ISSN 1070-4280, Russian Journal of Organic Chemistry, 2009, Vol. 45, No. 4, pp. 581–586. © Pleiades Publishing, Ltd., 2009.
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Asymmetric Oxidation of Verbenone Ethylene Dithioacetal

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Received June 16, 2008

Abstract—Asymmetric oxidation of verbenone ethylene dithioacetal with *m*-chloroperoxybenzoic acid at different substrate-to-oxidant ratios in methylene chloride at –10°C gave previously unknown (1*S*,1′*S*,2*S*,3′*S*,5*S*)-4,6,6-trimethylspiro[bicyclo[3.1.1]hept-3-ene-2,2′-[1,3]dithiolane] 1′,3′-dioxide, (1*S*,2*S*,3′*S*,5*S*)-4,6,6-trimethylspiro[bicyclo[3.1.1]hept-3-ene-2,2′-[1,3]dithiolane] 1′,1′,3′-trioxide, and (1*S*,5*S*)-4,6,6-trimethylspiro[bicyclo-[3.1.1]hept-3-ene-2,2′-[1,3]dithiolane] 1′,1′,3′,3′-tetraoxide whose structure was determined by X-ray analysis.

DOI: 10.1134/S1070428009040186

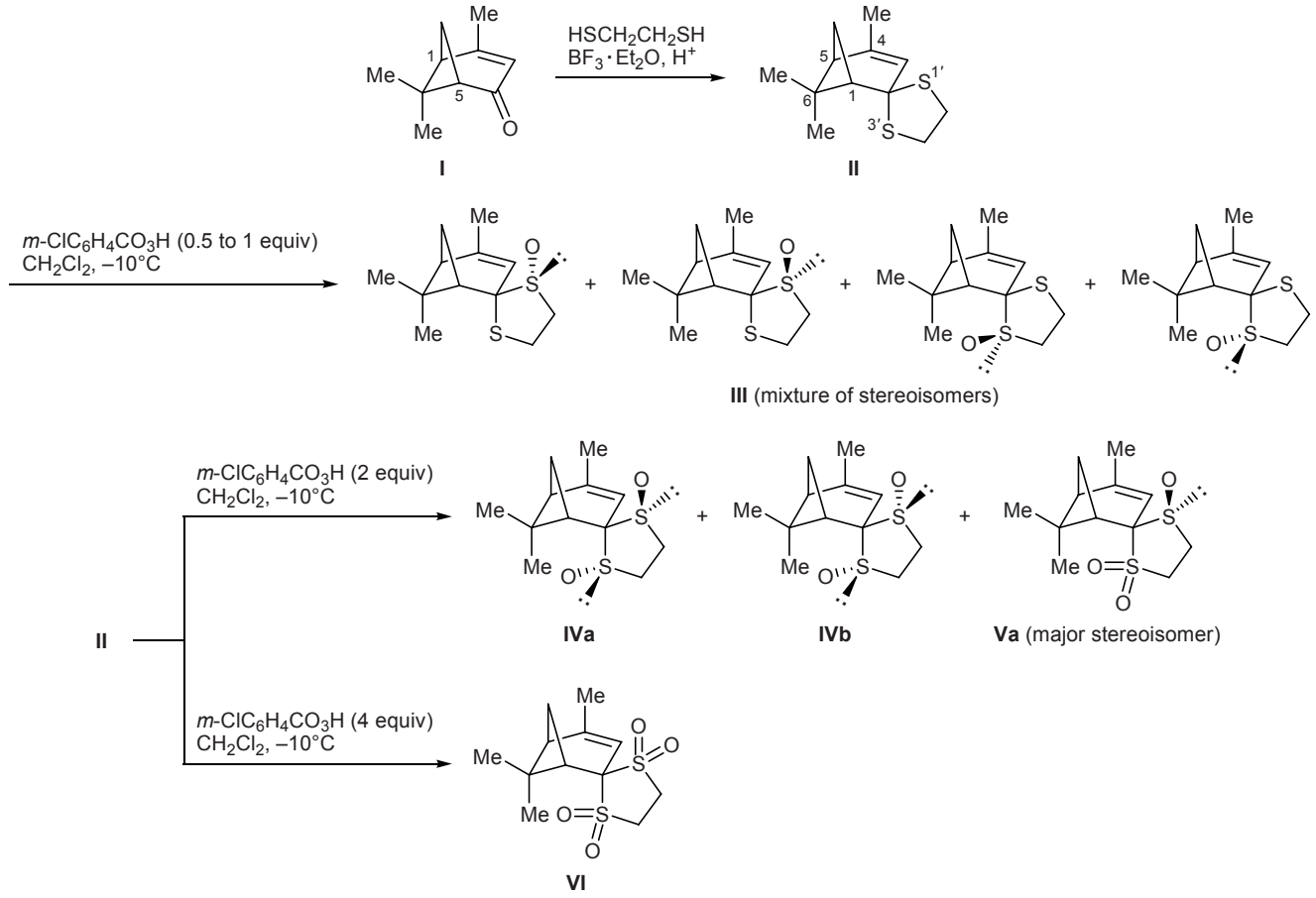
In the recent years, extensive studies have been performed in the field of modification of sulfur-containing biologically active compounds with a view to obtain their sulfoxide analogs. Synthetic sulfoxides or those isolated from natural sources possess practically important properties; for example, they are capable of acting as antioxidants and antidepressants [1] and are effective in the treatment of ulcers [2–4]. Therefore, development of efficient procedures for the synthesis of optically active sulfoxides has become an important problem. Such compounds may be prepared by oxidation of a chiral sulfide having prochiral centers [5].

1,3-Dithiolanes and 1,4-dithianes may be regarded as substrates capable of undergoing oxidation to chiral sulfoxides [6–10]. Oxidation of dithiolane derivatives containing a terpene fragment also attracts interest from the theoretical viewpoint due to structural diversity of possible oxidation products. Asymmetric oxidation of dithiolanes according to Kagan or Modena [6–10] is known to be successful; in addition, the Bolm catalytic system $VO(acac)_2$–oxidant [11–13], enzymatic catalysis, and biotransformations involving whole-cell cultures of microorganisms were reported [14–16].

In the present work we examined asymmetric oxidation of optically active verbenone ethylene dithioacetal possessing prochiral sulfur atoms with a view to obtain chiral sulfinyl- and sulfonyl-containing derivatives. As starting terpene compound we used commercially available (–)-(1*S*,5*S*)-verbenone [**I**, (1*S*,5*S*)-4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-one]. The reaction of ketone **I** with an equimolar amount of 1,2-ethanedithiol in diethyl ether in the presence of Lewis acid ($BF_3 \cdot Et_2O$) gave 80-85% of the corresponding dithioacetal **II** (Scheme 1). The IR spectrum of compound **II** lacked carbonyl absorption band at 1720 cm^{-1}, but a band at 880 cm^{-1} was present due to vibrations of the C–S bonds. The structure of **II** was confirmed by the NMR and mass spectra and elemental analysis. The ^{13}C NMR spectrum of compound **II** contained no signal at δ_C 220 ppm, which is typical of the carbonyl carbon atom in initial ketone **I**. Carbon nuclei in the methylene groups attached to sulfur resonated at δ_C 37.7 and 40.6 ppm), and signals from the corresponding methylene protons appeared in the ^1H NMR spectrum as multiplets in the region δ 3.10–3.40 ppm.

Compound **II** was converted into the corresponding sulfoxides and sulfones using *m*-chloroperoxybenzoic acid as oxidant. When the oxidation of **II** was performed at a substrate-to-oxidant ratio of 1:0.5 or 1:1, monosulfinyl derivative **III** was formed as a mixture of two diastereoisomer couples with an overall yield of 62–65%. According to the NMR data, the stereoisomer ratio was (1:1.6:1:2.9). Although we failed to isolate particular stereoisomers as individual substances, most signals in the ^1H and ^{13}C NMR spectra of their mixture were not overlapped, so that we were able to distin-

Scheme 1.



guish signals of two major diastereoisomers (see Experimental). The formation of stereoisomeric compounds **III** was confirmed by mass spectrometry.

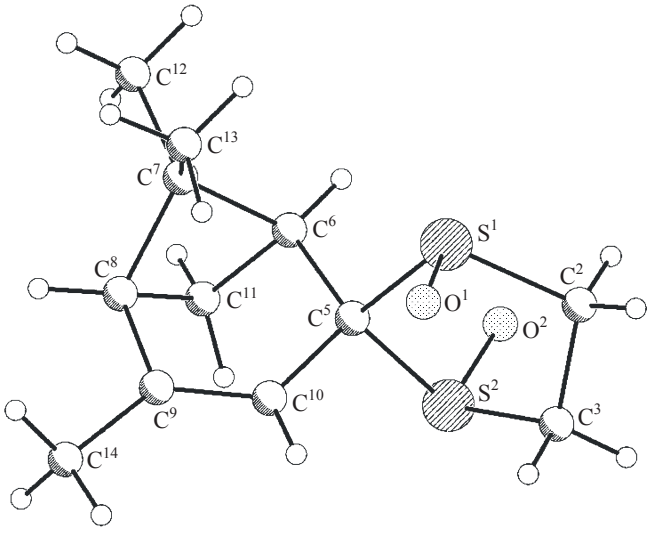


Fig. 1. Structure of the molecule of (1*S*,1′*S*,2*S*,3′*S*,5*S*)-4,6,6-trimethylspiro[bicyclo[3.1.1]hept-3-ene-2,2′-[1,3]dithiolane] 1′,3′-dioxide (**IVa**) according to the X-ray diffraction data.

The oxidation of compound **II** with 2 equiv of *m*-chloroperoxybenzoic acid at –10°C gave a mixture of the corresponding bis-sulfoxide and sulfinyl sulfonyl derivative, the conversion of verbenone dithioacetal **II** being 98%. By column chromatography we isolated two fractions: 35% of bis-sulfoxide **IV** and 27% of *S*,*S*,*S*′-trioxide **V**. According to the NMR data, the first fraction contained two diastereoisomers **IVa** and **IVb** at a ratio of 1.6:1 (diastereoisomer excess *de* = 23%). The major stereoisomer (**IVa**) was isolated by recrystallization from ethanol, and its preparative yield was 20–22%. The structure of **IVa** was determined by X-ray analysis. It was found that crystals of **IVa** belong to the $P2_12_12_1$ chiral space group. The dithiolane ring adopts an *envelope* conformation where the S^1, C^3, S^4, and C^5 atoms lie almost in one plane (Fig. 1). The sulfinyl oxygen atoms occupy *trans*-pseudoaxial positions.

The configuration of the second diastereoisomer (**IVb**) was assigned by comparing the NMR spectra of **IVa** and **IVb**. In the ^{1}H NMR spectra of **IVa** and **IVb**, signals from protons on C^3 and C^1 strongly differed in

their position. The 3-H signal in the spectrum of **IVb** appeared by 0.3 ppm upfield, whereas the signal from 1-H was displaced downfield by 0.25 ppm, relative to the corresponding signals of isomer **IVa**. Taking into account that the differences in the positions of the other proton signals were considerably smaller, we can conclude that diastereosiomers **IVa** and **IVb** differ just by the configuration of one sulfur atom ($S^{3'}$).

NMR analysis of the second fraction (**V**) showed the presence of three stereoisomers at a ratio of 4.5 : 1.6 : 1. The major stereoisomer (**Va**) was isolated in 17–20% yield by recrystallization from ethanol. Its IR spectrum displayed absorption bands typical of sulfonyl and sulfinyl groups at 1309 ($\nu_{as}SO_2$), 1126 (ν_sSO_2), and 1055 cm^{-1} (νSO). The structure of compound **Va** was unambiguously determined by X-ray analysis. On the whole, the configuration of molecule **Va** is similar to that of **IVa** with correction for introduction of an additional oxygen atom. The average S–O bond length in the sulfonyl group [1.434(3) Å] is appreciably smaller than the sulfinyl S–O bond length [1.485(3) Å]. The dithiolane ring has an *envelope* conformation with the C^2 atom deviating from the plane formed by the remaining four atoms (S^1, C^3, S^4, C^5; Fig. 2). The sulfinyl oxygen atom occupies *trans*-pseudoaxial position.

The reaction of dithioacetal **II** with excess (4 equiv) of *m*-chloroperoxybenzoic acid at –10°C resulted in the formation of sulfone **VI** in 70–75% yield. The IR spectrum of **VI** contained absorption bands due to stretching vibrations of the sulfonyl groups at 1328 ($\nu_{as}SO_2$) and 1130 cm^{-1} (ν_sSO_2). The structure of bis-sulfone **VI** was unambiguously determined by X-ray analysis. As in molecules **IVa** and **Va**, no appreciable deviations from standard bond lengths and bond angles were observed for compound **VI**. In particular, the S–O bond lengths in the sulfonyl groups range from 1.429(2) to 1.441(2) Å [average value 1.435(10) Å]. The dithiolane ring in **VI** has the same conformation as in molecules **IVa** and **Va** (Fig. 3). It should be noted that all three compounds **IVa**, **Va**, and **VI** are characterized by very similar unit cell parameters. They crystallize in orthorhombic system with $P2_12_12_1$ (chiral) space symmetry group, and the edges of their unit cells have approximately equal lengths (only slight extension is observed in going from less to more oxidized compounds). Obviously, introduction of additional oxygen atoms into the spiro-fused verbenone ethylene dithioacetal structure is accompanied by insignificant contribution to steric interactions.

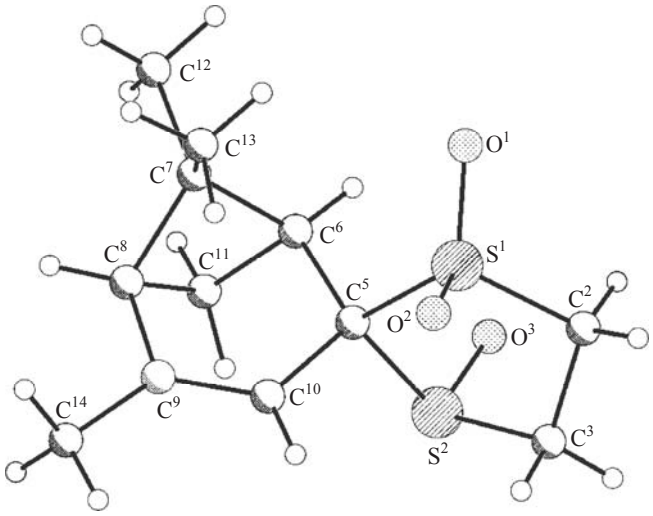


Fig. 2. Structure of the molecule of (1*S*,2*S*,3′*S*,5*S*)-4,6,6-trimethylspiro[bicyclo[3.1.1]hept-3-ene-2,2′-[1,3]dithiolane] 1′,1′,3′-trioxide (**Va**) according to the X-ray diffraction data.

The oxidation of dithioacetal **II** with *m*-chloroperoxybenzoic acid at room temperature was characterized by lower regio- and stereoselectivity, but the overall yield of the bis-sulfoxide and sulfoxide–sulfone fractions increased to 80–82%. By column chromatography we isolated 23–25% of stereoisomeric *S*,*S*′-dioxides **IV** and 57% of *S*,*S*,*S*′-trioxides **V**. The ratio of diastereoisomers **IVa** and **IVb** was estimated at 1.1 : 1 (*de* ≈ 5%) by NMR spectroscopy. It was also found (NMR) that fraction **V** contained four stereoisomers at a ratio of 1.5 : 1.3 : 1.1 : 1, whereas in the oxidation of **II** at –10°C only three stereoisomers were formed.

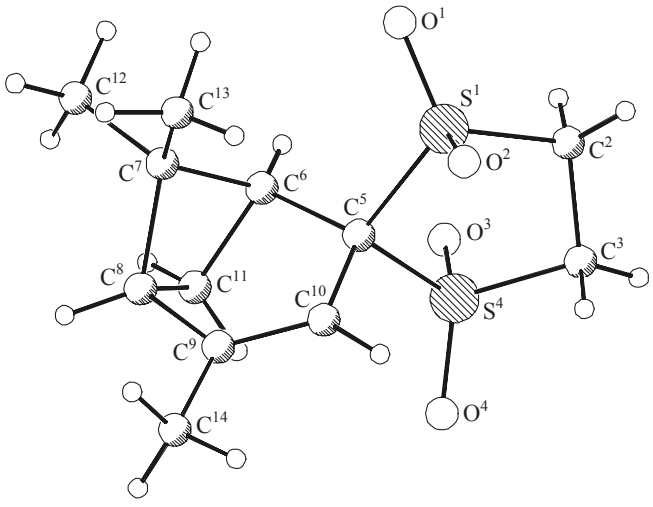


Fig. 3. Structure of the molecule of (1*S*,5*S*)-4,6,6-trimethylspiro[bicyclo[3.1.1]hept-3-ene-2,2′-[1,3]dithiolane] 1′,1′,3′,3′-tetraoxide (**VI**) according to the X-ray diffraction data.

Crystallographic data for compounds **IVa**, **Va**, and **VI** and parameters of X-ray diffraction experiments

Parameter	**IVa**	**Va**	**VI**
Formula	$C_{12}H_{18}O_2S_2$	$C_{12}H_{18}O_3S_2$	$C_{12}H_{18}O_4S_2$
Crystal habit, mm	0.51 × 0.43 × 0.39	0.48 × 0.36 × 0.31	0.51 × 0.42 × 0.23
Color		Colorless	
Crystal system		Orthorhombic	
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Unit cell parameters			
a, Å	8.1582(3)	8.1941(6)	8.3267(2)
b, Å	12.2987(4)	12.2900(8)	12.5084(3)
c, Å	12.3989(4)	12.5532(14)	12.5588(3)
V, Å^3	1244.05(7)	1264.18(19)	1308.05(5)
Z	4	4	4
d_{calc}, g/cm^3	1.380	1.442	1.475
μ, mm^{-1}	0.411	0.415	0.411
Number of independent reflections	4020 (R_{int} = 0.0188)	3917 (R_{int} = 0.0162)	4178 (R_{int} = 0.0123)
Number of reflections with $I > 2\sigma(I)$	2897	3242	3629
Completeness	99.4% (θ < 26.00°)	98.5% (θ < 26.00°)	98.7% (θ < 26.50°)
S	1.001	1.019	1.001
R_1 [$I > 2\sigma(I)$]	0.0273	0.0306	0.0259
wR_2 [$I > 2\sigma(I)$]	0.0580	0.0730	0.0648
Maximal/minimal electron density, e/Å^3	0.182/–0.220	0.206/–0.334	0.200/–0.213

EXPERIMENTAL

The IR spectra were recorded on a Shimadzu IR Prestige 21 spectrometer with Fourier transform from samples prepared as KBr pellets or neat substances. The melting points were determined on a Gallenkamp-Sanyo melting point apparatus. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance-II-300 spectrometer at 300.17 and 75.42 MHz, respectively, using $CDCl_3$ as solvent. Signals were assigned with the aid of two-dimensional homo- (^{1}H–^{1}H COSY, ^{1}H–^{1}H NOESY) and heteronuclear correlation techniques (HETCORR). Gas–liquid chromatography was performed on a Chrom-5 instrument equipped with a flame ionization detector and a 2000×4-mm column packed with 5% of Carbowax-20 on Chromaton-N-AW-DMCS; carrier gas helium; oven temperature programming from 50 to 250°C at a rate of 6 deg/min. The optical rotations were measured on a Kruss P3002RS automatic digital polarimeter. The mass spectra were recorded on a Finnigan Trace DSQ GC–MS system (TR-5MS column, 30 m; oven temperature programming from 50 to 220°C at a rate of 4 deg/min). Silufol and Sorbfil plates were used for thin-layer chromatography (eluent hexane–diethyl ether); spots were visualized by treatment with an alcoholic solution of vanillin or 5% solution of $KMnO_4$. The elemental compositions were determined using an EA 1110 CHNS-O automatic analyzer.

The X-ray diffraction data were acquired on an Xcalibur-3 automatic diffractometer at 295(2) K according to standard procedures (CCD detector, MoK_α irradiation, graphite monochromator, ω-scanning with a step of 1.0 deg). The structures were solved by the direct method and were refined by the least-squares procedure in full matrix anisotropic approximation (isotropic for hydrogen atoms) using SHELX97 software package. The crystallographic parameters of compounds **IVa**, **Va**, and **VI** and parameters of X-ray diffraction experiments are collected in table. The complete sets of crystallographic data were deposited to the Cambridge Crystallographic Data Centre (entry nos. CCDC 716504–716506) and are available for free (*www.ccdc.cam.ac.uk/data_request/cif*).

(1*S*,5*S*)-4,6,6-Trimethylbicyclo[3.1.1]hept-3-en-2-one [**I**, (–)-verbenone], $[\alpha]_D$ = –167.9° (c = 3.7, $CHCl_3$) was commercial product (Fluka).

(1*S*,5*S*)-4,6,6-Trimethylspiro[bicyclo[3.1.1]hept-3-ene-2,2′-[1,3]dithiolane] (II). (–)-Verbenone (**I**), 1 g

(6.67 mmol), was dissolved in 50 ml of diethyl ether, 0.56 ml (6.67 mmol) of ethane-1,2-dithiol and 0.85 ml (6.67 mmol) of boron trifluoride–ether complex were added, and the mixture was stirred for 24 h at room temperature. The mixture was then poured into water and extracted with diethyl ether, the extract was washed with a solution $NaHCO_3$, water, and a saturated solution of NaCl and dried over anhydrous sodium sulfate, the solvent was distilled off under reduced pressure, and the residue was purified by column chromatography using heptane–diethyl ether (50:1) as eluent. Yield 1.21 g (80%), oily substance, R_f 0.75 (hexane–diethyl ether, 1:2), $[\alpha]_D$ = –41.9° (*c* = 1.22, EtOH). IR spectrum: ν 880 cm^{-1} (C–S). ^1H NMR spectrum, δ, ppm: 0.96 s and 1.31 s (3H each, 6-CH_3), 1.44 d (1H, 7-H, *J* = 9.4 Hz), 1.68 d (3H, 4-CH_3, *J* = 1.2 Hz), 1.96 d.d.d (1H, 5-H, *J* = 5.4, 5.3 Hz), 2.45 d.d.d (1H, 1-H, *J* = 7.5, 5.8, 1.7 Hz), 2.55 d.d.d (1H, 7-H, *J* 9.4, 5.7, 5.5 Hz), 3.10–3.40 m (4H, 4′-H, 5′-H), 5.36 m (1H, 3-H, *J* = 1.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 22.6 (4-CH_3), 23.1 and 26.8 (6-CH_3), 36.8 (C^7, $C^{5'}$), 43.6 (C^6), 46.6 (C^5), 56.3 (C^1), 72.1 (C^2), 121.8 (C^3), 144.4 (C^4). Mass spectrum (70 eV), *m*/*z* (I_{rel}, %): 226 (82) $[M]^+$, 198 (77), 164 (59), 133 (100), 105 (39), 99 (55), 77 (24). Found, %: C 64.00; H 7.87; S 28.48. $C_{12}H_{18}S_2$. Calculated, %: C 63.72; H 7.96; S 28.32.

4,6,6-Trimethylspiro[bicyclo[3.1.1]hept-3-ene-2,2′-[1,3]dithiolane] 1′-oxide (III). The procedure for the synthesis and isolation was the same as that described below for compound **IVa** with the difference that the ratio **II**–*m*-$ClC_6H_4CO_3$ was 1:1. Yield 0.66–0.69 g (62–65%), colorless crystals, R_f 0.24–0.34 (hexane–diethyl ether 50:1). IR spectrum: ν 1047 cm^{-1} (S=O). ^1H NMR spectrum, δ, ppm: first stereoisomer: 0.97 s and 1.42 s (3H each, 6-CH_3), 1.77 d (3H, 4-CH_3, *J* = 1.6 Hz), 2.05–2.15 m (1H, 1-H, 5-H), 3.41 m and 3.93 m (4H, 4′-H, 7-H), 2.60–2.80 m (4H, 5′-H), 4.96 m (1H, 3-H, *J* = 1.6 Hz); second stereoisomer: 1.02 s and 1.38 s (3H each, 6-CH_3), 1.83 d (3H, 4-CH_3, *J* = 1.6 Hz), 2.05–2.15 m (1H, 1-H, 5-H), 3.52 m and 3.93 m (4H, 4′-H, 5′-H), 5.52 m (1H, 3-H, *J* = 1.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: first stereoisomer: 22.8, 23.0, 26.3 (CH_3); 36.0, 34.8, 41.8, 46.5, 48.0, 51.7, 85.4 (C^2), 116.6 (C^3), 149.9 (C^4); second stereoisomer: 23.1, 23.4, 26.7 (CH_3); 33.5, 35.1, 43.6, 46.4, 53.5, 51.4, 84.3 (C^2), 113.8 (C^3), 151.6 (C^4). Mass spectrum (70 eV), *m*/*z* (I_{rel}, %): 243 (5) $[M]^+$, 182 (11), 165 (21), 151 (35), 92 (41), 91 (87), 77 (100).

(1*S*,1′*S*,2*S*,3′*S*,5*S*)-4,6,6-Trimethylspiro[bicyclo-[3.1.1]hept-3-ene-2,2′-[1,3]dithiolane] 1′,3′-dioxide (IVa). A solution of 1 g (4.42 mmol) of compound **II** in 50 ml of methylene chloride was cooled to –10°C, a 70–75% solution of *m*-chloroperoxybenzoic acid in methylene chloride was added to attain a substrate-to-oxidant ratio of 1:2. The mixture was stirred for 5 h, anhydrous ammonia (prepared by heating its aqueous solution and dried over calcium chloride) was passed through the mixture using a gas-inlet tube, and the curdy precipitate of *m*-chloroperoxybenzoic acid ammonium salt was filtered off. The solvent was distilled off from the giltrate under reduced pressure, and the residue was subjected to column chromatography on silica gel using diethyl ether–heptane (1:25) as eluent. Yield 0.22–0.25 g (20–22%), colorless crystals, mp 189–190°C, R_f 0.05 (hexane–diethyl ether, 50:1), $[\alpha]_D$ = +49.1° (*c* = 1.76, EtOH). IR spectrum: ν 1035 cm^{-1} (S=O). ^1H NMR spectrum, δ, ppm: 1.13 s and 1.46 s (3H each, 6-CH_3), 1.84 d (1H, 7-H, *J* = 10.0 Hz), 1.89 d (3H, 4-CH_3, *J* = 1.6 Hz), 2.22 d.d.d (1H, 5-H, *J* = 6.1, 5.3, 1.0 Hz), 2.43 d.d.d (1H, 1-H, *J* = 7.8, 5.7, 2.1 Hz), 2.84 d.d.d (1H, 7-H, *J* = 10.0, 4.8, 1.0 Hz), 3.53 d.d (1H, 5′-H, *J* = 10.0, 1.5 Hz), 3.57 d.d (1H, 5′-H, *J* = 10.0, 4.0 Hz), 3.65 d.d.d (1H, 4′-H, *J* = 14.0, 3.0, 2.5 Hz), 3.78 d.d.d (1H, 4′-H, *J* = 14.0, 9.0, 4.0 Hz), 5.29 m (1H, 3-H, *J* = 1.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 22.4 and 26.3 (6-CH_3), 23.8 (4-CH_3), 35.4 (C^7), 42.4 (C^5), 42.6 (C^6), 45.9 (C^1), 48.1 ($C^{5'}$), 51.1 ($C^{4'}$), 97.4 (C^2), 107.7 (C^3), 154.3 (C^4). Mass spectrum (70 eV), *m*/*z* (I_{rel}, %): 258 (12) $[M]^+$, 182 (100), 165 (49), 140 (27), 92 (46), 91 (47), 77 (28). Found, %: C 54.99; H 7.14; S 25.05. $C_{12}H_{22}S_2O_2$. Calculated, %: C 55.58; H 6.98; S 24.81.

(1*S*,1′*S*,2*S*,3′*R*,5*S*)-4,6,6-Trimethylspiro[bicyclo-[3.1.1]hept-3-ene-2,2′-[1,3]dithiolane] 1′,3′-dioxide (IVb). Transparent crystals of stereoisomer **IVb** were separated manually from compound **IVa**. ^1H NMR spectrum, δ, ppm: 1.18 s and 1.42 s (3H each, 6-CH_3), 1.80 d (1H, 7-H, *J* = 9.8 Hz), 1.90 d (3H, 4-CH_3, *J* = 1.6 Hz), 2.22 d.d.d (1H, 5-H, *J* = 6.1, 5.5, 1.0 Hz), 2.43 d.d.d (1H, 1-H, *J* = 5.8, 5.5, 2.1 Hz), 2.78 d.d.d (1H, 7-H, *J* = 9.8, 6.1, 5.5 Hz), 3.45–3.85 m (4H, SCH_2), 3.57 m (1H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 22.5 and 24.0 (6-CH_3), 26.3 (4-CH_3), 33.4 (C^7), 42.5 (C^1), 44.4 (C^6), 46.3 (C^5), 48.6 and 51.8 ($C^{4'}$, $C^{5'}$), 98.5 (C^2), 106.9 (C^3), 156.4 (C^4).

(1*S*,2*S*,3′*S*,5*S*)-4,6,6-Trimethylspiro[bicyclo-[3.1.1]hept-3-ene-2,2′-[1,3]dithiolane] 1′,1′,3′-trioxide (Va). Yield 0.21–0.24 g (17–20%), colorless crystals, mp 192–193°C, R_f 0.20 (hexane–diethyl ether, 50:1), $[\alpha]_D$ = –40.1° (*c* = 1.12, EtOH). IR spectrum, ν, cm^{-1}: 1055 (S=O), 1309 ($\nu_{as}SO_2$), 1126 (ν_sSO_2).

^{1}H NMR spectrum, δ, ppm: 1.04 s and 1.46 s (3H each, 6-CH_3), 1.87 d (3H, 4-CH_3, J = 1.6 Hz), 1.90 d (1H, 7-H, J = 9.3 Hz), 2.12 d.d (1H, 5-H, J = 5.0, 4.6 Hz), 2.77 d.d.d (1H, 7-H, J = 10.0, 6.0, 5.3 Hz), 2.79 m (1H, 1-H), 3.15 d.d.d (1H, 5′-H, J = 14.3, 5.2, 5.0 Hz), 3.32 d.d.d (1H, 5′-H, J = 14.3, 5.3, 1.3 Hz), 3.65 d.d.d (1H, 4′-H, J = 14.0, 5.3, 1.3 Hz), 4.12 d.d.d (1H, 4′-H, J = 14.0, 6.0, 1.0 Hz), 5.25 s (1H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 22.7, 23.8, 26.1 (CH_3), 35.2 (C^7), 42.9 (C^6), 43.3 (C^5), 46.3 (C^1), 49.3 ($C^{5'}$), 40.7 ($C^{4'}$), 87.3 (C^2), 107.4 (C^3), 155.9 (C^4). Found, %: C 52.95; H 6.65; S 22.51. $C_{12}H_{22}S_2O_2$. Calculated, %: C 52.55; H 6.57; S 23.36.

(1*S*,5*S*)-4,6,6-Trimethylspiro[bicyclo[3.1.1]hept-3-ene-2,2′-[1,3]dithiolane] 1′,1′,3′,3′-tetraoxide (VI) was synthesized by oxidation of **II** (see above) using 4 equiv of *m*-chloroperoxybenzoic acid. Yield 0.90–0.96 g (70–75%), colorless crystals, mp 202–203°C, R_f 0.75 (hexane–diethyl ether, 50:1), $[\alpha]_D$ = –113° (c = 1.14, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1328 ($\nu_{as}SO_2$), 1130 (ν_sSO_2). ^{1}H NMR spectrum, δ, ppm: 0.95 s and 1.36 s (3H each, 6-CH_3), 1.83 d (3H, 4-CH_3, J = 1.5 Hz), 1.85 d (1H, 7-H, J = 10.0 Hz), 2.07 m (1H, 5-H), 2.52 d.d.d (1H, 7-H, J = 10.0, 6.0, 5.4 Hz), 2.63 d.d.d (1H, 1-H, J = 5.0, 2.0 Hz), 3.40–3.60 m (4H, 4′-H, 5′-H), 5.27 m (1H, 3-H, J = 1.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 23.0 and 26.3 (6-CH_3), 24.0 (4-CH_3), 33.9 (C^7), 40.1 (C^6), 45.1 (C^5), 46.3 (C^1), 47.5 ($C^{4'}$), 49.2 ($C^{5'}$), 83.2 (C^2), 107.2 (C^3), 157.7 (C^4). Mass spectrum (70 eV), m/z (I_{rel}, %): 291 (5) $[M]^+$, 198 (81), 156 (57), 149 (46), 119 (65), 92 (97), 91 (100), 77 (14). Found, %: C 49.65; H 6.35; S 21.85. $C_{12}H_{22}S_2O_2$. Calculated, %: C 49.66; H 6.21; S 22.07.

This study was performed under financial support by the President of the Russian Federation (Program for Support of Leading Scientific Schools, project no. NSh-4028.2008.3).

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