, ppm: 3.23 narrow m (2H, H$^{2',6'}$); 3.17 d (1H, *endo*-H^{6}, ^4J 5.5 Hz); 2.90 narrow m (2H, H^{1,5}); 2.92–2.75 m (1H, anti-H^{7}); 2.62 t (1H, H$^{7'}$, ^3J 3.5 Hz); 2.20–1.70 (6H, H^{2,3,4}); 1.60–1.25 m (7H, H$^{3',4',5'}$ and *syn*-H^{7}). ^{13}C NMR spectrum, δ, ppm: 14.8 (C^{3}); 18.5 (C$^{7'}$); 19.7 (C$^{3',5'}$); 19.9 (C$^{4'}$); 27.3 (C$^{1'}$); 29.3 (C^{7}); 30.3 (C^{2,4}); 36.0 (C^{1,5}); 47.6 (C$^{2',6'}$); 70.6 (C^{6}).

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