Regio- and Stereoselectivity of the SiO_2-Catalyzed Reaction of Thiocamphor (=1,7,7-Trimethylbicyclo[2.2.1]heptane-2-thione) with Optically Active Monosubstituted Oxiranes

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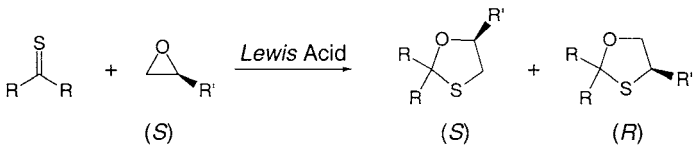
The reactions of the enolizable thioketone (1*R*,4*R*)-thiocamphor (=(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]-heptane-2-thione; **1**) with (*S*)-2-methyloxirane (**2**) in the presence of a *Lewis* acid such as $SnCl_4$ or SiO_2 in anhydrous CH_2Cl_2 led to two diastereoisomeric spirocyclic 1,3-oxathiolanes **3** and **4** with the Me group at C(5′), as well as the isomeric β-hydroxy thioether **5** (*Scheme 2*). The analogous reactions of **1** with (*RS*)-, (*R*)-, and (*S*)-2-phenyloxirane (**7**) yielded two isomeric spirocyclic 1,3-oxathiolanes **8** and **9** with Ph at C(4′), an additional isomer **13** bearing the Ph group at C(5′), and three isomeric β-hydroxy thioethers **10**, **11**, and **12** (*Scheme 4*). In the presence of HCl, the β-hydroxy thioethers **5**, **10**, **11**, and **12** isomerized to the corresponding 1,3-oxathiolanes **3** and **4** (*Scheme 3*), and **8**, **9**, and **13**, respectively (*Scheme 5*). Under similar conditions, an epimerization of **3**, **8**, and **9** occurred to yield the corresponding diastereoisomers **4**, **14**, and **15**, respectively (*Schemes 3* and *6*). The structures of **9** and **15** were confirmed by X-ray crystallography (*Figs. 1* and *2*). These results show that the *Lewis* acid-catalyzed addition of oxiranes to enolizable thioketones proceeds with high regio- and stereoselectivity *via* an S_N2-type mechanism.

1. Introduction. – The formation of 1,3-oxathiolanes *via* the *Lewis* acid-catalyzed reactions of non-enolizable thiocarbonyl compounds with racemic or optically active oxiranes has been investigated in recent years [1–5]. All results reported previously indicate that the reactions proceed with high regio- and stereoselectivity *via* an S_N2-type mechanism (*Scheme 1*). For example, the reactions with monosubstituted oxiranes lead to 5- and 4-substituted 1,3-oxathiolanes with retention and inversion of the configuration, respectively.

Scheme 1

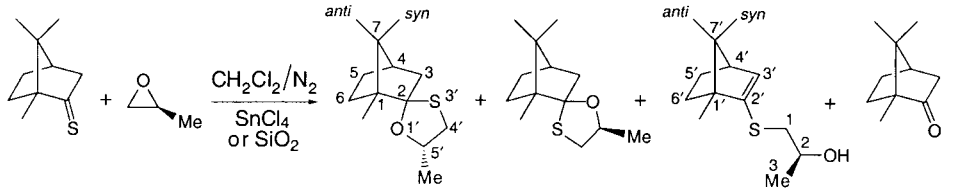


With the aim of establishing the scope and limitation of the formation of 1,3-oxathiolanes, the reactions of some enolizable thioketones with asymmetrically substituted oxiranes were carried out. In the present paper, the results of the reactions of (1*R*,4*R*)-thiocamphor (=1,7,7-trimethylbicyclo[2.2.1]heptane-2-thione; **1**) with (*S*)-2-methyloxirane (**2**), and (*RS*)-, (*R*)-, and (*S*)-phenyloxirane (**7**) are described.

[1]) Part II of the projected Ph.D. thesis of *C. F.*, University of Zurich. For Part I, see [1].

2. Results. – 2.1. *Reaction of (1*R*,4*R*)-Thiocamphor* (**1**) *with (*S*)-2-Methyloxirane* (**2**). On dropping 4 equiv. of **2** into a soln. of **1** and 0.6 equiv. of $SnCl_4$ in anhydrous CH_2Cl_2 at $-78°$ under an N_2 atmosphere, the color of the yellow soln. turned slowly to light yellow. After 8 min, the reaction was quenched by addition of H_2O. Chromatographic separation of the mixture gave two diastereoisomeric spirocyclic 1,3-oxathiolanes **3** and **4**, and camphor (**6**) in 51, 8, and 10% yield, respectively, as well as an unexpected open-chain product **5** in 18% yield. When the reaction was repeated at room temperature in the presence of silica gel, after 1 d, only **3** and the isomer **5** were obtained in 16 and 48% yield, respectively. Furthermore, the starting material **1** was recovered in 10% yield (*Scheme 2* and *Table 1*).

Scheme 2



1 **2** **3** **4** **5** **6**

Table 1. *$SnCl_4$- and SiO_2-Catalyzed Reactions of* **1** *with* **2** *in CH_2Cl_2*

Lewis acid	Temp.	Reaction time	Yield of products [%]				
			3	**4**	**5**	**6**	**1**
$SnCl_4$	$-78°$	8 min	51	8	18	10	–
SiO_2	r.t.	1 d	16	–	48	–	10

The structures of **3**, **4**, and **5** were assigned on the basis of elemental analyses, ^{1}H-, ^{13}C-, and 2D-NMR, and mass spectra, and by comparison with those of similar compounds described previously [1–5]. The configurations at C(2) and C(5′) of **3** and **4** were determined by means of NOESY spectra relative to the known absolute configuration of the bicyclic skeleton of the starting material **1**. The examination of a *Dreiding* model of **3** shows that the spatial distances between H–C(5′) and the Me–C(1) group, and between the Me–C(5′) group and H_{endo}–C(3) are small, which corresponds well with the NOESY spectrum (600 MHz, C_6D_6) of **3**, which shows one relevant cross-signal between H–C(5′) at 4.02–3.99 ppm and Me–C(1) at 1.11 ppm, and a smaller relevant cross-signal between Me–C(5′) at 1.08 ppm and H_{endo}–C(3) at 1.95 ppm. It is worth mentioning that the difference between the chemical shifts of H_{endo}–C(6) at 2.32 ppm and H_{exo}–C(6) at 1.45 ppm is large ($\Delta\delta = 0.85$ ppm) due to the proximity of the electronegative O-atom, which means that the O-atom is close to H_{endo}–C(6), *i.e.*, in the *endo* position. These analyses indicate that the absolute configuration of **3** is (1*R*,2*R*,4*R*,5′*S*). Similarly, the examination of the *Dreiding* model of the diastereoisomer **4** shows that the distance between H–C(5′) and H_{exo}–C(3) is small, in accordance with the NOESY spectrum (500 MHz, $CDCl_3$) of **4**, which shows a relevant cross-signal between H–C(5′) at 4.18–4.13 ppm and H_{exo}–C(3) at 2.33 ppm.

In addition, H_{endo}–C(6) and H_{exo}–C(6) both absorbed at 1.63–1.56 ppm, which implies that the O-atom is *exo*-oriented. Therefore, the absolute configuration of **4** is (1*R*,2*S*,4*R*,5′*S*).

Acid-Catalyzed Isomerization of **5** *with HCl.* A solution of **5** in Et_2O at −20° was treated with 4 drops of conc. HCl, and the mixture was stirred for 8 h. After the usual workup, column chromatography yielded 73% of **3** and 8% of **4**. The isomerization of **5** also occurred smoothly in $CDCl_3$, which contained traces of DCl, at room temperature, leading to different ratios of **3** and **4**, depending on the conditions. In the absence of DCl, *i.e.*, after filtration of $CDCl_3$ through Al_2O_3, no isomerization of **5** was observed (*Scheme 3* and *Table 2*). On the other hand, irradiation of this solution with sunlight led to extensive isomerization.

Scheme 3

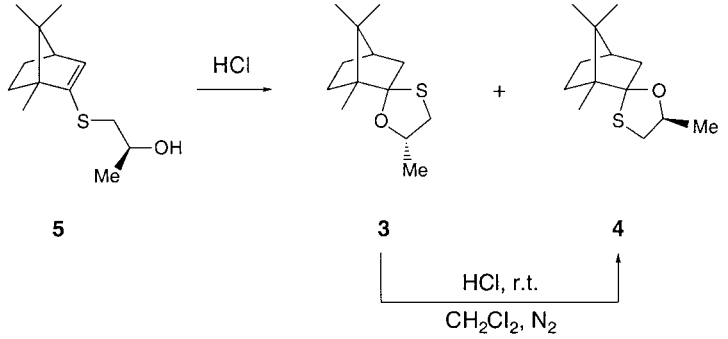


Table 2. *Acid-Catalyzed Isomerzation of* **5** *to Give* **3** *and* **4**

Solvent	Conditions	Temp.	Reaction time	Ratio of products	
				3	**4**
Et_2O	addition of HCl	−20°	8 h	73	8[a])
$CDCl_3$		r.t.	5 min	1 :	3.8
$CDCl_3$		r.t.	12 h	1 :	1.8
$CDCl_3$	filtered through Al_2O_3	r.t.	12 h	no reaction	
$CDCl_3$	filtered through Al_2O_3, *hv*	r.t.	2 h	1 :	3.5
C_6D_6		r.t.	12 h	no reaction	

[a]) Yields of isolated products.

Epimerization of **3** *with HCl.* To a solution of **3** in CH_2Cl_2, five drops of conc. HCl were added at room temperature. After stirring the mixture for 7.5 h and the usual workup, chromatographic separation gave the diastereoisomer **4** in 73% yield, and the starting material **3** was recovered in 7% yield (*Scheme 3*).

2.2. *Reaction of* **1** *with 2-Phenyloxirane* (**7**). The analogous $SnCl_4$-catalyzed reaction of **1** with (*RS*)-**7** in CH_2Cl_2 at −78° for 17 min led to two diastereoisomeric 1,3-oxathiolanes **8** and **9** in 37 and 21% yield, respectively, whereas the reaction of **1** with (*R*)-**7** under the same conditions gave only diastereoisomer **8** in 79% yield (*Scheme 4*). The reaction of **1** with (*R*)-**7** was repeated at −78° for 20 min, whereupon **8** was formed

in 62% yield. In addition, the β-hydroxy thioether **10** was isolated in 8% yield. After 17 min at $-78°$, the reaction of **1** with (*S*)-**7** gave the two diastereoisomers **8** and **9** in 1 and 45% yield, respectively, as well as a β-hydroxy thioether **11** in 44% yield.

The SiO_2-catalyzed reaction of **1** with (*R*)-**7** was carried out at room temperature for 3 days, and chromatographic separation gave the diastereoisomer **8**, and two unexpected isomers **12** and **13** in 58, 5, and 2% yield, respectively. At 0°, after 3 days, the reaction yielded 51, 6, 10, and 0.7% of **8**, **10**, **12**, and **13**, repectively. In addition, the starting material **1** was recovered in 18% yield (*Scheme 4* and *Table 3*).

Scheme 4

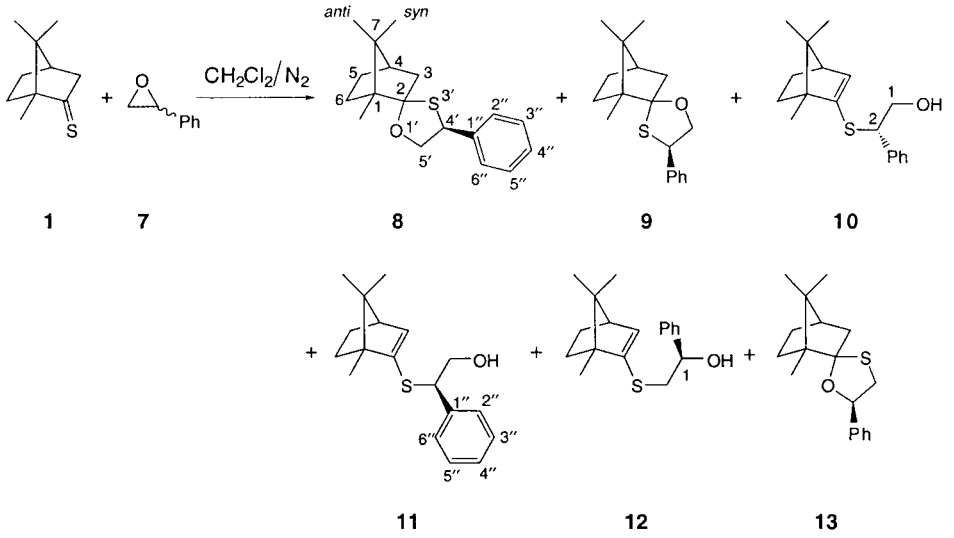
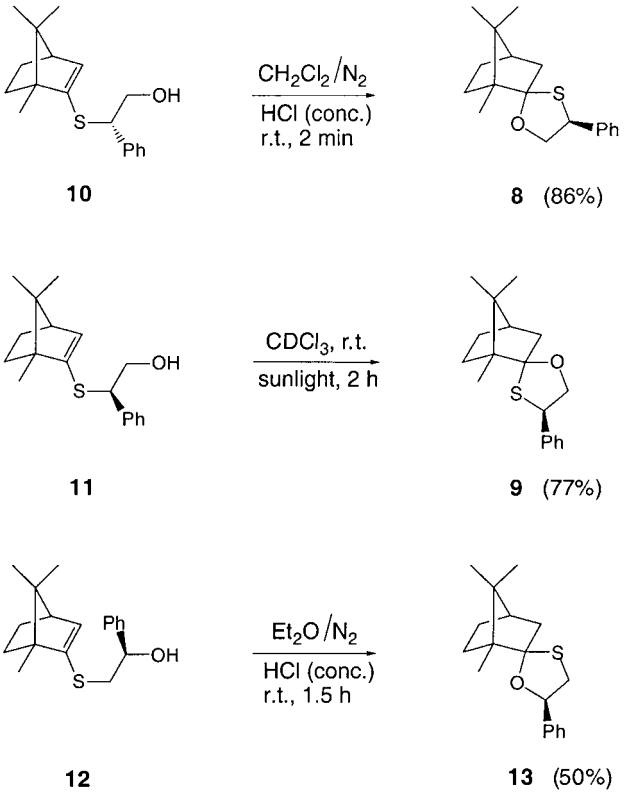


Table 3. *$SnCl_4$- and SiO_2-Catalyzed Reactions of* **1** *with* **7** *in CH_2Cl_2*

Lewis acid	**7**	Temp.	Reaction time	Yield of products [%]						
				8	**9**	**10**	**11**	**12**	**13**	**1**
$SnCl_4$	(*RS*)	−78°	17 min	37	21	–	–	–	–	–
	(*R*)	−78°	17 min	79	–	–	–	–	–	–
	(*R*)	−78°	20 min	62	–	8	–	–	–	–
	(*S*)	−78°	17 min	1	45	–	44	–	–	–
SiO_2	(*R*)	r.t.	3 d	58	–	–	–	5	2	–
	(*R*)	0°	3 d	51	–	6	–	10	0.7	18

Isomerization of **10**, **11**, *and* **12**. A solution of **10** in CH_2Cl_2 under N_2 was treated with one drop of conc. HCl for 2 min at room temperature. The usual workup by preparative TLC yielded 86% of the spirocyclic compound **8**. Similar treatment of **12** in Et_2O with two drops of conc. HCl for 1.5 h at room temperature gave **13** in 50% yield. The analogous isomerization of **11** in $CDCl_3$ proceeded smoothly at room temperature by irradiation with sunlight for 2 h, leading to **9** in 77% yield. (*Scheme 5*).

Scheme 5

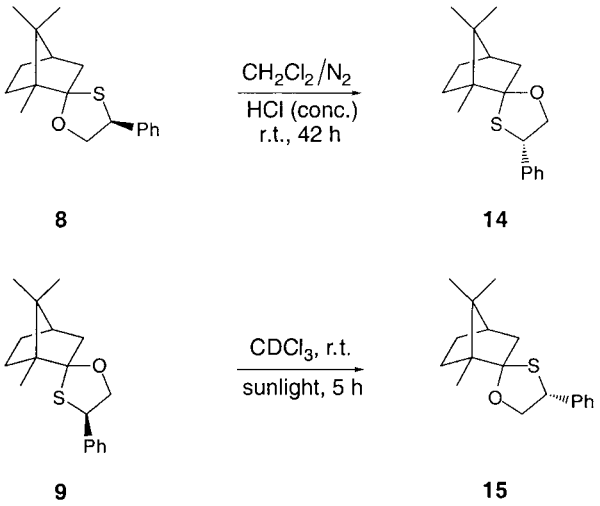


Epimerization of **8** *to* **14**, *and of* **9** *to* **15**. Addition of seven drops of conc. HCl to a CH_2Cl_2 solution of **8** at room temperature and stirring the mixture for 42 h yielded 67% of **14**, and 21% of the starting material **8** was recovered. An analogous epimerization of **9** in $CDCl_3$ occurred upon irradiation with sunlight for 5 h at room temperature and led to **15** in 42% yield. In addition, 32% of the starting material **9** was recovered (*Scheme 6*).

The structures of **8**–**15** were assigned on the basis of their elemental analyses, ^{1}H-, ^{13}C-, and 2D-NMR, and mass spectra, and by comparison with those of similar compounds described previously (see [1–5] and *Sect. 2.1*). The configurations of the spirocyclic 1,3-oxathiolanes **8**, **9**, **13**, **14**, and **15** were determined by means of NOESY spectra, relative to the known absolute configuration of the bicyclic skeleton of the starting material **1**.

The examination of a *Dreiding* model of **8** shows that the distances between H–C(2″) and H–C(6″) of the Ph group and the Me group at C(1) are small, in agreement with the NOESY spectrum (600 MHz, C_6D_6) of **8**, which shows one cross-signal between H–C(2″)/H–C(6″) at 7.31 ppm and Me–C(1) at 1.16 ppm. In addition, $\Delta\delta$ of H_{endo}–C(6) at 2.47 ppm and H_{exo}–C(6) at $\approx$1.50 ppm is 0.97 ppm, which demonstrates that the O-atom is close to H_{endo}–C(6), *i.e.*, the O-atom is in the *endo*-

Scheme 6



position. Therefore, the absolute configuration of **8** has been established as (1*R*,2*R*,4*R*,4′*S*). Similarly, the NOESY spectrum of **9** (600 MHz, $CDCl_3$) shows one relevant cross-signal between H–C(2″)/H–C(6″) at 7.42–7.40 ppm and Me–C(1) at 1.08 ppm, but the signals of H_{endo}–C(6) and H_{exo}–C(6) overlap at 1.62–1.54 ppm, which implies that the O-atom is *exo*-oriented. Therefore, it can be deduced that **9** possesses the absolute configuration of (1*R*,2*S*,4*R*,4′*R*). The structure of **9** was confirmed by X-ray crystallography (*Fig. 1*).

The crystals of **9** were enantiomerically pure, and the absolute configuration of the molecule has been confidently determined independently by the diffraction experiment. The enantiomer defined this way is in agreement with the known configuration of the camphor moiety, and the configuration of the Ph-substituted C(4′) is (*R*). The configuration at the spiro C-atom is (*S*). Therefore, the absolute configuration deduced by NOESY spectra is in agreement with the X-ray analysis.

The NOESY spectrum (600 MHz, $CDCl_3$) of **13** shows two relevant cross-signals between H–C(2″)/H–C(6″) at 7.40–7.39 ppm and H_{endo}–C(6) at 2.26 ppm and Me–C(1) at 1.04 ppm, as well as one relevant cross-signal between H–C(5′) at 4.86 ppm and H_{endo}–C(3) at 1.82 ppm. In addition, $\Delta\delta$ of H_{endo}–C(6) (2.26 ppm) and H_{exo}–C(6) (*ca.* 1.51 ppm) is 0.75 ppm, which suggests an *endo*-oriented O-atom. Therefore, the absolute configuration of **13** should be (1*R*,2*R*,4*R*,5′*R*).

The NOESY spectrum (500 MHz, $CDCl_3$) of **14** shows one relevant cross-peak between H–C(2″)/H–C(6″) at 7.45–7.43 ppm and H_{endo}–C(3) at 2.20 ppm, as well as one relevant cross-signal between H–C(4′) at 4.51 ppm and Me–C(1) at 0.99 ppm. In addition, the signals of H_{endo}–C(6) and H_{exo}–C(6) overlap (1.65–1.55 ppm), which indicates an *exo*-oriented O-atom. So, it can be inferred that **14** has the absolute configuration (1*R*,2*S*,4*R*,4′*S*), *i.e.*, it is the C(2) epimer of **8**.

The NOESY spectrum (500 MHz, $CDCl_3$) of **15** shows two relevant cross-peaks between H–C(2″)/H–C(6″) (7.42–7.41 ppm) and H_{exo}–C(3) (2.61 ppm) as well as

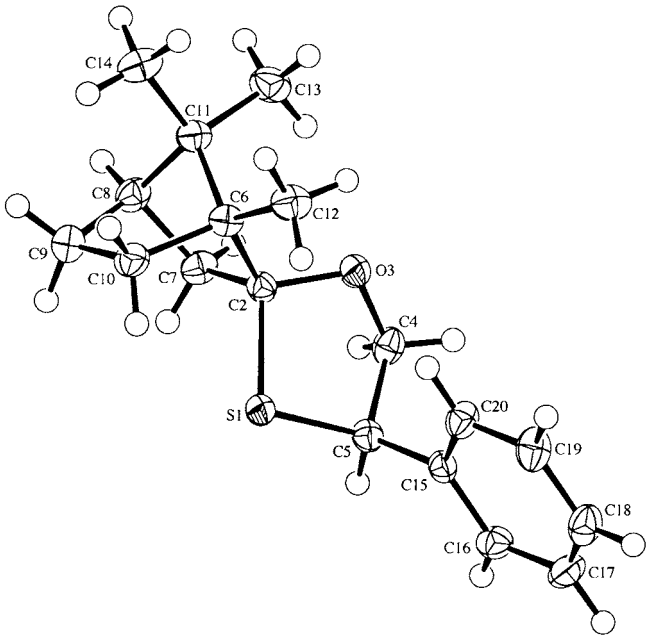


Fig. 1. *ORTEP Plot* [6] *of the molecular structure of* **9** (arbitrary numbering of the atoms; 50% probability ellipsoids)

H_{endo}–C(3) (1.86 ppm), and one relevant cross-signal between H–C(4′) (4.46 ppm) and Me–C(1) (1.02 ppm). The $\Delta\delta$ of H_{endo}–C(6) (2.13 ppm) and H_{exo}–C(6) (*ca.* 1.48 ppm) amounts to 0.65 ppm, which indicates an *endo*-oriented O-atom. According to the results mentioned above, it can be concluded that the absolute configuration of **15** is (1*R*,2*R*,4*R*,4′*R*), *i.e.*, **15** is the C(2) epimer of **9**. This result was confirmed by X-ray crystallography (*Fig. 2*).

The crystals of **15** were enantiomerically pure, and the absolute configuration of the molecule has been confidently determined independently by the diffraction experiment. The enantiomer defined this way is in agreement with the known configuration of the camphor moiety. The configurations at the Ph-substituted C(4′) and the spiro C-atom are both (*R*).

3. Discussion and Conclusions. – The results presented show that the enolizable thioketone **1** reacts with the optically active monosubstituted oxiranes **2** and **7** in the presence of a *Lewis* acid to yield spirocyclic 1,3-oxathiolanes, as well as open-chain enethiol ethers, with high regio- and stereoselectivity. The reactions proceed *via* an S_N2-type mechanism, whereby the nucleophilic thiocarbonyl S-atom preferentially attacks the less hindered C(3)-atom of the activated (*S*)-2-methyloxirane (**1**) (O–C(3) cleavage), leading to products with retention of configuration (*Scheme 2*). In the case of 2-phenyloxirane (**7**), the preferred attack takes place at C(2) (O–C(2) cleavage) with inversion of configuration (*Scheme 4*).

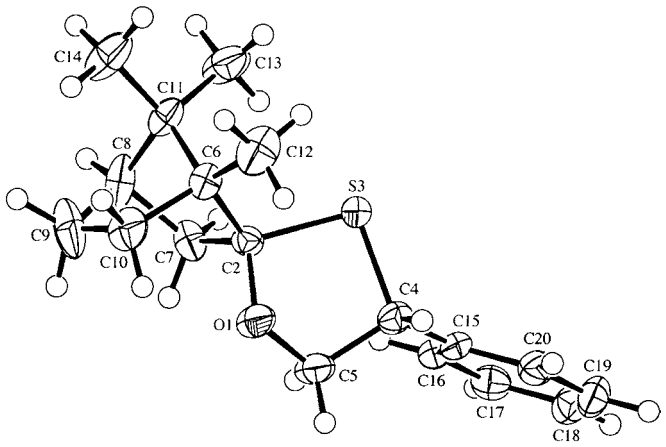
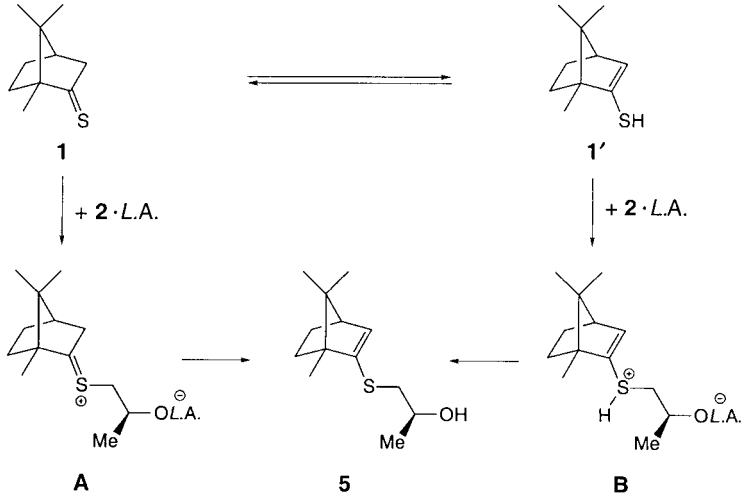


Fig. 2. *ORTEP Plot* [6] *of the molecular structure of one of the three symmetry-independent molecules of* **15** (arbitrary numbering of the atoms; 50% probability ellipsoids)

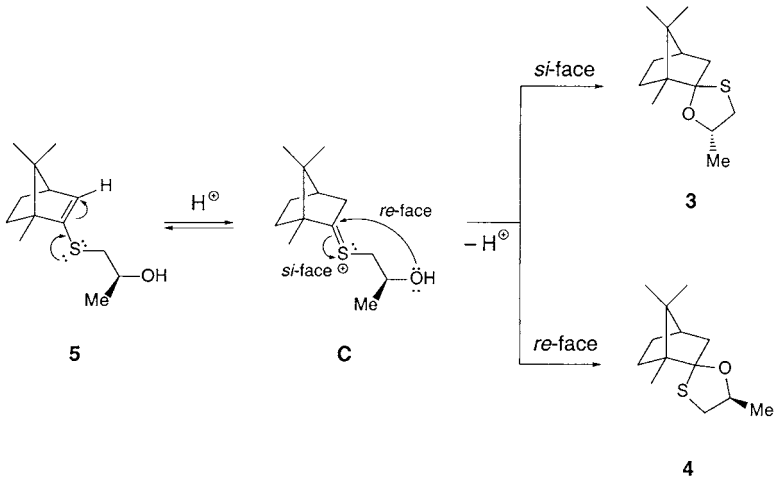
In contrast to the analogous reaction with non-enolizable thioketones, enethiol ethers **5**, **10**, **11**, and **12** are formed with thiocamphor (**1**). Their formation can be rationalized *via* intermediates of type **A** or **B** (*Scheme 7*). In the case of non-enolizable thioketones, the analogous intermediates undergo ring closure to give 1,3-oxathiolanes exclusively (*cf.* [1–5]).

Scheme 7



The enethiol ethers isomerize smoothly to give the corresponding spirocyclic 1,3-oxathiolanes in the presence of traces of HCl or DCl (*Schemes 3* and *5*). The mechanism of the isomerization of **5** is depicted in *Scheme 8*. The C=C bond of the sulfanylalkene of **5** is protonated, leading to the thiocarbonylium ion **C**. The cyclization of **C** and subsequent release of a proton yields the spirocyclic 1,3-oxathiolanes **3** and **4**,

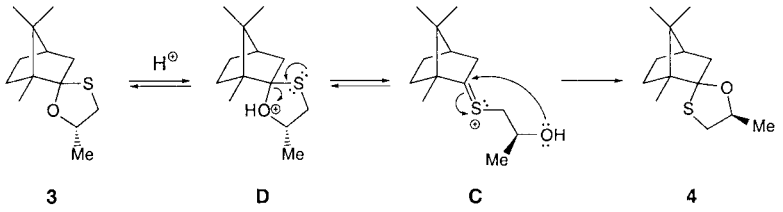
Scheme 8



depending upon the nucleophilic attack of the OH group from the *si*- and *re*-face side, respectively (*Scheme 8*).

The observed epimerizations in the cases of **3**/**4**, **8**/**14**, and **9**/**15** (*Schemes 3* and *6*) can be explained by the acid-catalyzed ring opening of the spirocyclic 1,3-oxathiolanes according to the mechanism described by *Pihlaja* [7]. The ring opening of the oxonium ion **D** leads to the thiocarbonylium ion **C**, which undergoes a cyclization by nucleophilic attack of the OH group from the opposite side to yield the thermodynamically more stable epimer **4** (*Scheme 9*).

Scheme 9



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Experimental Part

1. *General*. See [8]. Optical rotations were recorded on a *Perkin-Elmer-241* polarimeter ($c = 1$, in THF). HPLC on a *Chiralcel OD-H* column. IR Spectra: film, in cm^{-1}. NMR Spectra: at 300 (^1H) and 75.5 MHz (^{13}C) in $CDCl_3$, if not otherwise stated. Assignment of signals based on 2D NMR spectra.

2. *General Procedures for the Reactions of (1*R,*4*R*)-Thiocamphor* (=1,7,7-Trimethylbicylo[2.2.1]heptane-2-thione; **1**) *with Oxiranes* (S)-**2** *and* **7**. *Procedure 1*. To the soln. of **1** (*ca.* 1 mmol) in anh. CH_2Cl_2 (10–15 ml) under N_2 atmosphere, 0.5 equiv. of $SnCl_4$ was added at $-78°$. This led to little change in the color of the soln. After stirring the mixture for 15 min at $-78°$, *ca.* 2 equiv. of oxirane (*S*)-**2** or **7** were added dropwise, whereby

the color of the soln. changed moderately in most cases. Then, the reaction was quenched by addition of H_2O, and the mixture was washed with sat. aq. NaCl soln. (3×). The combined org. layers were dried ($MgSO_4$) and evaporated *in vacuo*. The products were separated by chromatography (SiO_2; hexane/Et_2O or hexane/CH_2Cl_2; CC, prep. TLC (PLC)).

Procedure 2. To a soln. of **1** (*ca.* 1 mmol) and oxirane (*S*)-**2** or (**7**) (*ca.* 2 mmol) in dry CH_2Cl_2 (10–15 ml) under an N_2 atmosphere, 4.5 g of silica gel were added at r.t. After stirring the suspension for 2–3 d at r.t., the mixture was filtered, and the residue was washed with CH_2Cl_2 (4×). Then, the combined filtrate was evaporated *in vacuo*. The products were separated as described above.

3. *Reactions of* **1**. 3.1. *With (*S*)-2-Methyloxirane* ((*S*)-**2**). Reaction of **1** (168 mg, 1 mmol) with **2** (232 mg, 4 mmol, or 116 mg, 2 mmol) and 0.6 mmol of $SnCl_4$ (or 4.5 g of SiO_2) at −78° or r.t. (CC (hexane/CH_2Cl_2 10:1 and hexane/Et_2O 3:1)) yielded *(1*R,*2*R,*4*R,*5′*S*)-1,5′,7,7-tetramethylspiro[bicyclo[2.2.1]heptane-2,2′-[1,3]oxathiolane]* (**3**), *(1*R,*2*S,*4*R,*5′*S*)-1,5′,7,7-tetramethylspiro[bicyclo[2.2.1]heptane-2,2′-[1,3]oxathiolane]* (**4**), *(2*S*)-1-[(1′*R*,4′*R*)-(1′,7′,7′-trimethylbicyclo[2.2.1]hept-2′-en-2′-yl)sulfanyl]propan-2-ol* (**5**), and *camphor* (**6**). In addition, the starting material **1** was partly recovered in the case of SiO_2 as catalyst (*Scheme 2* and *Table 1*).

Data of **3**: Yield: 116 (36) mg (51 (16)%). Colorless oil. $[\alpha]_D^{22} = +$ 44.3. IR: 2952*s*, 2932*s*, 2883*m*, 1475*m*, 1454*s*, 1389*s*, 1373*s*, 1348*w*, 1332*w*, 1306*m*, 1274*w*, 1250*w*, 1234*w*, 1195*m*, 1178*w*, 1149*m*, 1112*s*, 1092*s*, 1060*s*, 1046*s*, 1023*w*, 1012*w*, 998*m*, 953*m*, 938*m*, 884*m*, 823*w*, 803*m*, 747*w*. ^{1}H-NMR (600 MHz, C_6D_6): 4.02–3.99 (*m*, H−C(5′)); 2.65 (*ddd*, *J* = 14.1, 4.4, 3.4, H_{exo}−C(3)); 2.62 (*dd*, *J* = 9.9, 5.4, 1 H−C(4′)); 2.44 (*dd*, *J* = 9.8, 7.2, 1 H−C(4′)); 2.32 (*ddd*, *J* = 12.8, 9.3, 3.7, H_{endo}−C(6)); 1.95 (*d*, *J* = 14.1, H_{endo}−C(3)); 1.67–1.66 (*m*, H_{exo}−C(5)); 1.56 (*t*, *J* = 4.6, H−C(4)); 1.45 (*ddd*, *J* = 12.2, 7.4, 4.8, H_{exo}−C(6)); 1.37–1.33 (*m*, H_{endo}−C(5)); 1.11 (*s*, Me−C(1)); 1.08 (*d*, *J* = 6.0, Me−C(5′)); 1.05 (*s*, Me_{syn}); 0.78 (*s*, Me_{anti}). ^{13}C-NMR (150.9 MHz, C_6D_6): 103.8 (*s*, C(2)); 78.7 (*d*, C(5′)); 55.7 (*s*, C(1)); 50.6 (*t*, C(3)); 49.5 (*s*, C(7)); 46.6 (*d*, C(4)); 40.7 (*t*, C(4′)); 30.5 (*t*, C(6)); 28.0 (*t*, C(5)); 21.3 (*q*, Me_{syn}); 21.1 (*q*, Me_{anti}); 20.4 (*q*, Me−C(5′)); 15.3 (*q*, Me−C(1)). CI-MS (NH_3): 228 (15), 227 (100, $[M+H]^+$), 171 (8), 170 (67), 169 (7), 153 (7). Anal. calc. for $C_{13}H_{22}OS$ (226.38): C 68.97, H 9.80, S 14.16; found: C 68.92, H 9.66, S 14.07.

Data of **4**: Yield: 18 mg (8%). Colorless oil. $[\alpha]_D^{25} = +$ 50.9. IR: 2955*s*, 2930*s*, 2880*s*, 1480*m*, 1450*m*, 1440*m*, 1390*m*, 1380*m*, 1370*m*, 1348*w*, 1335*w*, 1305*w*, 1275*w*, 1255*w*, 1220*w*, 1200*w*, 1175*m*, 1165*m*, 1143*m*, 1130*m*, 1110*m*, 1095*s*, 1080*s*, 1030*s*, 998*w*, 950*m*, 928*w*, 880*m*, 865*w*, 855*w*, 840*w*, 805*w*, 762*w*, 740*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.18–4.13 (*m*, H−C(5′)); 2.92 (*dd*, *J* = 9.7, 4.9, 1 H−C(4′)); 2.43 (*t*, *J* = 9.7, 1 H−C(4′)); 2.33 (*ddd*, *J* = 13.4, 4.3, 3.4, H_{exo}−C(3)); 1.91 (*d*, *J* = 13.4, H_{endo}−C(3)); 1.76 (*t*-like, *J* ≈ 4.5, H−C(4)); 1.74–1.68 (*m*, H_{exo}−C(5)); 1.63–1.56 (*m*, 2 H−C(6)); 1.34 (*d*, *J* = 6.0, Me−C(5′)); 1.22–1.17 (*m*, H_{endo}−C(5)); 1.03 (*s*, Me_{syn}); 0.89 (*s*, Me−C(1)); 0.87 (*s*, Me_{anti}). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 104.8 (*s*, C(2)); 77.6 (*d*, C(5′)); 53.3 (*s*, C(1)); 51.7 (*t*, C(3)); 48.1 (*s*, C(7)); 45.9 (*d*, C(4)); 38.2 (*t*, C(4′)); 34.7 (*t*, C(6)); 27.2 (*t*, C(5)); 21.1 (*q*, Me_{anti}); 20.8 (*q*, Me_{syn}); 19.5 (*q*, Me−C(5′)); 10.0 (*q*, Me−C(1)). CI-MS (NH_3): 228 (6), 227 (40, $[M+H]^+$), 171 (11), 170 (100), 153 (10). Anal. calc. for $C_{13}H_{22}OS$ (226.38): C 68.97, H 9.80, S 14.16; found: C 69.04, H 9.98, S 13.88.

Data of **5**: Yield: 41 (108) mg (18 (48)%). Colorless oil. $[\alpha]_D^{22} = -22.2$. IR: 3356*m* (br., OH), 3059*w*, 2954s, 2872s, 1561*m*, 1453*m*, 1386*m*, 1375*m*, 1365*m*, 1298*m*, 1255*w*, 1186*w*, 1125*m*, 1107*m*, 1074*m*, 1044*m*, 983*m*, 935*m*, 906*w*, 876*w*, 820*w*, 776*w*, 714*w*. ^{1}H-NMR: 5.57 (*d*, *J* = 3.4, H−C(3′)); 4.00–3.94 (*m*, H−C(2)); 2.85 (*dd*, *J* = 13.4, 4.0, 1 H−C(1)); 2.67 (*dd*, *J* = 13.4, 8.1, 1 H−C(1)); 2.35 (*t*, *J* = 3.5, H−C(4′)); 2.17 (*d*, *J* = 3.5, OH); 1.92–1.83 (*m*, H_{exo}−C(5′)); 1.55–1.48 (*m*, H_{exo}−C(6′)); 1.27 (*d*, *J* = 6.2, 3 H−C(3)); 1.13–0.97 (*m*, H_{endo}−C(5′), H_{endo}−C(6′)); 1.01 (*s*, Me−C(1)); 0.81 (*s*, Me_{syn}); 0.78 (*s*, Me_{anti}). ^{13}C-NMR: 143.3 (*s*, C(2′)); 125.3 (*d*, C(3′)); 65.9 (*d*, C(2)); 56.5 (*s*, C(1′)); 56.4 (*s*, C(7′)); 52.1 (*d*, C(4′)); 40.4 (*t*, C(1)); 31.7 (*t*, C(6′)); 26.4 (*t*, C(5′)); 22.3 (*q*, C(3)); 19.7 (*q*, Me_{anti}); 19.5 (*q*, Me_{syn}); 11.3 (*q*, Me−C(1′)). EI-MS: 226 (24, $M^{+\bullet}$), 198 (50), 184 (16), 169 (24), 168 (43), 167 (50), 165 (13), 155 (13), 153 (11), 152 (12), 151 (12), 141 (11), 140 (42), 139 (15), 138 (10), 135 (14), 133 (12), 125 (46), 123 (18), 121 (11), 119 (19), 116 (15), 111 (13), 109 (26), 108 (74), 107 (34), 106 (12), 105 (30), 97 (13), 95 (65), 93 (37), 91 (51), 85 (16), 83 (23), 81 (42), 80 (11), 79 (27), 77 (30), 74 (14), 71 (10), 69 (36), 67 (27), 65 (17), 59 (17), 57 (26), 55 (45), 53 (22), 45 (32), 43 (40), 41 (100).

Isomerization of **5** *to* **3** *and* **4**. Treatment of **5** (60 mg, 0.27 mmol) with 4 drops of conc. HCl in Et_2O (15 ml) at −20° (8 h, CC (hexane/CH_2Cl_2 10:1)) yielded 44 mg (73%) of **3** and 5 mg (8%) of **4**. Moreover, the isomerization of **5** to **3** and **4** proceeded very smoothly in NMR tubes in the presence of traces of DCl with different ratios of **3** to **4**, depending upon the conditions, but without DCl ($CDCl_3$ filtered through Alox (basic)), **5** did not change at all (*Scheme 3* and *Table 2*).

Epimerization of **3** *to* **4**. Treatment of **3** (106 mg, 0.47 mmol) with 5 drops of conc. HCl in CH_2Cl_2 (6 ml) at r.t. (7.5 h, CC (hexane/CH_2Cl_2 10:1)) yielded 77 mg (73%) of **4**, and 8 mg (7%) of the starting material **3** was recovered (*Scheme 3*).

3.2. *With 2-Phenyloxirane* (**7**). Reaction of **1** (168 mg, 1 mmol) with **7** (240 mg, 2 mmol) and 0.5 mmol $SnCl_4$ (or 4.5 g of SiO_2) at $-78°$, 0°, or r.t. (CC (hexane/CH_2Cl_2 10:1 and hexane/Et_2O 3:1)) gave *(1*R*,2*R*,4*R*,4′*S*)-1,7,7-trimethyl-4′-phenylspiro[bicyclo[2.2.1]heptane-2,2′-[1,3]oxathiolane]* (**8**), *(1*R*,2*S*,4*R*,4′*R*)-1,7,7-trimethyl-4′-phenylspiro[bicyclo[2.2.1]heptane-2,2′-[1,3]oxathiolane]* (**9**), *(2*S*)-2-phenyl-2-[(1′*R*,4′*R*)-(1′,7′,7′-trimethylbicyclo[2.2.1]hept-2′-en-2′-yl)sulfanyl]ethanol* (**10**), *(2*R*)-2-phenyl-2-[(1′*R*,4′*R*)-(1′,7′,7′-trimethylbicyclo[2.2.1]hept-2′-en-2′-yl)sulfanyl]ethanol* (**11**), *(1*R*)-1-phenyl-2-[(1′*R*,4′*R*)-(1′,7′,7′-trimethylbicyclo[2.2.1]hept-2′-en-2′-yl)sulfanyl]ethanol* (**12**), and *(1*R*,2*R*,4*R*,5′*R*)-1,7,7-trimethyl-5′-phenylspiro[bicyclo[2.2.1]heptane-2,2′-[1,3]oxathiolane]* (**13**). In addition, the starting material **1** was partly recovered when SiO_2 was used as a catalyst at 0° (*Scheme 4*; for yields see *Table 3*).

Data of **8**: Colorless oil. $[\alpha]_D^{23} = -119.0$. IR: 3080*w*, 3058*w*, 3020*m*, 2980*s*, 2950*s*, 2865*s*, 1600*m*, 1583*w*, 1490*m*, 1472*m*, 1450*s*, 1388*s*, 1369*m*, 1350*w*, 1304*m*, 1272*m*, 1250*m*, 1191*m*, 1150*w*, 1111*m*, 1078*s*, 1040*m*, 1025*m*, 1015*m*, 1000*w*, 985*w*, 958*m*, 935*m*, 911*w*, 880*m*, 860*w*, 810*m*, 795*w*, 758*m*, 724*w*, 700*s*. ^{1}H-NMR (600 MHz, C_6D_6): 7.31 (*d*-like, $J = 7.2$, H–C(2″), H–C(6″)); 7.10 (*t*-like, $J \approx 7.7$, H–C(3″), H–C(5″)); 7.02 (*t*-like, $J \approx 7.3$, H–C(4″)); 4.36 (*dd*, $J = 5.8, 2.8$, H–C(4′)); 4.01 (*dd*, $J = 9.4, 2.8$, 1 H–C(5′)); 3.77 (*dd*, $J = 9.4, 5.9$, 1 H–C(5′)); 2.54 (*ddd*, $J = 13.7, 7.8, 3.2$, H_{exo}–C(3)); 2.47 (*ddd*, $J = 12.8, 9.3, 3.6$, H_{endo}–C(6)); 1.79 (*d*, $J = 13.7$, H_{endo}–C(3)); 1.69–1.63 (*m*, H_{exo}–C(5), H–C(4)); 1.52–1.47 (*m*, H_{exo}–C(6)); 1.32–1.28 (*m*, H_{endo}–C(5)); 1.16 (*s*, Me–C(1)); 1.03 (*s*, Me_{syn}); 0.78 (*s*, Me_{anti}). ^{13}C-NMR (150.9 MHz, C_6D_6): 143.6 (*s*, C(1″)); 129.0 (*d*, C(3″), C(5″)); 128.2 (*d*, C(2″), C(6″)); 127.5 (*d*, C(4″)); 106.1 (*s*, C(2)); 75.8 (*t*, C(5′)); 54.9 (*s*, C(1)); 54.0 (*d*, C(4′)); 51.0 (*t*, C(3)); 49.0 (*s*, C(7)); 47.0 (*d*, C(4)); 31.2 (*t*, C(6)); 28.0 (*t*, C(5)); 21.6 (*q*, Me_{syn}); 20.6 (*q*, Me_{anti}); 14.9 (*q*, Me–C(1)). CI-MS (NH_3): 290 (21), 289 (100, $[M+H]^+$), 202 (11), 170 (42), 104 (12). Anal. calc. for $C_{18}H_{24}OS$ (288.45): C 74.95, H 8.39, S 11.12; found: C 74.87, H 8.13, S 10.88.

Data of **9**: Colorless crystals. M.p. 79.4–79.7°. $[\alpha]_D^{23} = +86.5$. IR (KBr): 3060*w*, 3031*w*, 3012*w*, 2985*m*, 2956*s*, 2884*m*, 2886*s*, 1616*w*, 1602*w*, 1540*w*, 1498*w*, 1490*w*, 1480*m*, 1456*s*, 1387*m*, 1370*m*, 1351*w*, 1342*w*, 1304*w*, 1277*w*, 1246*w*, 1156*w*, 1137*w*, 1112*w*, 1082*s*, 1057*w*, 1042*s*, 1011*m*, 990*w*, 953*m*, 937*m*, 913*w*, 871*m*, 836*m*, 807*m*, 772*m*, 757*m*, 735*w*, 701*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.42–7.40 (*m*, H–C(2″), H–C(6″)); 7.32–7.29 (*m*, H–C(3″), H–C(5″)); 7.24–7.21 (*m*, H–C(4″)); 4.49 (*dd*, $J = 6.0, 3.9$, H–C(4′)); 4.28 (*dd*, $J = 9.4, 6.1$, 1 H–C(5′)); 4.18 (*dd*, $J = 9.4, 3.9$, 1 H–C(5′)); 2.45 (*ddd*, $J = 13.4, 4.4, 3.3$, H_{exo}–C(3)); 2.03 (*d*, $J = 13.4$, H_{endo}–C(3)); 1.82 (*t*, $J = 4.5$, H–C(4)); 1.77–1.72 (*m*, H_{exo}–C(5)); 1.62–1.54 (*m*, 2 H–C(6)); 1.27–1.22 (*m*, H_{endo}–C(5)); 1.08 (2*s*, Me_{syn}, Me–C(1)); 0.91 (*s*, Me_{anti}). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 142.5 (*s*, C(1″)); 128.7 (*d*, C(3″), C(5″)); 127.8 (*d*, C(2″), C(6″)); 127.3 (*d*, C(4″)); 107.6 (*s*, C(2)); 77.1 (*t*, C(5′)); 54.2 (*s*, C(1)); 51.2 (*t*, C(3)); 51.1 (*d*, C(4′)); 48.6 (*s*, C(7)); 46.0 (*d*, C(4)); 34.9 (*t*, C(6)); 27.2 (*t*, C(5)); 21.2 (*q*, Me_{anti}); 20.9 (*q*, Me_{syn}); 10.7 (*q*, Me–C(1)). CI-MS (NH_3): 290 (6), 289 (78, $[M+H]^+$), 256 (9), 202 (8), 171 (11), 170 (100), 164 (49), 104 (9). Anal. calc. for $C_{18}H_{24}OS$ (288.45): C 74.95, H 8.39, S 11.12; found: C 75.08, H 8.15, S 10.94.

Crystals of **9** suitable for the X-ray crystal-structure determination were grown from Et_2O/MeOH.

Data of **10**: Colorless oil. $[\alpha]_D^{22} = +69.4$. IR: 3385*m* (br., OH), 3062*w*, 3029*w*, 2982*m*, 2953*s*, 2871*s*, 1601*w*, 1582*w*, 1561*w*, 1493*m*, 1470*m*, 1453*s*, 1386*m*, 1375*m*, 1365*m*, 1290*w*, 1279*w*, 1253*w*, 1202*w*, 1184*w*, 1134*w*, 1106*w*, 1075*m*, 1054*s*, 1018*m*, 981*m*, 906*w*, 875*w*, 820*w*, 783*w*, 757*w*, 737*w*, 715*w*, 698*s*. ^{1}H-NMR: 7.35–7.18 (*m*, 5 arom. H); 5.58 (*d*, $J = 3.4$, H–C(3′)); 4.11 (*t*, $J = 6.6$, H–C(2)); 3.85–3.79 (br. *s*, 2 H–C(1)); 2.24 (*t*, $J = 3.5$, H–C(4′)); 1.81–1.74 (*m*, OH, H_{exo}–C(5′)); 1.47–1.39 (*m*, H_{exo}–C(6′)); 1.05–0.89 (*m*, H_{endo}–C(5′), H_{endo}–C(6′)); 0.94 (*s*, Me–C(1)); 0.69 (*s*, Me_{syn}); 0.67 (*s*, Me_{anti}). ^{13}C-NMR: 142.0 (*s*, C(1″)); 139.0 (*s*, C(2′)); 128.7 (*d*, C(3″), C(5″)); 128.5 (*d*, C(4″)); 128.0 (*d*, C(2″), C(6″)); 127.7 (*d*, C(3′)); 65.8 (*t*, C(1)); 56.9 (*s*, C(1′)); 56.0 (*s*, C(7′)); 52.2 (*d*, C(2)); 52.1 (*d*, C(4′)); 31.5 (*t*, C(6′)); 26.3 (*t*, C(5′)); 19.6 (*q*, Me_{anti}); 19.4 (*q*, Me_{syn}); 11.4 (*q*, Me–C(1′)). CI-MS (NH_3): 290 (20), 289 (100, $[M+H]^+$), 170 (8), 169 (14).

Data of **11**: Colorless oil. $[\alpha]_D^{22} = -185.2$. IR: 3377*m* (br., OH), 3062*w*, 3029*w*, 2985*m*, 2953*s*, 2870*s*, 1601*w*, 1584*w*, 1561*m*, 1492*m*, 1471*m*, 1452*s*, 1386*s*, 1374*m*, 1365*m*, 1297*m*, 1253*w*, 1205*w*, 1185*w*, 1134*w*, 1106*w*, 1056*s*, 1019*m*, 981*m*, 933*w*, 906*w*, 875*w*, 821*w*, 784*w*, 757*w*, 737*w*, 716*w*, 698*s*. ^{1}H-NMR: 7.38–7.22 (*m*, 5 arom. H); 5.61 (*d*, $J = 3.4$, H–C(3′)); 4.24 (*t*, $J = 6.7$, H–C(2)); 3.92 (*t*, $J = 6.5$, 2 H–C(1)); 2.28 (*t*, $J = 3.5$, 1 H–C(4′)); 1.85 (*t*, $J = 6.6$, OH); 1.79–1.70 (*m*, H_{exo}–C(5′)); 1.41 (*ddd*, $J = 12.1, 8.6, 3.3$, H_{exo}–C(6′)); 1.00 (*s*, Me–C(1)); 0.91–0.68 (*m*, H_{endo}–C(5′), H_{endo}–C(6′)); 0.78 (*s*, Me_{syn}); 0.74 (*s*, Me_{anti}). ^{13}C-NMR: 141.4 (*s*, C(1″)); 139.1 (*s*, C(2′)); 128.5 (*d*, C(3″), C(5″)); 128.2 (*d*, C(4″)); 127.9 (*d*, C(2″), C(6″)); 127.5 (*d*, C(3′)); 65.9 (*t*, C(1)); 56.6 (*s*, C(1′)); 55.8 (*s*, C(7′)); 52.5 (*d*, C(2)); 52.1 (*d*, C(4′)); 31.1 (*t*, C(6′)); 26.0 (*t*, C(5′)); 19.5 (*q*, Me_{anti}); 19.3 (*q*, Me_{syn}); 11.2 (*q*, Me–C(1′)). CI-MS (NH_3): 291 (7), 290 (20), 289 (100, $[M+H]^+$), 169 (18). Anal. calc. for $C_{18}H_{24}OS$ (288.45): C 74.95, H 8.39, S 11.12; found: C 74.79, H 8.26, S 11.03.

Data of **12**: Colorless oil. $[\alpha]_D^{22} = -1.0$. IR: 3407*m* (br., OH), 3063*w*, 3028*w*, 2982*m*, 2953*s*, 2871*m*, 1561*w*, 1495*w*, 1472*w*, 1455*m*, 1386*m*, 1373*w*, 1365*w*, 1298*w*, 1189*w*, 1133*w*, 1106*w*, 1080*w*, 1054*m*, 1046*m*, 1027*m*, 983*m*, 908*w*, 875*w*, 820*w*, 777*w*, 754*w*, 713*w*, 698*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.39–7.35 (*m*, 4 arom. H); 7.31–7.28 (*m*,

1 arom. H); 5.69 (*d*, *J* = 3.4, H–C(3′)); 4.76 (*dd*, *J* = 9.6, 1.7, 1 H–C(1)); 3.08 (*dd*, *J* = 13.7, 3.2, 1 H–C(2)); 2.85 (*dd*, *J* = 13.7, 9.7, 1 H–C(2)); 2.68 (br. *s*, OH); 2.39 (*t*, *J* = 3.4, H–C(4′)); 1.92–1.89 (*m*, H_{exo}–C(5′)); 1.55–1.51 (*m*, H_{exo}–C(6′)); 1.09–1.01 (*m*, H_{endo}–C(5′), H_{endo}–C(6′)); 1.04 (*s*, Me–C(1)); 0.84 (*s*, Me_{syn}); 0.80 (*s*, Me_{anti}). ^{13}C-NMR (105.9 MHz, $CDCl_3$): 142.5 (*s*, C(1″)); 142.3 (*s*, C(2′)); 128.6 (*d*, C(3″), C(5″)); 127.9 (*d*, C(4″)); 127.2 (*d*, C(3′)); 125.8 (*d*, C(2″), C(6″)); 71.3 (*d*, C(1)); 56.8 (*s*, C(1′)); 56.0 (*s*, C(7′)); 52.2 (*d*, C(4′)); 40.9 (*t*, C(2)); 31.5 (*t*, C(6′)); 26.5 (*t*, C(5′)); 19.7 (*q*, Me_{anti}); 19.5 (*q*, Me_{syn}); 11.4 (*q*, Me–C(1′)). CI-MS (NH_3): 291 (6), 290 (20), 289 (100, $[M+H]^+$), 171 (13).

Data of **13**: Colorless oil. $[\alpha]_D^{22} = -116.7$. IR: 3088*w*, 3066*w*, 3031*w*, 2984*s*, 2952*s*, 2928*s*, 2873*m*, 1607*w*, 1498*w*, 1477*w*, 1454*s*, 1433*w*, 1390*m*, 1371*m*, 1320*w*, 1305*w*, 1273*w*, 1251*w*, 1211*w*, 1193*m*, 1143*w*, 1113*m*, 1082*s*, 1070*s*, 1049*m*, 1029*m*, 997*w*, 960*w*, 936*w*, 919*w*, 888*w*, 832*w*, 806*w*, 765*m*, 742*m*, 697*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.40–7.39 (*m*, H–C(2″), H–C(6″)); 7.36–7.34 (*m*, H–C(3″), H–C(5″)); 7.31–7.28 (*m*, H–C(4″)); 4.86 (*dd*, *J* = 10.5, 4.5, H–C(5′)); 3.22 (*dd*, *J* = 10.2, 4.5, 1 H–C(4′)); 2.70 (*t*, *J* = 10.4, 1 H–C(4′)); 2.45 (*ddd*, *J* = 13.8, 4.7, 3.0, H_{exo}–C(3)); 2.26 (*ddd*, *J* = 13.0, 9.3, 3.8, H_{endo}–C(6)); 1.82 (*d*, *J* = 13.8, H_{endo}–C(3)); 1.77 (*t*, *J* = 4.7, H–C(4)); 1.74–1.68 (*m*, H_{exo}–C(5)); 1.53–1.48 (*m*, H_{exo}–C(6)); 1.26 (*ddd*, *J* = 12.3, 9.4, 4.8, H_{endo}–C(5)); 1.04 (*s*, Me–C(1)); 0.98 (*s*, Me_{syn}); 0.91 (*s*, Me_{anti}). ^{13}C-NMR (105.9 MHz, $CDCl_3$): 139.9 (*s*, C(1″)); 128.5 (*d*, C(3″), C(5″)); 127.9 (*d*, C(4″)); 126.0 (*d*, C(2″), C(6″)); 102.9 (*s*, C(2)); 82.1 (*d*, C(5′)); 54.3 (*s*, C(1)); 50.8 (*t*, C(3)); 48.2 (*s*, C(7)); 46.6 (*d*, C(4)); 41.7 (*t*, C(4′)); 30.4 (*t*, C(6)); 27.0 (*t*, C(5)); 21.0 (*q*, Me_{syn}); 20.2 (*q*, Me_{anti}); 12.6 (*q*, Me–C(1)). CI-MS (NH_3): 289 (37, $[M+H]^+$), 171 (12), 170 (100). Anal. calc. for $C_{18}H_{24}OS$ (288.45): C 74.95, H 8.39, S 11.12; found: C 74.72, H 8.08, S 11.41.

Isomerization of **10** *to* **8**, *of* **11** *to* **9**, *and of* **12** *to* **13**. Treatment of **10** (21 mg, 0.07 mmol) with 1 drop of conc. HCl in CH_2Cl_2 (10 ml) at r.t. (2 min, prep. TLC (hexane/CH_2Cl_2 4:1)) yielded 18 mg (86%) of **8**. Irradiation of **11** (13 mg, 0.045 mmol) in $CDCl_3$ (1 ml) with sunlight at r.t. (2 h, prep. TLC (hexane/CH_2Cl_2 4:1)) gave 10 mg (77%) of **9**. Treatment of **12** (30 mg, 0.10 mmol) with 2 drops of conc. HCl in Et_2O (15 ml) at r.t. (1.5 h, prep. TLC (hexane/CH_2Cl_2 20:1)) yielded 15 mg (50%) of **13** (*Scheme 5*).

Epimerization of **8** *to* **14**, *and of* **9** *to* **15**. Treatment of **8** (82 mg, 0.28 mmol) with 7 drops of conc. HCl in CH_2Cl_2 (10 ml) at r.t. (42 h, PLC (hexane/CH_2Cl_2 15:1)) yielded 55 mg (67%) of *(1*R*,2*S*,4*R*,4′*S*)-1,7,7-trimethyl-4′-phenylspiro[bicyclo[2.2.1]heptane-2,2′-[1,3]oxathiolane]* (**14**), and 17 mg (21%) of the starting material **8** was recovered. An analogous epimerization of **9** (143 mg, 0.50 mmol) in $CDCl_3$ (5 ml) by irradiation with sunlight at r.t. (5 h, prep. HPLC (chiral phase, hexane)) gave 60 mg (42%) of *(1*R*,2*R*,4*R*,4′*R*)-1,7,7-trimethyl-4′-phenylspiro[bicyclo[2.2.1]heptane-2,2′-[1,3]oxathiolane]* (**15**), and 46 mg (32%) of the starting material **9** was recovered (*Scheme 6*).

Data of **14**: Colorless oil. $[\alpha]_D^{22} = -43.2$. IR: 3080*w*, 3060*w*, 3025*m*, 2950*s*, 2930*s*, 2880*s*, 1600*m*, 1490*m*, 1480*m*, 1450*s*, 1388*s*, 1370*m*, 1355*w*, 1330*w*, 1305*m*, 1293*w*, 1278*w*, 1245*w*, 1205*w*, 1195*w*, 1160*w*, 1140*w*, 1110*m*, 1085*s*, 1050*s*, 1025*m*, 1015*m*, 1000*m*, 955*m*, 945*m*, 915*w*, 874*m*, 860*w*, 838*m*, 805*m*, 760*s*, 736*w*, 699*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.45–7.43 (*m*, H–C(2″), H–C(6″)); 7.35–7.31 (*m*, H–C(3″), H–C(5″)); 7.28–7.24 (*m*, H–C(4″)); 4.51 (*dd*, *J* = 8.6, 6.2, H–C(4′)); 4.39 (*dd*, *J* = 9.4, 6.2, 1 H–C(5′)); 3.89 (*t*-like, *J* ≈ 9.0, 1 H–C(5′)); 2.52 (*ddd*, *J* = 13.4, 4.5, 3.2, H_{exo}–C(3)); 2.20 (*d*, *J* = 13.4, H_{endo}–C(3)); 1.85 (*t*, *J* = 4.5, H–C(4)); 1.80–1.73 (*m*, H_{exo}–C(5)); 1.65–1.55 (*m*, 2 H–C(6)); 1.30–1.25 (*m*, H_{endo}–C(5)); 1.07 (*s*, Me_{syn}); 0.99 (*s*, Me–C(1)); 0.91 (*s*, Me_{anti}). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 139.4 (*s*, C(1″)); 128.5 (*d*, C(3″), C(5″)); 128.0 (*d*, C(2″), C(6″)); 127.4 (*d*, C(4″)); 107.4 (*s*, C(2)); 77.3 (*t*, C(5′)); 54.0 (*s*, C(1)); 52.6 (*d*, C(4′)); 51.7 (*t*, C(3)); 48.3 (*s*, C(7)); 45.9 (*d*, C(4)); 34.7 (*t*, C(6)); 27.1 (*t*, C(5)); 21.1 (*q*, Me_{anti}); 20.7 (*q*, Me_{syn}); 10.1 (*q*, Me–C(1)). CI-MS (NH_3): 290 (7), 289 (35, $[M+H]^+$), 202 (16), 171 (11), 170 (100), 104 (8). Anal. calc. for $C_{18}H_{24}OS$ (288.45): C 74.95, H 8.39, S 11.12; found: C 74.84, H 8.21, S 11.15.

Data of **15**: Colorless crystals. M.p. 43.5–45.0°. $[\alpha]_D^{22} = +29.6$. IR: 3085*w*, 3063*w*, 3029*m*, 2985*s*, 2954*s*, 2870*s*, 1601*m*, 1493*m*, 1477*m*, 1452*s*, 1390*s*, 1372*m*, 1331*w*, 1305*m*, 1273*m*, 1249*w*, 1205*m*, 1193*m*, 1164*w*, 1113*m*, 1084*s*, 1051*m*, 1037*m*, 1019*m*, 1002*m*, 976*m*, 956*m*, 936*m*, 913*w*, 881*m*, 861*m*, 820*m*, 808*m*, 759*s*, 698*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.42–7.41 (*m*, H–C(2″), H–C(6″)); 7.32–7.29 (*m*, H–C(3″), H–C(5″)); 7.25–7.22 (*m*, H–C(4″)); 4.46 (*dd*, *J* = 9.3, 5.8, H–C(4′)); 4.33 (*dd*, *J* = 9.2, 5.8, 1 H–C(5′)); 3.68 (*t*, *J* = 9.3, 1 H–C(5′)); 2.61 (*ddd*, *J* = 13.8, 4.6, 3.1, H_{exo}–C(3)); 2.13 (*ddd*, *J* = 13.0, 9.3, 3.7, H_{endo}–C(6)); 1.86 (*d*, *J* = 13.8, H_{endo}–C(3)); 1.79 (*t*, *J* = 4.7, H–C(4)); 1.74–1.70 (*m*, H_{exo}–C(5)); 1.51–1.45 (*m*, H_{exo}–C(6)); 1.29–1.25 (*m*, H_{endo}–C(5)); 1.02 (*s*, Me–C(1)); 0.96 (*s*, Me_{syn}); 0.90 (*s*, Me_{anti}). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 138.4 (*s*, C(1″)); 128.8 (*d*, C(3″), C(5″)); 128.4 (*d*, C(2″), C(6″)); 127.7 (*d*, C(4″)); 105.6 (*s*, C(2)); 76.1 (*t*, C(5′)); 55.0 (*d*, C(4′)); 54.6 (*s*, C(1)); 51.0 (*t*, C(3)); 48.6 (*s*, C(7)); 46.5 (*d*, C(4)); 30.0 (*t*, C(6)); 27.3 (*t*, C(5)); 21.2 (*q*, Me_{syn}); 20.4 (*q*, Me_{anti}); 13.3 (*q*, Me–C(1)). CI-MS (NH_3): 290 (6), 289 (26, $[M+H]^+$), 171 (12), 170 (100), 104 (7). Anal. calc. for $C_{18}H_{24}OS$ (288.45): C 74.95, H 8.39, S 11.12; found: C 75.10, H 8.22, S 11.04.

Crystals of **15** suitable for X-ray crystal-structure determination were grown from EtOH.

6. *X-Ray Crystal-Structure Determination of* **9** *and* **15** (*Table 4*, and *Figs. 1* and *2*)[2]). All measurements were performed on a *Nonius KappaCCD* diffractometer [9] with graphite-monochromated MoK_α radiation ($\lambda =$ 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler. The data collection and refinement parameters are given in *Table 4*, and views of the molecules are shown in *Figs. 1 and 2*. Data reduction was performed with *HKL Denzo* and *Scalepack* [10]. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. The structures were solved by direct methods with SIR92 [11], which revealed the positions of all non-H-atoms. There are three symmetry-independent molecules in the asymmetric unit of **15**. The atomic coordinates of the molecules were tested carefully for a relationship from a higher-symmetry space group with the program PLATON [12], but none could be found. All are of the same stereoisomer, and molecules B and C have almost identical conformations. Molecule A differs slightly by a twist of *ca.* 18° in the orientation of the Ph ring with respect to its orientation in molecules B and C. The non-H-atoms of each structure were refined anisotropically. All of the H-atoms were placed in geometrically idealized positions, and each was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.2 U_{eq} for the Me

Table 4. *Crystallographic Data of Compounds* **9** *and* **15**

		9	**15**
Crystallized from		Et_2O/MeOH	EtOH
Empirical formula		$C_{18}H_{24}OS$	$C_{18}H_{24}OS$
Formula weight [g mol^{-1}]		288.45	288.45
Crystal color, habit		colorless, needle	colorless, prism
Crystal dimensions [mm]		$0.10 \times 0.12 \times 0.28$	$0.25 \times 0.28 \times 0.32$
Temp. [K]		160(1)	160(1)
Crystal system		orthorhombic	orthorhombic
Space group		$P2_12_12_1$	$P2_12_12_1$
Z		4	12
Reflections for cell determination		2597	6085
2θ Range for cell determination [°]		4 – 60	4 – 55
Unit cell parameters	a [Å]	7.4031(1)	11.1418(1)
	b [Å]	10.0944(1)	15.8380(2)
	c [Å]	20.6428(3)	27.0675(3)
	V [Å^3]	1542.63(3)	4776.43(9)
D_X [g cm^{-3}]		1.242	1.203
μ (MoK_α) [mm^{-1}]		0.204	0.198
$2\theta_{max}$ [°]		60	55
Scan type		ϕ and ω	ϕ and ω
Total reflections measured		37157	61270
Symmetry-independent reflections		4501	10952
Reflections with $I > 2\sigma(I)$		3640	7086
Parameters refined		183	551
R [on F; $I > 2\sigma(I)$ reflections]		0.0407	0.0449
wR		0.0353[a])	0.0846[b])
Goodness-of-fit		1.547	0.969
Secondary extinction coefficient		$1.3(2) \times 10^{-6}$	$1.4(2) \times 10^{-3}$
Final Δ_{max}/σ		0.0003	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]		0.31; −0.33	0.34; −0.25

[a]) $wR(F)$ $(w = [\sigma^2(F_o) + (0.01F_o)^2]^{-1}$, $I > 2\sigma(I)$ reflections). [b]) $wR(F^2)$ $(w = [\sigma^2(F_o^2) + (0.0258P)^2]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$, all independent reflections).

[2]) CCDC-203514 and -203515 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44-(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

groups in **15**). Refinement of the structure was carried out on F (for **9**) and F^2 (for **15**) by full-matrix least-squares procedures, which minimized the function $\Sigma w(|F_o|-|F_c|)^2$ and $\Sigma w(F_o^2-F_c^2)^2$, resp. A correction for secondary extinction was applied in each case. Refinement of the absolute structure parameter [13] yielded values of 0.01(5) and −0.03(4), resp., which confidently confirms that the refined coordinates represent the true enantiomorph. Neutral-atom-scattering factors for non-H-atoms were taken from [14a], and the scattering factors for H-atoms were taken from [15]. Anomalous dispersion effects were included in F_c [16]; the values for f' and f'' were those of [14b]. The values of the mass attenuation coefficients are those of [14c]. All calculations for **9** were performed with the teXsan crystallographic software package [17], and those for **15** employed SHELXL97 [18].

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