Regioselectivity of the 1,3-Oxathiolane Formation in the *Lewis* Acid-Catalyzed Reaction of Thioketones with Asymmetrically Substituted Oxiranes

by **Changchun Fu**[1]), **Anthony Linden**, and **Heinz Heimgartner***

Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

Dedicated to Professor *André M. Braun* on the occasion of his 60th birthday

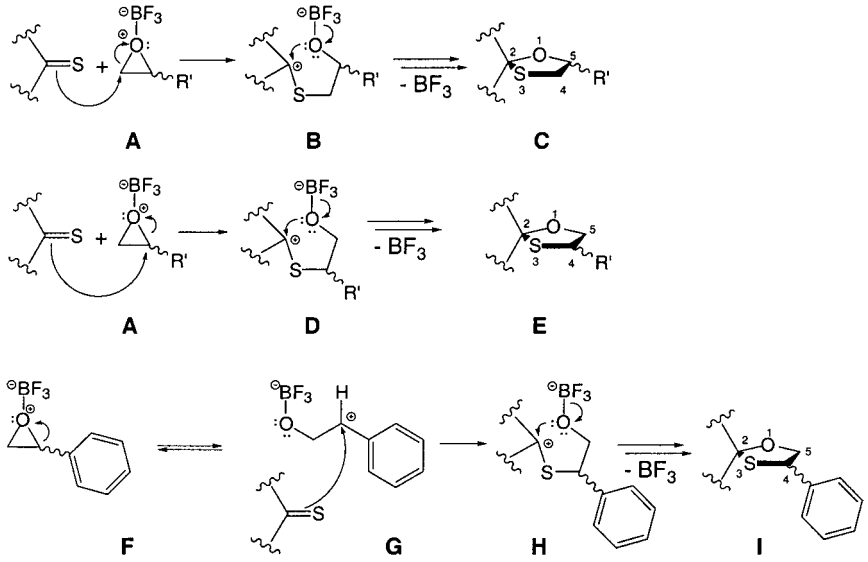
The reactions of the aromatic thioketone 4,4′-dimethoxythiobenzophenone (**1**) with three monosubstituted oxiranes **3a**–**c** in the presence of $BF_3 \cdot Et_2O$ or $SnCl_4$ in dry CH_2Cl_2 led to the corresponding 1:1 adducts, *i.e.*, 1,3-oxathiolanes **4a**–**b** with R at C(5) and **8c** with Ph at C(4). In addition, 1,3-dioxolanes **7a** and **7c**, and the unexpected 1:2 adducts **6a**–**b** were obtained (*Scheme 2* and *Table 1*). In the case of the aliphatic, nonenolizable thioketone 1,1,3,3-tetramethylindane-2-thione (**2**) and **3a**–**c** with $BF_3 \cdot Et_2O$ as catalyst, only 1:1 adducts, *i.e.* 1,3-oxathiolanes **10a**–**b** with R at C(5) and **11a**–**c** with R or Ph at C(4), were formed (*Scheme 6* and *Table 2*). In control experiments, the 1:1 adducts **4a** and **4b** were treated with 2-methyloxirane (**3a**) in the presence of $BF_3 \cdot Et_2O$ to yield the 1:2 adduct **6a** and 1:1:1 adduct **9**, respectively (*Scheme 5*). The structures of **6a**, **8c**, **10a**, **11a**, and **11c** were confirmed by X-ray crystallography (*Figs. 1–5*). The results described in the present paper show that alkyl and aryl substituents have significant influence upon the regioselectivity in the process of the ring opening of the complexed oxirane by the nucleophilic attack of the thiocarbonyl S-atom: the preferred nucleophilic attack occurs at C(3) of alkyl-substituted oxiranes (O–C(3) cleavage) but at C(2) of phenyloxirane (O–C(2) cleavage).

1. Introduction. – 1,3-Oxathiolanes are easily prepared *via* the *Lewis* acid catalyzed reaction of oxiranes with thioketones. This direct formation of 1,3-oxathiolanes is favorable, because oxiranes as well as thiocarbonyl derivatives are easily accessible. In our recent publications, the reactions of 1,3-thiazole-5(4*H*)-thiones [1][2], trithiocarbonates [3], aromatic thioketones, and nonenolizable aliphatic thioketones [4][5] with mono- and disubstituted oxiranes were described as a new access to 1,3-oxathiolanes. Different regioselectivities were observed in the reactions of 1,3-thiazole-5(4*H*)-thiones and trithiocarbonates with alkyl- and aryl-oxiranes, respectively.

For the *Lewis* acid catalyzed addition of oxiranes to C=S bonds to form 1,3-oxathiolanes, the following mechanisms were proposed (*Scheme 1*): the O-atom of the oxirane forms a complex with the *Lewis* acid (*e.g.*, BF_3), whereby positive charges at the two C-atoms of the oxirane develop. This facilitates the nucleophilic attack by the thiocarbonyl S-atom. The oxirane complex **A** reacts with the C=S bond *via* an S_N2-type process to form **B** and **D**, whereby the preferred attack occurs at C(3) of the oxirane because of steric factors, *i.e.*, **B** is favorably formed. The cyclizations of **B** or **D**, and subsequent release of the *Lewis* acid lead to the 5-alkyl derivative **C** as the major and the 4-alkyl derivative **E** as the minor products. In contrast, the Ph group in the oxirane

[1]) Diploma thesis of *C. F.*, Universität Zürich, 2001.

Scheme 1



complex **F** favors a primary ring opening to yield **G**, which is attacked by the thiocarbonyl S-atom. The mechanism for the formation of **H** and, therefore, of **I** corresponds to an S_N1-type reaction due to the stabilization of the positive charge by π-conjugation. According to the postulated mechanism, the stability of the intermediates **B**, **D**, and **H** might determine the rate of the reactions, *i.e.*, the more easily the intermediates are formed, the faster the reactions would proceed.

To obtain more insight into the regioselectivity of the ring opening of oxiranes in the formation of 1,3-oxathiolanes and, in particular, to establish the influence of alkyl and aryl substituents, reactions of asymmetrical Me-, Bu-, and Ph-substituted oxiranes with nonenolizable thioketones were carried out. In the present paper, the results of the reactions with 4,4′-dimethoxythiobenzophenone (**1**) and 1,1,3,3-tetramethylindane-2-thione (**2**) are described.

2. Results. – 2.1. *Reactions of 4,4′-Dimethoxythiobenzophenone* (**1**) *with Oxiranes.* On dropping 5 equiv. of 2-methyloxirane (**3a**) into a solution of **1** and 1.1 equiv. $BF_3 \cdot Et_2O$ in dry CH_2Cl_2 at $-78°$ under N_2, the violet solution turned rapidly to light yellow. After 1 min, the reaction was quenched with H_2O. Chromatographic separation gave 1:1 adduct **4a** and 4,4′-dimethoxybenzophenone (**5**) in 27 and 68% yield, respectively, as well as an unexpected 1:2 adduct **6a** in 2% yield. The reaction was repeated at $-90°$ and 0°, whereby **4a**, **5**, and **6a** were obtained in 17, 62, and 10%, and in 1, 80, and 1% yields, respectively. In addition, a second unusual product **7a** was isolated in 14% yield from the reaction performed at 0° (*Scheme 2* and *Table 1*).

The structures of **4a** and **7a** were assigned by means of elemental analyses, MS, ^{1}H- and ^{13}C-NMR spectra, and by comparison with the analogues described previously [1–5]. The novel product **6a** corresponds to a 1:2 adduct, a 1,3-dioxa-6-thiacyclooctane on the basis of elemental analysis, and CI- and ESI-MS spectra. The NMR

Scheme 2

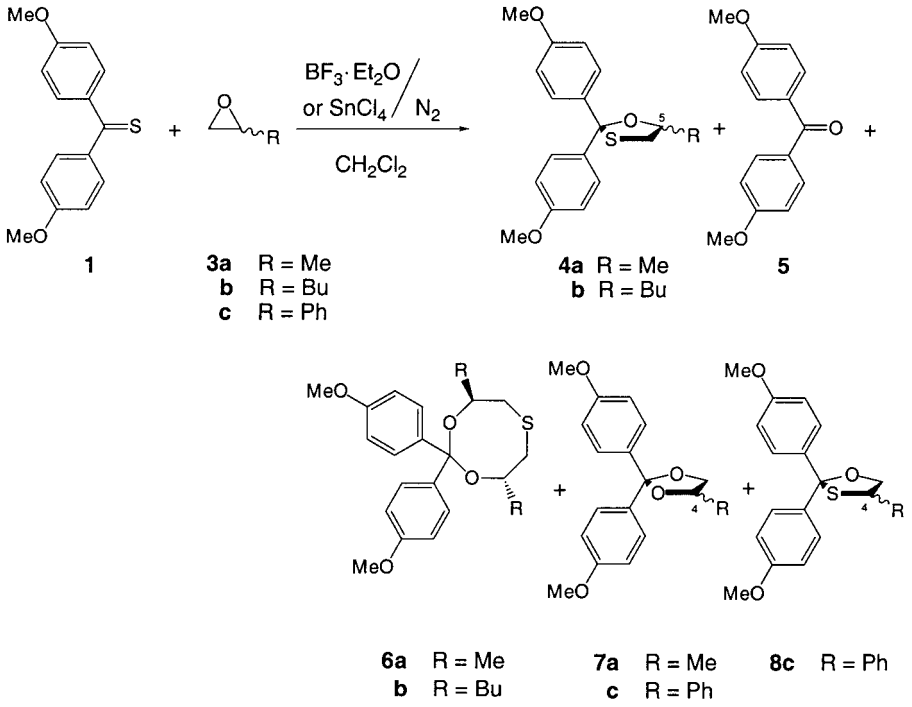


Table 1. *BF_3- and $SnCl_4$-Catalyzed Reactions of* **1** *with* **3** *in CH_2Cl_2*

	3	R	Temp. [°]	Yields [%] of Products				
				4	**5**	**6**	**7**	**8**
$BF_3 \cdot Et_2O$	**a**	Me	−90	17	62	10	–	–
			−78	27	68	2	–	–
			0	1	80	1	14	–
	b	Bu	−90	4	84	7	–	–
			−78	22	74	3	–	–
	c	Ph	−78	–	76	–	10	13
$SnCl_4$	**a**	Me	−78	52	26	1	–	–
	b	Bu	−78	25	42	3	–	–
	c	Ph	−78	–	27	–	–	71

data are in agreement with the structure of the eight-membered ring of type **6**; the ^{1}H- and ^{13}C-NMR spectra indicate a symmetric molecule. The compound shows an uncommon broad signal in the ^{1}H-NMR spectrum for the H-atoms of the Ph group between 7.80–7.40 ppm and a *d* ($J = 8.5$ Hz) at 6.76 ppm. For the two MeO groups only one *s* appears at 3.29 ppm. The ^{13}C-NMR spectrum shows 2 *s* at 159.4 and 136.1 ppm, 1 br. *d* at 129.0 ppm and 1 *d* at 113.3 ppm for two Ph groups, as well as only 1 *q* at 54.6 ppm for two MeO. All these data indicate a symmetric molecule. Apart from that, one fine-structured *m* for two C*H*(Me)O appears at *ca.* 4.0 ppm in the ^{1}H-NMR spectrum, while the protons of two CH_2S groups absorb as 2 *dd* at 2.74 and 2.46 ppm. The latter signals present the typical values of geminal coupling (14.6 Hz), and *cis*- and *trans*-coupling (3.0 and 5.5 Hz) in eight-membered rings. The signal intensities of C*H*(Me)O and MeO are in a ratio of 1:3. The structure of **6a** has been confirmed by X-ray crystal-structure analysis (see *Fig. 1*).

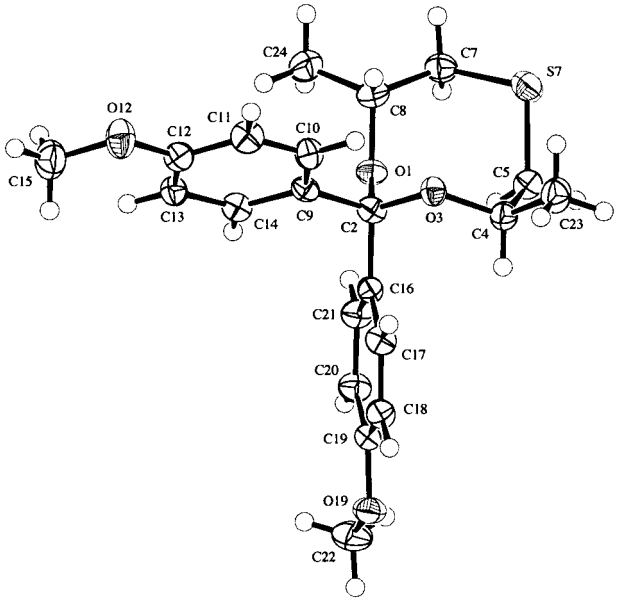


Fig. 1. *ORTEP Plot* [6] *of one of the two symmetry-independent molecules of* **6a** (arbitrary numbering of the atoms; 50% probability ellipsoids)

It is worth mentioning how the most important ions in the CI-MS, and the ions $[M+\mathrm{MeOH}+\mathrm{Na}]^+$, $[M+\mathrm{K}]^+$, and $[M+\mathrm{Na}]^+$ in the ESI-MS spectra of **6a** could be formed (*Scheme 3*).

Analogously, the $BF_3 \cdot Et_2O$-catalyzed reaction of **1** with **3b** at $-78°$ led to **4b**, **5**, and **6b** in 22, 74, and 3% yields, respectively. In the ^{1}H-NMR spectrum, the 1:2 adduct **6b** also shows signals for the CH_2S group with typical values of geminal coupling (14.6 Hz), and *cis*- and *trans*-coupling (3.2 and 5.3 Hz) in eight-membered rings. In the ESI-MS the most important peaks appear at *m/z* 513 ($[M+\mathrm{MeOH}+\mathrm{Na}]^+$), 481 ($[M+\mathrm{Na}]^+$), and 497 ($[M+\mathrm{K}]^+$). When the same reaction was performed at $-90°$, the yield of **6b** increased to 7%.

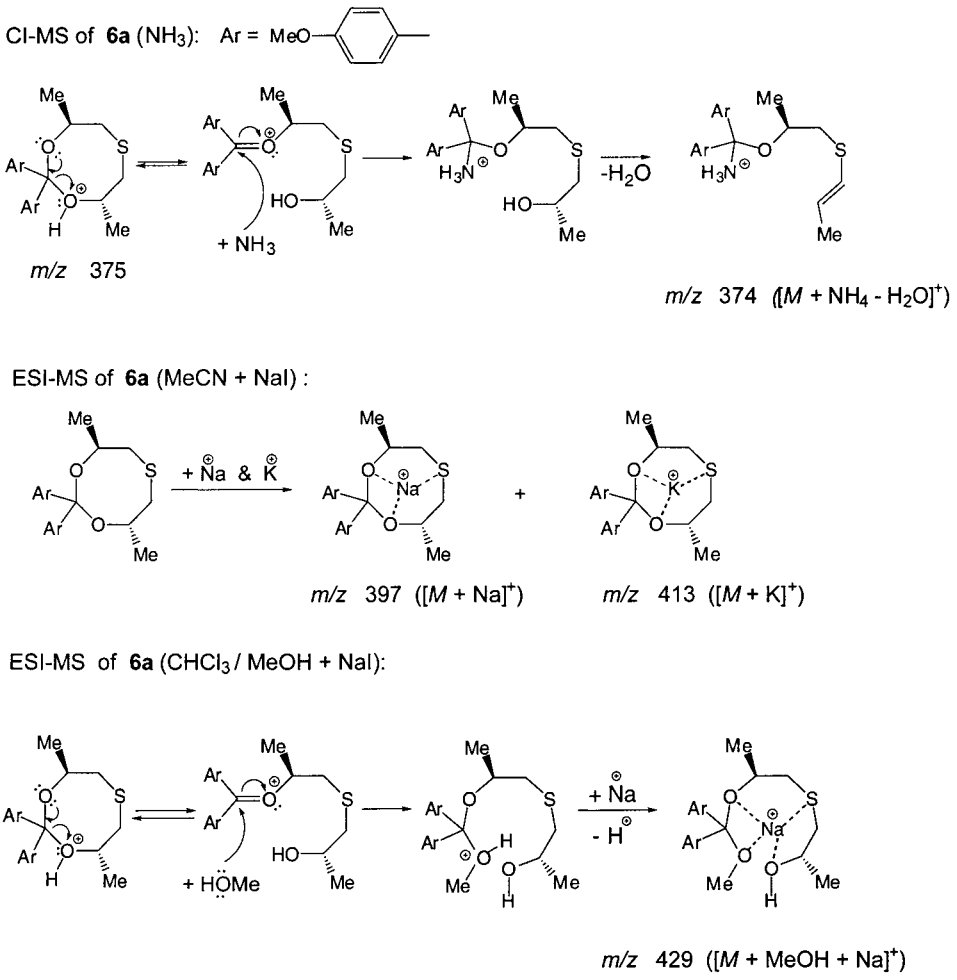
The corresponding reaction of **1** with **3c** at $-78°$ led to **8c**, **5**, and the unusual product **7c** in 13, 76, and 10% yields, respectively (see *Scheme 2* and *Table 1*).

The structures of **4b**, **6b**, **7c**, and **8c** were assigned on the basis of the elemental analyses, NMR and MS data, and that of **8c** was confirmed by X-ray crystallography (see *Fig. 2*).

For the formation of 1,3-dioxolanes of type **7**, an addition of the corresponding oxirane to 4,4′-dimethoxybenzophenone (**5**) was proposed. To verify this proposal, a mixture of **3c** and **5** in CH_2Cl_2 at $-60°$ was treated with $BF_3 \cdot Et_2O$. After stirring for 15 min, separation of the products by column chromatography gave **7c** in 66% yield, and **5** was recovered in 23% yield (*Scheme 4*).

Repetition of the reaction of **1** with **3a–c** in the presence of $SnCl_4$ at $-78°$ led to **6a** and **6b** in low yields. On the other hand, the yields of **4a**, **4b**, and **8c** increased to 52, 25, and 71%, respectively. By means of TLC analysis, no 1,3-dioxolane could be detected in these cases (see *Table 1*).

Scheme 3



2.2. *Reactions of* **4a** *and* **4b** *with 2-Methyloxirane* (**3a**). To explain the formation of the unexpected product **6a**, the 1:1 adduct **4a** was reacted with **3a** at $-90°$ in the presence of $BF_3 \cdot Et_2O$. After chromatographic separation, the 1:2 adduct **6a** was obtained in 11% yield (*Scheme 5*).

The analogous reaction of **4b** with **3a** under the conditions mentioned above gave the 1:1:1 adduct **9** in 4% yield (*Scheme 5*). The structure of **9** was assigned on the basis of its ^{1}H- and ^{13}C-NMR, and ESI mass spectra. The ^{1}H-NMR spectrum shows a signal (*dd*) at 3.12 ppm for 1 H of CH_2S, again with the typical value of a geminal coupling (14.7 Hz) in eight-membered rings.

2.3. *Reactions of 1,1,3,3-Tetramethylindane-2-thione* (**2**) *with Oxiranes.* To a solution of **2** and 1.1 equiv. $BF_3 \cdot Et_2O$ in dry CH_2Cl_2 at 0° under N_2, 5 equiv. of 2-methyloxirane (**3a**) were added dropwise. The color of the mixture changed from orange to pale pink.

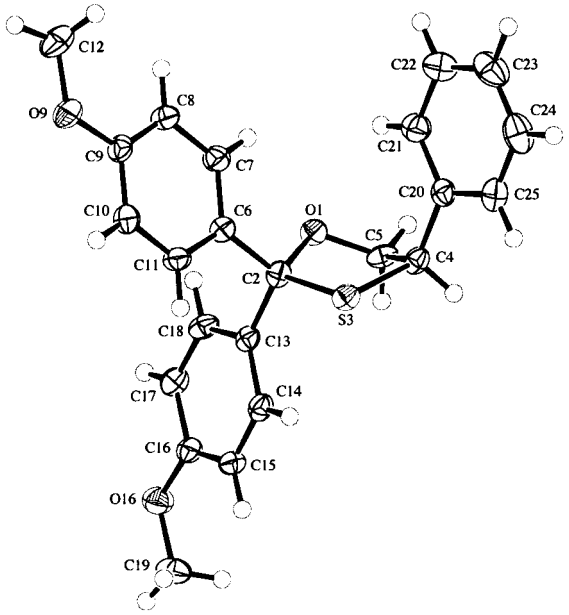
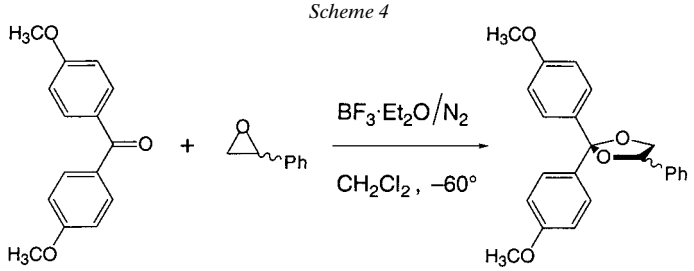


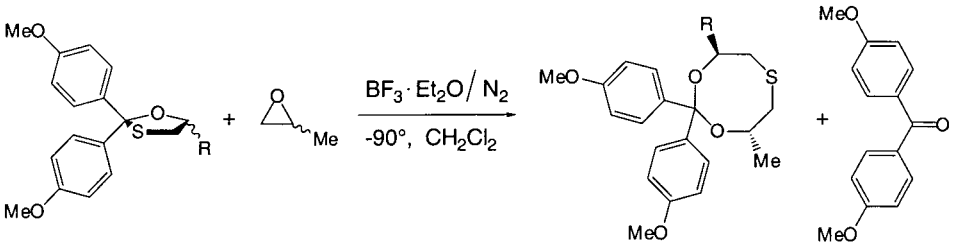
Fig. 2. *ORTEP Plot* [6] *of the molecular structure of* **8c** (arbitrary numbering of the atoms; 50% probability ellipsoids)

Scheme 4



5 **3c** **7c** (66%)

Scheme 5

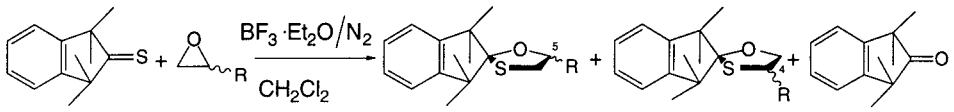


trans-(R,R or S,S)

4a R = Me **3a** **6a** R = Me (11%) **5** (83%)
b R = Bu **9** R = Bu (4%) (81%)

After 4 min, the reaction was quenched by addition of H_2O. Chromatographic separation gave two isomeric 1:1 adducts **10a** and **11a**, as well as ketone **12** in 44, 5, and 29% yields, respectively. The starting material **2** was recovered in only 5% yield (see *Scheme 6* and *Table 2*). The reaction was repeated at −78°, room temperature, and 40°. It is remarkable that **10a** was the exclusive product at −78°, but, with rising reaction temperature the yield of its isomer **11a** and ketone **12** increased significantly (see *Table 2*).

Scheme 6



2 **3a** R = Me, **b** R = Bu, **c** R = Ph; **10a** R = Me, **b** R = Bu; **11a** R = Me, **b** R = Bu, **c** R = Ph; **12**

Table 2. *BF_3-Catalyzed Reactions of* **2** *with* **3** *in CH_2Cl_2*

3	R	Temp. [°]	Reaction time [min]	Yields [%] of products			
				10	**11**	**12**	**2**
a	Me	−78	20	28	–	–	54
		0	4	44	5	29	5
		r.t.	1	39	9	24	4
		40	1	38	11	43	3
b	Bu	0	60	28	9	62	1
c	Ph	−60	25	–	56	–	31
		0	45	–	24	–	64

The $BF_3 \cdot Et_2O$-catalyzed reaction of **2** with **3b** gave similar results. At 0°, the ratio **10b**/**11b** amounted to *ca.* 3:1 (CC). Due to the extended reaction time, **12** was isolated in 62% yield.

The corresponding reaction of **2** with **3c** led only to a 1:1 adduct **11c** at −60° and at 0° in 56 and 24% yield, respectively. In this case, no **12** could be observed; however, a larger amount of starting material **2** was recovered (see *Table 2*).

The structures of the products were assigned on the basis of ^{1}H- and ^{13}C-NMR spectra, elemental analyses, and EI-MS; the structures of compounds **10a**, **11a**, and **11c** were confirmed by means of X-ray crystallography (*Figs. 3–5*).

3. Discussion and Conclusion. – The results presented show that the asymmetric 2-alkyl- and 2-phenyloxiranes **3a–c**, in the presence of a *Lewis* acid, react with the nonenolizable thioketones **1** and **2** to yield 1,3-oxathiolanes. The results support fundamentally the reaction mechanisms depicted in *Scheme 1*.

The reactions of **1** and **2** with **3c** proceeded with high regioselectivity, and so did those of **1** with **3a** and **3b** (*Tables 1* and *2*). However, different results were obtained in the cases of **2** with **3a** and **3b** (*Table 2*). The reaction of **2** with **3a** at −78° gave exclusively **10a**, while both isomers **10a** and **11a** were formed at 0°, room temperature

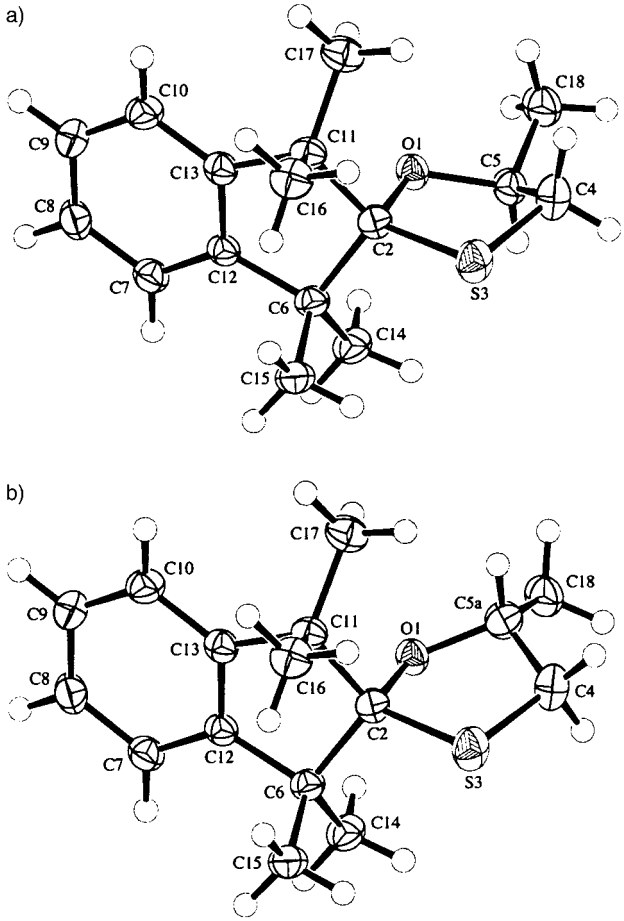


Fig. 3. *ORTEP Plot* [6] *of the molecular structure of* **10a**, *showing both disordered configurations* (arbitrary numbering of the atoms; 50% probability ellipsoids; a) major component (75%); b) minor component (25%))

and 40°, *i.e.*, the regioselectivity decreased with increasing temperature. It is worth mentioning that the ratio **10a**/**11a** is always in favor of **10a**, in good agreement with the mechanisms depicted in *Scheme 1*. The nucleophilic attack at the oxirane is favored at the unsubstituted, the sterically less hindered C-atom.

Under the chosen reaction conditions, the aromatic thioketone **1** is more reactive than the aliphatic thioketone **2**. On the other hand, **2** is more stable than **1**, as it was partially recovered by chromatographic separation even if the reaction was performed at 0° and 40°, while not even traces of **1** could be detected after 1 min at −90°.

The control experiments showed that 1,3-oxathiolanes decompose easily in the presence of mineral or *Lewis* acids. The mechanism of the decomposition under acidic conditions has been described by *Pihlaja* [7]. An analogous mechanism is proposed for the *Lewis* acid catalysis, whereby the C−O bond of the *Lewis* acid-complexed 1,3-

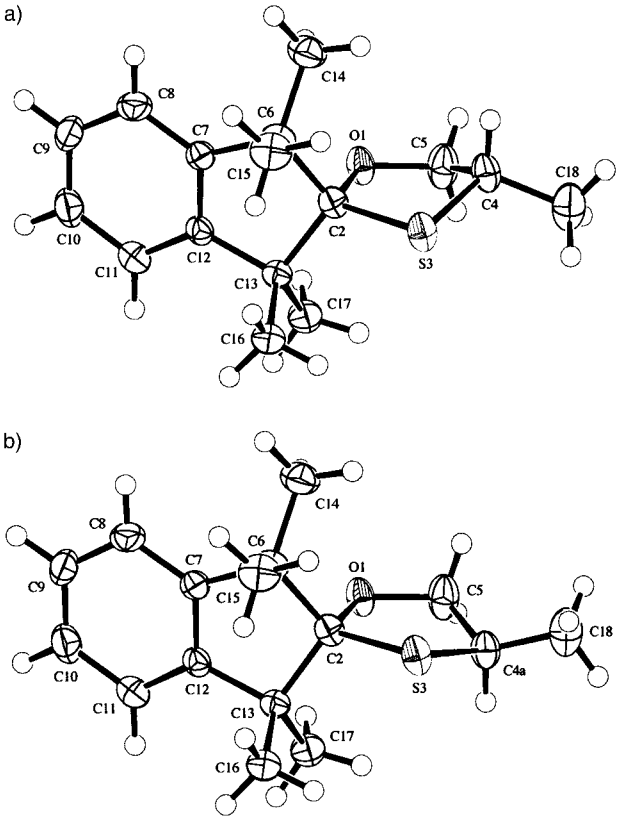


Fig. 4. *ORTEP Plot* [6] *of the molecular structure of* **11a**, *showing both disordered configurations* (arbitrary numbering of the atoms; 50% probability ellipsoids; a) major component (60%); b) minor component (40%))

oxathiolane is preferentially broken (*Scheme 7*). The more stable the intermediate **J** is, the faster is the decomposition to the ketones **5** and **12**. Therefore, the reaction of **1** led to a significantly higher yield of ketone than that of **2**, since **J** in the case of **1** is stabilized by the delocalization of the positive charge through the π-conjugation of the 4-methoxyphenyl groups.

On the basis of the results of the control experiments shown in *Scheme 5*, the formation of **6a** and **9** can be explained as follows (*Scheme 8*, *a*): the zwitterion **K** is formed by the nucleophilic attack of the S-atom of the 1,3-oxathiolane **4** at C(3) of the complexed oxirane. Then, the cleavage of the C–S bond of **K** gives a new zwitterion **L**. The following cyclization leads to the 1:2 adduct **6** or the 1:1:1 adduct **9**. It is remarkable that, in the reaction with racemic starting materials **4** and **3a**, only the *trans*-substituted products were found, *i.e.*, (*R*)-1,3-oxathiolane **4** does not react with (*S*)-oxirane ((*S*)-**3a**), but only with the (*R*)-enantiomer, and *vice versa*.

For the formation of **6** and **9**, another mechanism is also conceivable (*Scheme 8*, *b*): after complexation of the S-atom of **4** with BF_3, first the C–S bond is cleaved, leading to the zwitterion **M**. The attack of the S-atom of **M** at C(3) of the BF_3-complexed **3a**

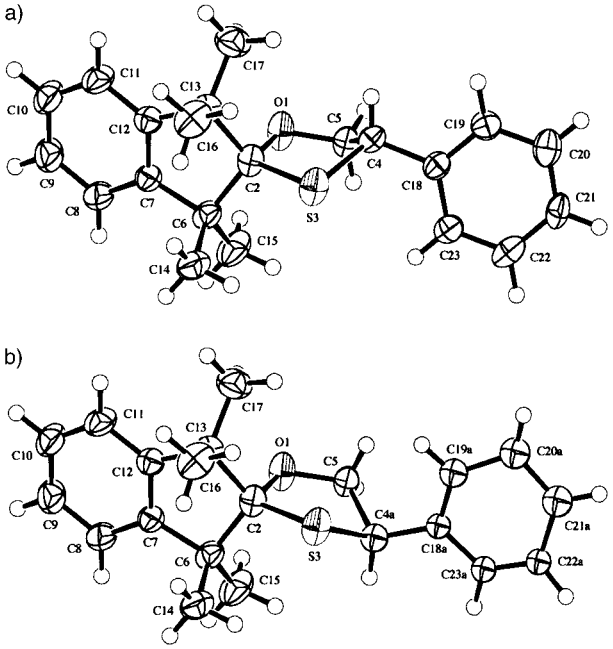
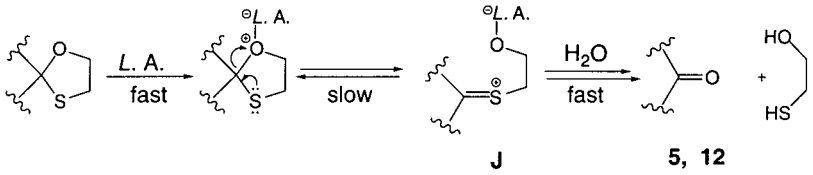


Fig. 5. *ORTEP Plot* [6] *of the molecular structure of* **11c**, *showing both disordered configurations* (arbitrary numbering of the atoms; 50% probability ellipsoids; a) major component (80%); b) minor component (20%))

Scheme 7



yields the zwitterion **L**, which undergoes cyclization to the product. However, in this mechanism, the first step is not in accordance with that described by *Pihlaja* [7]. In addition, the complexation of 1,3-oxathiolanes with BF_3 should occur preferentially at the O-atom according to the HSAB principle. Therefore, the second mechanism can be discarded.

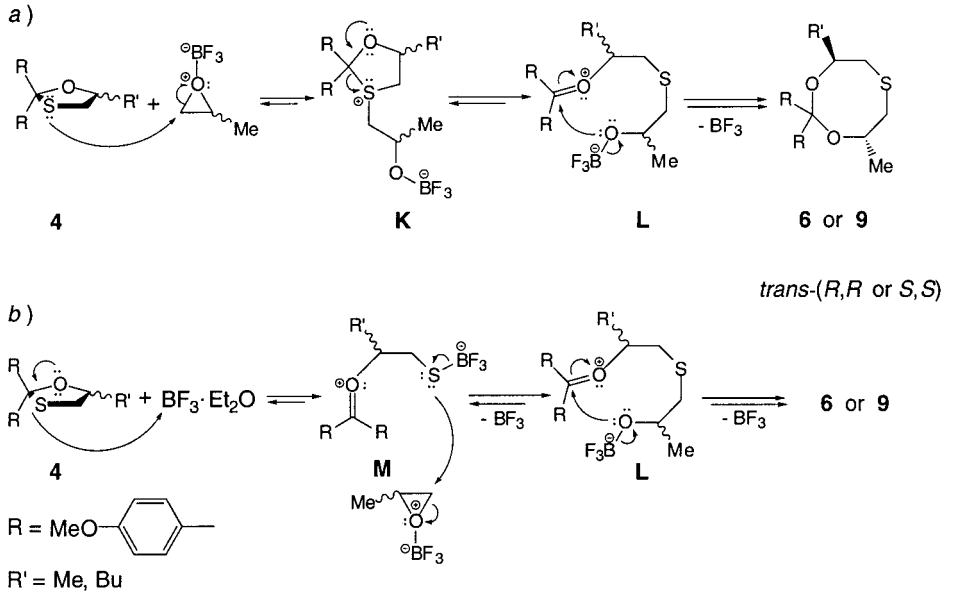
We thank the analytical units of our institute for spectra and analyses and Mr. *J. Tödtli* for his assistance with the determination of the crystal structures. Financial support of this work by the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, is gratefully acknowledged. *C. F.* thanks the *Betty Sassella-Keller-Legat* for financial support.

Experimental Part

1. *General.* See [8]. IR Spectra in $CHCl_3$, NMR spectra at 300 (^1H) and 75.5 MHz (^{13}C) in C_6D_6, if not otherwise stated.

2. *Synthesis of the Starting Materials.* The thioketones used were prepared according to described procedures: 4,4′-dimethoxythiobenzophenone (**1**) [9] was extracted by means of a *Soxhlet* extractor with

Scheme 8



pentane, the extracts were concentrated *i.v.*, and the residue was recrystallized from AcOEt (yield 97%); for *1,1,3,3-tetramethylindane-2-thione* (**2**), see [10].

3. *General Procedure for the Reactions of Thioketones* **1** *and* **2** *with Oxiranes* **3**. To the soln. of **1** or **2** (*ca.* 1 mmol) in dry CH_2Cl_2 (10–15 ml) under N_2, 1.1 equiv. of a *Lewis* acid ($BF_3 \cdot Et_2O$ or $SnCl_4$) was added at $-90°$, $-78°$, $0°$, r.t., and $40°$, resp. In general, this led to a more or less pronounced change in the color of the soln. After stirring the mixture for 15 min at the selected temp., *ca.* 5 equiv. of oxirane **3** was added dropwise, whereby the color of the soln. changed rapidly 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 *i.v.* The products were separated by chromatography (SiO_2; hexane/Et_2O or hexane/CH_2Cl_2; CC or prep. TLC (PLC)).

4. *Reactions of* **1**. 4.1. *With 2-Methyloxirane* (**3a**). Reaction of **1** (258 mg, 1 mmol) with **3a** (290 mg, 5 mmol) and 1.1 mmol $BF_3 \cdot Et_2O$ (or $SnCl_4$) at different temperatures (1 min, CC (hexane/Et_2O 10:1)) yielded *2,2-bis(4-methoxyphenyl)-5-methyl-1,3-oxathiolane* (**4a**), trans-*2,2-bis(4-methoxyphenyl)-4,8-dimethyl-1,3,6-dioxathiocane* (**6a**), *2,2-bis(4-methoxyphenyl)-4-methyl-1,3-dioxolane* (**7a**), and *4,4′-dimethoxybenzophenone* (**5**) (see *Table 1*).

Data of **4a**: Colorless oil. IR: 2955*w*, 2930*w*, 2900*w*, 2835*w*, 1607*s*, 1580*w*, 1507*s*, 1464*w*, 1440*w*, 1410*w*, 1380*w*, 1300*m*, 1250*s*, 1200 (sh), 1174*s*, 1090*m*, 1030*s*, 820*s*. ^{1}H-NMR ($CDCl_3$): 7.53 (*d*, *J* = 8.9, 2 arom. H); 7.31 (*d*, *J* = 9.0, 2 arom. H); 6.87 (*d*, *J* = 8.9, 2 arom. H); 6.79 (*d*, *J* = 9.0, 2 arom. H); 4.30–4.19 (*m*, H–C(5)); 3.80, 3.75 (2*s*, 2 MeO); 3.18 (*dd*, *J* = 9.9, 5.4, 1 H–C(4)); 2.97 (*dd*, *J* = 9.9, 8.9, 1 H–C(4)); 1.50 (*d*, *J* = 6.0, Me). ^{13}C-NMR ($CDCl_3$): 159.0, 158.9 (2*s*, 2 arom. C); 137.5, 137.4 (2*s*, 2 arom. C); 128.6, 127.9 (2*d*, 4 arom. CH); 113.5, 113.2 (2*d*, 4 arom. CH); 98.6 (*s*, C(2)); 78.3 (*d*, C(5)); 55.3 (*q*, 2 MeO); 41.4 (*t*, C(4)); 19.6 (*q*, Me). CI-MS (NH_3): 319 (6), 318 (19), 317 (100, $[M+H]^+$), 243 (31). Anal. calc. for $C_{18}H_{20}O_3S$ (316.42): C 68.33, H 6.37, S 10.13; found: C 68.33, H 6.44, S 10.17.

Data of **6a**: Colorless crystals. M.p. 106.5–107.4°. IR: 2965*w*, 2925*w*, 2835*w*, 1610*m*, 1585*w*, 1508*s*, 1465*w*, 1440*w*, 1410*w*, 1375*w*, 1334*w*, 1312*w*, 1301*w*, 1245*s*, 1205 (sh), 1172*s*, 1128*w*, 1080*m*, 1030*s*, 1010*m*, 975*w*, 829*m*. ^{1}H-NMR: 7.80–7.40 (br. *s*, 4 arom. H); 6.76 (*d*, *J* = 8.5, 4 arom. H); 4.02–3.98 (*m*, H–C(4), H–C(8)); 3.29 (*s*, 2 MeO); 2.73 (*dd*, *J* = 14.6, 3.0, 2 H, CH_2(5), CH_2(7)); 2.46 (*dd*, *J* = 14.6, 5.5, 2 H, CH_2(5), CH_2(7)); 1.00 (*d*, *J* = 6.4, 2 Me). ^{13}C-NMR: 159.4 (*s*, 2 arom. C); 136.1 (*s*, 2 arom. C); 129.0 (br. *d*, 4 arom. CH); 113.3 (*d*, 4 arom. CH); 102.7 (*s*, C(2)); 69.8 (*d*, C(4), C(8)); 54.6 (*q*, 2 MeO); 38.7 (*t*, C(5), C(7)); 21.6 (*q*, 2 Me). CI-MS (NH_3): 509 (26), 508 (32), 507 (100), 375 (15, $[M+H]^+$), 374 (23, $[M+NH_4-H_2O]^+$), 331 (7), 330 (32), 135 (8), 133

(49). ESI-MS ($CHCl_3$/MeOH + NaI): 429 (32, $[M + MeOH + Na]^+$), 258 (18), 257 (100). ESI-MS (MeCN + NaI): 414 (19), 413 (62, $[M + K]^+$), 399 (10), 398 (24), 397 (100, $[M + Na]^+$), 265 (21). Anal. calc. for $C_{21}H_{26}O_4S$ (374.50): C 67.35, H 7.00, S 8.56; found: C 67.19, H 6.79, S 8.77.

Crystals of **6a** suitable for the X-ray crystal-structure analysis were grown from Et_2O/MeOH.

Data of **7a**: Colorless oil. IR: 3000*w*, 2960*w*, 2930*w*, 2905*w*, 2820*w*, 1610*s*, 1580*w*, 1500*m*, 1460*m*, 1440*w*, 1410*w*, 1380*w*, 1300*m*, 1240*s*, 1200 (sh), 1170*s*, 1110*w*, 1090 (sh), 1070*s*, 1030*s*, 1010*w*, 985*w*, 955*w*, 930*w*, 910*w*, 830*s*. ^{1}H-NMR: 7.64, 7.63 (2*d*, $J = 8.9$, 4 arom. H); 6.80, 6.77 (2*d*, $J = 8.9$, 4 arom. H); 4.10–4.00 (*m*, H–C(4)); 3.82 (*dd*, $J = 7.5$, 6.3, 1 H–C(5)); 3.37 (*t*, $J = 7.4$, 1 H–C(5)); 3.30, 3.26 (2*s*, 2 MeO); 1.07 (*d*, $J = 6.1$, Me). ^{13}C-NMR: 159.9 (*s*, 2 arom. C); 136.5, 136.3 (2*s*, 2 arom. C); 128.2, 128.0 (2*d*, 4 arom. CH); 113.8, 113.6 (2*d*, 4 arom. CH); 110.2 (*s*, C(2)); 72.8 (*d*, C(4)); 71.4 (*t*, C(5)); 54.8 (*q*, 2 MeO); 18.7 (*q*, Me). ESI-MS (CH_2Cl_2/MeOH + NaI): 413 (47), 323 (9, $[M + Na]^+$), 301 (13, $[M + H]^+$), 257 (27), 243 (100), 135 (24). Anal. calc. for $C_{18}H_{20}O_4$ (300.35): C 71.98, H 6.71; found: C 71.97, H 6.57.

4.2. *With 2-Butyloxirane* (**3b**). Reaction of **1** (258 mg, 1 mmol) with **3b** (500 mg, 5 mmol) and 1.1 mmol $BF_3 \cdot Et_2O$ (or $SnCl_4$) at $-90°$ or $-78°$ (1 min, CC (hexane/Et_2O 10:1)) yielded *5-butyl-2,2-bis(4-methoxyphenyl)-1,3-oxathiolane* (**4b**), trans-*4,8-dibutyl-2,2-bis(4-methoxyphenyl)-1,3,6-dioxathiocane* (**6b**), and **5** (see *Table 1*).

Data of **4b**: Colorless oil. IR: 2990*w*, 2950*m*, 2930*m*, 2860*w*, 2835*w*, 1608*s*, 1584*w*, 1508*s*, 1464*m*, 1440*w*, 1410*w*, 1375*w*, 1304*m*, 1250*s*, 1200 (sh), 1174*s*, 1112*w*, 1034*s*, 1010*w*, 885*w*, 825*m*. ^{1}H-NMR ($CDCl_3$): 7.52 (*d*, $J =$ 8.8, 2 arom. H); 7.29 (*d*, $J = 8.9$, 2 arom. H); 6.87 (*d*, $J = 8.8$, 2 arom. H); 6.78 (*d*, $J = 8.9$, 2 arom. H); 4.12–4.01 (*m*, H–C(5)); 3.80, 3.75 (2*s*, 2 MeO); 3.15 (*dd*, $J = 9.8$, 5.5, 1 H–C(4)); 3.00 (*t*, $J = 9.4$, 1 H–C(4)); 1.96–1.84, 1.78–1.65 (2*m*, 2 H of Bu); 1.09–1.25 (*m*, 4 H of Bu); 0.96–0.91 (*t*-like, $J \approx 7.1$, Me). ^{13}C-NMR ($CDCl_3$): 159.0, 158.9 (2*s*, 2 arom. C); 137.6, 137.5 (2*s*, 2 arom. C); 128.5, 127.9 (2*d*, 4 arom. CH); 113.3, 113.2 (2*d*, 4 arom. CH); 98.4 (*s*, C(2)); 82.4 (*d*, C(5)); 55.3 (*q*, 2 MeO); 39.9 (*t*, C(4)); 34.0, 28.6, 22.7 (3*t*, 3 CH_2); 14.0 (*q*, Me). CI-MS (NH_3): 361 (7), 360 (21), 359 (100, $[M + H]^+$), 244 (10), 243 (76). Anal. calc. for $C_{21}H_{26}O_3S$ (358.50): C 70.36, H 7.31, S 8.94; found: C 70.34, H 7.38, S 9.06.

Data of **6b**: Colorless oil. IR: 3000*m*, 2955*s*, 2935*s*, 2870*m*, 2860*m*, 2840*m*, 1610*s*, 1584*w*, 1507*s*, 1465*m*, 1440*w*, 1410*w*, 1378*w*, 1348*w*, 1314*m*, 1302*m*, 1245*s*, 1205 (sh), 1172*s*, 1110*s*, 1078*s*, 1030*s*, 1010*m*, 942*w*, 835*s*, 810*w*. ^{1}H-NMR: 7.85–7.35 (br. *s*, 4 arom. H); 6.78 (*d*, $J = 8.7$, 4 arom. H); 3.97–3.91 (*m*, H–C(4), H–C(8)); 3.29 (*s*, 2 MeO); 2.95 (*dd*, $J = 14.5$, 3.2, 2 H, CH_2(5), CH_2(7)); 2.55 (*dd*, $J = 14.6$, 5.3, 2 H, CH_2(5), CH_2(7)); 1.74–1.71 (*m*, 2 H of 2 Bu); 1.30–1.11 (*m*, 10 H of 2 Bu); 0.79 (*t*, $J = 7.1$, 2 Me). ^{13}C-NMR: 159.6 (*s*, 2 arom. C); 136.3 (*s*, 2 arom. C); 129.3 (br. *d*, 2 arom. CH); 113.4 (br. *d*, 2 arom. CH); 102.9 (*s*, C(2)); 73.7 (*d*, C(4), C(8)); 54.8 (*q*, 2 MeO); 37.3 (*t*, C(5), C(7)); 35.7, 28.0, 23.0 (3*t*, 6 CH_2); 14.2 (*q*, 2 Me). ESI-MS (MeOH/CH_2Cl_2 + NaI): 513 (18, $[M + MeOH + Na]^+$), 258 (20), 257 (100). ESI-MS (MeCN + NaI): 497 (7, $[M + K]^+$), 481 (100, $[M + Na]^+$), 265 (10). Anal. calc. for $C_{27}H_{38}O_4S$ (458.66): C 70.70, H 8.35, S 6.99; found: C 70.65, H 8.02, S 7.03.

4.3. *With 2-Phenyloxirane* (**3c**). Reaction of **1** (258 mg, 1 mmol) with **3c** (600 mg, 5 mmol) and 1.1 mmol $BF_3 \cdot Et_2O$ (or $SnCl_4$) at $-78°$ (1 min, CC (hexane/Et_2O 10:1) and CC (C_6H_6/hexane 4:1)) yielded *2,2-bis(4-methoxyphenyl)-4-phenyl-1,3-oxathiolane* (**8c**), *2,2-bis(4-methoxyphenyl)-4-phenyl-1,3-dioxolane* (**7c**), and **5** (see *Table 1*).

Data of **8c**: Colorless crystals. M.p. 136.3–137.3°. IR: 3031*w*, 3009*w*, 2960*w*, 2935*w*, 2910*w*, 2875*w*, 2840*w*, 1609*s*, 1584*m*, 1508*s*, 1465*m*, 1455*m*, 1442*m*, 1414*w*, 1305*m*, 1250*s*, 1205 (sh), 1175*s*, 1063*m*, 1035*s*, 1013*m*, 978*w*, 940*w*, 912*w*, 878*w*, 860*w*, 824*s*, 715 (sh), 700*w*. ^{1}H-NMR ($CDCl_3$): 7.50 (*d*, $J = 9.0$, 2 arom. H); 7.43 (*d*, $J = 9.0$, 2 arom. H); 7.36–7.23 (*m*, 5 arom. H); 6.86 (*d*, $J = 9.0$, 2 arom. H); 6.83 (*d*, $J = 9.0$, 2 arom. H); 4.86 (*t*, $J = 6.7$, H–C(4)); 4.40 (*dd*, $J = 9.4$, 6.6, 1 H–C(5)); 4.08 (*dd*, $J = 9.4$, 6.91, 1 H–C(5)); 3.80, 3.78 (2*s*, MeO). ^{13}C-NMR ($CDCl_3$): 159.1 (*s*, 2 arom. C); 139.8, 137.0, 136.8 (3*s*, 3 arom. C); 128.6, 128.4, 128.4, 128.1, 127.5 (5*d*, 9 arom. CH); 113.4, 113.3 (2*d*, 4 arom. CH); 100.9 (*s*, C(2)); 76.9 (*t*, C(5)); 55.8 (*d*, C(4)); 55.3 (2*q*, 2 MeO). ESI-MS (CH_2Cl_2/MeOH): 379 (93, $[M + H]^+$), 275 (29), 259 (100), 243 (34). Anal. calc. for $C_{23}H_{22}O_3S$ (378.49): C 72.99, H 5.86, S 8.47; found: C 72.69, H 5.84, S 8.71.

Crystals of **8c** suitable for the X-ray crystal-structure analysis were grown from Et_2O/MeOH.

Data of **7c**: Colorless oil. IR: 3002*w*, 2960*w*, 2938*w*, 2910*w*, 2840*w*, 1610*s*, 1585*w*, 1510*s*, 1465*m*, 1455*w*, 1442*w*, 1415*w*, 1305*m*, 1250*s*, 1205 (sh), 1172*s*, 1080*s*, 1035*s*, 1013*m*, 955*w*, 928*w*, 835*s*, 700*w*. ^{1}H-NMR: 7.73, 7.69 (2*d*, $J =$ 8.9, 4 arom. H); 7.31–7.03 (*m*, 5 arom. H); 6.84, 6.79 (2*d*, $J = 8.9$, 4 arom. H); 5.02 (*t*, $J = 7.0$, H–C(4)); 4.08 (*dd*, $J = 7.8$, 6.8, 1 H–C(5)); 3.78 (*t*, $J = 7.5$, 1 H–C(5)); 3.32, 3.27 (2*s*, 2 MeO). ^{13}C-NMR: 159.9 (*s*, 2 arom. C); 140.0 (*s*, 1 arom. C); 135.8 (*s*, 2 arom. C); 128.6, 128.2, 128.1, 128.0, 126.8 (5*d*, 9 arom. CH); 113.8, 113.7 (2*d*, 4 arom. CH); 111.0 (*s*, C(2)); 78.7 (*d*, C(4)); 72.3 (*t*, C(5)); 54.7, 54.6 (2*q*, 2 MeO). ESI-MS (CH_2Cl_2/MeOH + NaI): 535 (12), 519 (36), 465 (8), 385 (100, $[M + Na]^+$). Anal. calc. for $C_{23}H_{22}O_4$ (362.43): C 76.22, H 6.12; found: C 76.10, H 6.12.

4.4. *Reaction of* **3c** *with* **5**. An analogous reaction of **5** (242 mg, 1 mmol) with **3c** (600 mg, 5 mmol) in the presence of 1.1 mmol $BF_3 \cdot Et_2O$ at $-60°$ (15 min), yielded 211 mg (66%) of **7c**, and 49 mg (23%) of **5** were recovered.

4.5. *Reactions of* **4a** *and* **4b** *with* **3a**. Treatment of **4a** (133 mg, 0.42 mmol) with **3a** (122 mg, 2.1 mmol) in the presence of 0.378 mmol $BF_3 \cdot Et_2O$ at $-90°$ (20 min, CC (hexane/Et_2O 10:1)) yielded 18 mg (11%) of **6a**.

An analogous reaction of **4b** (180 mg, 0.5 mmol) with **3a** (145 mg, 2.5 mmol) under the conditions mentioned above yielded 9 mg (4%) of trans-*4-butyl-2,2-bis(4-methoxyphenyl)-8-methyl-1,3,6-dioxathiocane* (**9**), 98 mg (81%) of **5**, and 6 mg (3%) of **4b** were recovered.

Data of **9**: Colorless oil. IR: 3000*w*, 2960*m*, 2935*m*, 2875*m*, 2860*w*, 2840*w*, 1610*s*, 1585*w*, 1508*s*, 1465*w*, 1442*w*, 1412*w*, 1375*w*, 1315*w*, 1304*w*, 1246*s*, 1200 (sh), 1174*s*, 1129*w*, 1102*w*, 1092*w*, 1079*m*, 1034*s*, 1012*m*, 974*w*, 945*w*, 860*w*, 835*m*. ^{1}H-NMR: 7.84–7.42 (br. *s*, 4 arom. H); 6.79 (*d*, $J = 8.8$, 4 arom. H); 4.19–4.13, 3.78–3.73 (2*m*, H–C(4), H–C(8)); 3.29, 3.28 (2*s*, 2 MeO); 3.12 (*dd*, $J = 14.7$, 3.9, 1 H, CH_2(5), CH_2(7)); 2.61–2.43 (*m*, 3 H, CH_2(5), CH_2(7)); 1.94–1.90 (*m*, 1 H of Bu); 1.44–1.16 (*m*, 5 H of Bu); 0.91 (*d*, $J = 6.4$, Me); 0.85–0.81 (*t*-like, $J \approx 7.0$, Me). ^{13}C-NMR: 159.4 (*s*, 2 arom. C); 136.6, 135.6 (2*s*, 2 arom. C); 129.0 (br. *d*, 4 arom. CH); 113.2 (br. *d*, 4 arom. CH); 102.7 (*s*, C(2)); 72.4 (*d*, C(4)); 71.1 (*d*, C(8)); 54.6 (*q*, 2 MeO); 39.0, 37.3 (2*t*, C(5), C(7)); 35.4, 28.2, 22.9 (3*t*, 3 CH_2); 22.0, 14.1 (2*q*, 2 Me). ESI-MS (MeCN + NaI): 456 (7), 455 (19, $[M+K]^+$), 441 (12), 440 (26), 439 (100, $[M+Na]^+$).

5. *Reactions of* **2**. 5.1. *With* **3a**. Reaction of **2** (204 mg, 1 mmol) with **3a** (290 mg, 5 mmol) and 1.1 mmol $BF_3 \cdot Et_2O$ at different temp. (CC (hexane/CH_2Cl_2 10:1) and PLC) yielded *1,1,3,3-tetramethyl-5′-methylspiro-[indane-2,2′-[1,3]oxathiolane]* (**10a**), *1,1,3,3-tetramethyl-4′-methylspiro[indane-2,2′-[1,3]oxathiolane]* (**11a**), and *1,1,3,3-tetramethylindan-2-one* (**12**). In addition, the starting material **2** was partly recovered (see *Table 2*).

Data of **10a**: Colorless crystals. M.p. 77.6–79.0°. IR: 3070*w*, 2985*s*, 2965*s*, 2932*s*, 2900*m*, 2870*m*, 1588*w*, 1480*s*, 1450*s*, 1380*s*, 1364*m*, 1350*w*, 1338*w*, 1314*w*, 1180*w*, 1170*w*, 1143*m*, 1122*w*, 1090*s*, 1050*s*, 1028*w*, 1020*w*, 998*m*, 970*w*, 958*m*, 912*w*, 900*w*, 850*w*. ^{1}H-NMR: 7.16–7.04 (*m*, 4 arom. H); 4.09–4.02 (*m*, H–C(5′)); 2.43 (*dd*, $J = 10.3$, 4.5, 1 H–C(4′)); 2.33 (*t*, $J = 10.2$, 1 H–C(4′)); 1.48, 1.41, 1.37, 1.34 (4*s*, 4 Me); 0.93 (*d*, $J = 5.9$, Me). ^{13}C-NMR: 149.3, 148.7 (2*s*, 2 arom. C); 127.1, 127.0, 122.7, 122.5 (4*d*, 4 arom. CH); 112.4 (*s*, C(2)); 80.4 (*d*, C(5′)); 51.8, 51.6 (2*s*, C(1), C(3)); 39.8 (*t*, C(4′)); 32.5, 30.2, 24.1, 22.5, 18.6 (5*q*, 5 Me). EI-MS: 262 (6, $M^{+\cdot}$), 188 (52), 173 (26), 160 (61), 145 (100), 131 (16), 130 (11), 129 (22), 128 (23), 127 (11), 117 (21), 115 (20). Anal. calc. for $C_{16}H_{22}OS$ (262.42): C 73.23, H 8.45, S 12.22; found: C 72.85, H 8.57, S 11.94.

Crystals of **10a** suitable for the X-ray crystal-structure analysis were grown from MeOH/pentane.

Data of **11a**: Colorless crystals. M.p. 87.4–89.3°. IR: 3070*w*, 2990*m*, 2965*s*, 2930*s*, 2870*s*, 1600*w*, 1588*w*, 1479*s*, 1450*m*, 1378*s*, 1362*m*, 1314*w*, 1262*w*, 1170*w*, 1130*m*, 1092*s*, 1019*s*, 1026*w*, 1006*w*, 978*m*, 957*m*, 914*m*, 870*w*. ^{1}H-NMR: 7.15–7.05 (*m*, 4 arom. H); 3.82–3.78 (*m*, 1 H–C(5′)); 3.30–3.22 (*m*, 1 H–C(5′), H–C(4′)); 1.46, 1.43, 1.37, 1.35 (4*s*, 4 Me); 0.97 (*d*, $J = 6.1$, Me). ^{13}C-NMR: 149.0, 148.6 (2*s*, 2 arom. C); 127.1, 127.0 (2*d*, 2 arom. CH); 122.7, 122.5 (2*d*, 2 arom. CH); 114.0 (*s*, C(2)); 78.8 (*t*, C(5′)); 52.4, 51.5 (2*s*, C(1), C(3)); 44.1 (*d*, C(4′)); 32.1, 30.7, 23.7, 22.3, 16.5 (5*q*, 5 Me). EI-MS: 262 (31, $M^{+\cdot}$), 220 (7), 205 (10), 189 (21), 188 (100), 187 (17), 173 (27), 160 (53), 145 (61), 131 (14), 129 (13), 91 (10). Anal. calc. for $C_{16}H_{22}OS$ (262.42): C 73.23, H 8.45, S 12.22; found: C 73.15, H 8.44, S 12.25.

Crystals of **11a** suitable for the X-ray crystal-structure analysis were grown from Et_2O/MeOH.

5.2. *With* **3b**. Reaction of **2** (204 mg, 1 mmol) with **3b** (500 mg, 5 mmol) and 1.1 mmol $BF_3 \cdot Et_2O$ at 0° (1 h, CC (hexane/CH_2Cl_2 10:1) and PLC) yielded *1,1,3,3-tetramethyl-5′-butylspiro[indane-2,2′-[1,3]oxathiolane]* (**10b**), *1,1,3,3-tetramethyl-4′-butylspiro[indane-2,2′-[1,3]oxathiolane]* (**11b**), and **12**. In addition, the starting material **2** was partly recovered (see *Table 2*).

Data of **10b**: Colorless oil. IR: 3060*w*, 2990*s*, 2960*s*, 2930*s*, 2862*s*, 1600*w*, 1585*w*, 1478*s*, 1466*s*, 1455*s*, 1450*s*, 1375*s*, 1362*s*, 1344*w*, 1312*m*, 1250*w*, 1175*w*, 1158*w*, 1139*w*, 1124*w*, 1110*w*, 1100*w*, 1050*s*, 1025*m*, 1005*w*, 995*w*, 970*m*, 955*s*, 938*w*, 923*w*, 900*w*, 868*w*. ^{1}H-NMR ($CDCl_3$): 7.25–7.14 (*m*, 4 arom. H); 4.26–4.17 (*m*, H–C(5′)); 2.95 (*dd*, $J = 10.3$, 4.4, 1 H–C(4′)); 2.70 (*t*, $J = 10.2$, 1 H–C(4′)); 1.78–1.30 (*m*, 3 CH_2); 1.42, 1.41, 1.34, 1.31 (4*s*, 4 Me); 0.91–0.86 (*t*-like, $J \approx 7.0$, Me). ^{13}C-NMR ($CDCl_3$): 149.1, 148.5 (2*s*, 2 arom. C); 126.8, 126.7, 122.4, 122.2 (4*d*, 4 arom. CH); 111.7 (*s*, C(2)); 84.8 (*d*, C(5′)); 51.7, 51.5 (2*s*, C(1), C(3)); 38.2 (*t*, C(4′)); 33.5, 28.4, 22.6 (3*t*, 3 CH_2); 32.4, 30.1, 23.9, 22.3, 13.8 (5*q*, 5 Me). EI-MS: 305 (6), 304 (22, $M^{+\cdot}$), 303 (12), 220 (6), 205 (11), 189 (26), 188 (100), 187 (21), 173 (13), 160 (28), 145 (32), 129 (6), 117 (7), 91 (5). Anal. calc. for $C_{19}H_{28}OS$ (304.50): C 74.95, H 9.27, S 10.53; found: C 74.63, H 9.39, S 10.32.

Data of **11b**: Colorless oil. IR: 3060*w*, 2985*m*, 2955*s*, 2930*s*, 2860*s*, 1584*w*, 1475*s*, 1465*s*, 1450 (sh), 1375*s*, 1360*m*, 1310*w*, 1260*w*, 1170*w*, 1150*w*, 1125*w*, 1078*s*, 1000*w*, 965*w*, 953*m*, 910*m*. ^{1}H-NMR ($CDCl_3$): 7.22–7.11 (*m*, 4 arom. H); 4.25 (*dd*, $J = 8.2$, 5.2, 1 H–C(5′)); 3.67–3.50 (*m*, 1 H–C(5′), H–C(4′)); 1.75–1.57 (*m*, 2 H of Bu); 1.45–1.25 (*m*, 4 H of Bu, 4 Me); 0.96–0.91 (*t*-like, $J \approx 7.0$, Me). ^{13}C-NMR ($CDCl_3$): 148.5, 148.1 (2*s*, 2 arom. C);

126.9, 126.8, 122.5, 122.3 (4*d*, 4 arom. CH); 112.9 (*s*, C(2)); 77.3 (*t*, C(5′)); 52.1, 51.3 (2*s*, C(1), C(3)); 50.1 (*d*, C(4′)); 32.3, 31.5, 22.6 (3*t*, 3 CH_2); 31.8, 30.4, 23.3, 22.1, 13.8 (5*q*, 5 Me). EI-MS: 304 (7, $M^{+\cdot}$), 205 (11), 189 (18), 188 (100), 173 (30), 161 (11), 160 (69), 146 (15), 145 (75), 131 (16), 129 (17), 128 (13), 117 (20), 115 (15), 91 (15). Anal. calc. for $C_{19}H_{28}OS$ (304.50): C 74.95, H 9.27, S 10.53; found: C 74.87, H 9.13, S 10.23.

5.3. *With* **3c**. Reaction of **2** (204 mg, 1 mmol) with **3c** (600 mg, 5 mmol) and 1.1 mmol $BF_3 \cdot Et_2O$ at $-60°$ or $0°$ (25 min or 45 min, resp., CC (hexane/CH_2Cl_2 10:1)) yielded *1,1,3,3-tetramethyl-4′-phenylspiro[indane-2,2′-[1,3]oxathiolane]* (**11c**). In addition, the starting material **2** was partly recovered (see *Table 2*).

Data of **11c**: Colorless crystals. M.p. 103.5–104.0°. IR: 2960*w*, 2995*m*, 2962*s*, 2935*m*, 2870*m*, 1600*m*, 1575*w*, 1490*m*, 1478*s*, 1450*s*, 1378*s*, 1362*m*, 1312*w*, 1128*m*, 1075*s*, 1025*w*, 995*m*, 965*w*, 952*m*, 915*m*, 860*w*, 698*m*. ^{1}H-NMR ($CDCl_3$): 7.52 (*d*, *J* = 7.3, 2 arom. H); 7.40–7.21 (*m*, 7 arom. H); 4.73 (*dd*, *J* = 10.2, 5.9, H–C(4′)); 4.44 (*dd*, *J* = 8.9, 5.9, 1 H–C(5′)); 4.06–4.00 (br. *t*, *J* ≈ 10.3, 9.1, 1 H–C(5′)); 1.50, 1.44, 1.40, 1.39 (4*s*, 4 Me). ^{13}C-NMR ($CDCl_3$): 148.4, 148.0, 136.2 (3*s*, 3 arom. C); 128.6, 128.0, 127.9, 127.0, 126.9, 122.5, 122.3 (7*d*, 9 arom. CH); 113.9 (*s*, C(2)); 78.8 (*t*, C(5′)); 53.8 (*d*, C(4′)); 52.1, 51.7 (2*s*, C(1), C(3)); 31.9, 30.3, 23.5, 22.4 (4*q*, 4 Me). EI-MS: 324 (12, $M^{+\cdot}$), 220 (33), 205 (16), 188 (21), 173 (16), 160 (49), 145 (86), 136 (100), 135 (58), 104 (85), 91 (45), 77 (18). Anal. calc. for $C_{21}H_{24}OS$ (324.49): C 77.73, H 7.46, S 9.88; found: C 77.59, H 7.41, S 9.99.

Crystals of **11c** suitable for the X-ray crystal-structure analysis were grown from THF.

6. *X-Ray Crystal-Structure Determination of* **6a**, **8c**, **10a**, **11a**, *and* **11c** (see *Table 3* and *Figs. 1–5*)[2]). All measurements were made on a *Rigaku AFC5R* diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71069 Å) and a 12-kW rotating anode generator. The $\omega/2\theta$ scan mode was employed for data collection. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. Data collection and refinement parameters are given in the *Table 3*, views of the molecules are shown in *Figs. 1–5*.

The structures were solved by direct methods using SHELXS97 [11] for **8c** or SIR92 [12] for **6a**, **10a**, **11a**, and **11c**, which revealed the positions of all non-H-atoms. For each structure, all non-H-atoms were refined anisotropically (except for the atoms of the minor disordered conformation of **11c** (see below), which were refined isotropically). All of the H-atoms were fixed in geometrically calculated positions (d(C–H) = 0.95 Å), and each was assigned a fixed isotropic displacement parameter with a value equal to 1.2Ueq of its parent C-atom. Refinement of each structure was carried out on F using full-matrix least-squares procedures, which minimized the function $\Sigma w(|Fo| - |Fc|)^2$. A correction for secondary extinction was applied in each case.

Neutral atom scattering factors for non-H atoms were taken from [13a], and the scattering factors for H-atoms were taken from [14]. Anomalous dispersion effects were included in F_C [15]; the values for f' and f'' were those of [13b]. The values of the mass attenuation coefficients are those of [13c]. All calculations were performed using the teXsan crystallographic software package [16].

For **6a**, which is racemic, there are two symmetry-independent molecules in the asymmetric unit; however, there are no significant conformational differences between the molecules, and they both represent the same stereoisomer in which the two Me substituents in the eight-membered ring lie *trans* to one another.

The crystals of **8c** are enantiomerically pure, and the absolute configuration of the molecule has been confidently determined independently by the diffraction experiment (absolute structure parameter = 0.01(6)) [17]. The configuration at C(4) is (*R*). The heterocyclic ring has a half-chair conformation twisted on O(1)–C(5), but distorted significantly towards an envelope conformation with C(5) as the envelope flap.

Compounds **10a**, **11a**, and **11c** are all racemic, as dictated by the space-group symmetry. However, each structure is disordered in that the sites of one enantiomer in the crystal are also partially occupied by the opposite enantiomer, and *vice versa*. In the refined model, this manifests itself in the substituted C-atom of the heterocyclic five-membered ring occupying two disordered positions, above and below the mean ring plane, with the configuration about this atom in one position being inverted in the alternate position. In **10a** and **11a**, the position of the C-atom of the associated Me substituent is not disordered, but is common to both configurations (*Figs. 3* and *4*). In **11c**, the associated Ph substituent is necessarily disordered, and the two orientations of this ring interpenetrate so that they occupy approximately the same space in the crystal lattice (*Fig. 5*). The disordered sites in each structure are not equally occupied, and the relative site-occupation factors of the disordered sites are 0.75:0.25, 0.6:0.4 and 0.8:0.2 for **10a**, **11a**, and **11c**, respectively.

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[2]) Crystallographic data (excluding structure factors) for the structures of **6a**, **8c**, **10a**, **11a**, and **11c** have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publications No. CCDC 167151–167155. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 3. *Crystallographic Data of Compounds* **6a**, **8c**, **10a**, **11a**, *and* **11c**

	6a	**8c**	**10a**	**11a**	**11c**
Crystallized from	Et_2O/MeOH	Et_2O/MeOH	MeOH/pentane	Et_2O/MeOH	THF
Empirical formula	$C_{21}H_{26}O_4S$	$C_{23}H_{22}O_3S$	$C_{16}H_{22}OS$	$C_{16}H_{22}OS$	$C_{21}H_{24}OS$
Formula weight [g mol^{-1}]	374.49	378.48	262.41	262.41	324.48
Crystal color, habit	colorless, prism	colorless, prism	colorless, prism	colorless, prism	colorless, prism
Crystal dimensions [mm]	$0.18 \times 0.33 \times 0.43$	$0.28 \times 0.33 \times 0.39$	$0.25 \times 0.28 \times 0.48$	$0.33 \times 0.43 \times 0.43$	$0.43 \times 0.45 \times 0.50$
Temp. [K]	173(1)	173(1)	173(1)	173(1)	173(1)
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	4	2	4	4	4
Reflections for cell determination	25	25	25	25	25
2θ Range for cell determination [°]	24 – 26	36 – 40	35 – 40	27 – 39	35 – 39
Unit-cell parameters a [Å]	12.447(2)	11.573(3)	12.841(4)	8.659(2)	14.635(5)
b [Å]	14.647(3)	5.750(2)	10.635(4)	22.499(3)	7.926(3)
c [Å]	11.417(4)	15.225(2)	11.706(3)	8.158(2)	16.860(3)
α [°]	108.64(2)	90	90	90	90
β [°]	94.19(2)	111.29(1)	117.16(2)	112.97(2)	110.24(2)
γ [°]	85.54(2)	90	90	90	90
V [Å^3]	1963.7(9)	944.0(4)	1422.3(8)	1463.4(6)	1835(1)
Dx [g cm^{-3}]	1.267	1.331	1.225	1.191	1.174
$\mu(\mathrm{Mo}K_\alpha)$ [mm^{-1}]	0.187	0.192	0.214	0.208	0.179
$2\theta_{(\max)}$ [°]	50	55	55	55	55
Total reflections measured	6170	4990	4326	3692	4684
Symmetry-independent reflections	5820	4328	3276	3365	4206
Reflections used [$I > 2\sigma(I)$]	4580	3814	2545	2161	2968
Parameters refined	470	245	173	173	237
Final R	0.0373	0.0389	0.0449	0.0544	0.0543
wR ($w = [\sigma^2(Fo) + (0.005Fo)^2]^{-1}$)	0.0359	0.0375	0.0453	0.0480	0.0500
Goodness-of-fit	1.740	1.837	2.311	2.029	2.211
Secondary extinction coefficient	$6.4(6) \times 10^{-7}$	$6(1) \times 10^{-7}$	$8(1) \times 10^{-7}$	$2.2(9) \times 10^{-7}$	$2.8(7) \times 10^{-7}$
Final $\Delta_{\max}/\sigma$	0.0007	0.0004	0.0004	0.0004	0.001
$\Delta\rho$(max; min) [e Å^{-3}]	0.20; −0.19	0.34; −0.32	0.32; −0.22	0.37; −0.38	0.49; −0.46

REFERENCES

[1] P.-C. Tromm, H. Heimgartner, *Helv. Chim. Acta* **1990**, *73*, 2287.
[2] M. Blagoev, A. Linden, H. Heimgartner, *Helv. Chim. Acta*. **1999**, *82*, 1458.
[3] V. Oremus, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1991**, *74*, 1500.
[4] M. Blagoev, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1999**, *82*, 2316.
[5] M. Blagoev, A. Linden, H. Heimgartner, *Helv. Chim. Acta,* **2000**, *83*, 3163.
[6] C. K. Johnson, 'ORTEP II. Report ORNL-5138', Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.
[7] K. Pihlaja, *J. Am. Chem. Soc*. **1972**, *94*, 3330.
[8] D. Moya Argilagos, R. W. Kunz, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1998**, *81*, 2388.
[9] B. S. Pedersen, S. Scheibye, N. H. Nilsson, S.-O. Lawesson, *Bull. Soc. Chim. Belg*. **1978**, *87*, 223.
[10] C. P. Klages, J. Voß, *Chem. Ber*. **1980**, *133*, 2255; E. Langhals, H. Langhals, *Tetrahedron Lett*. **1990**, *31*, 859; G. Mlostoń, J. Romański, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1995**, *78*, 1067.
[11] G. M. Sheldrick, 'SHELXS97, Program for the Solution of Crystal Structures', University of Göttingen, Germany 1997.
[12] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, SIR92, *J. Appl. Crystallogr.* **1994**, *27*, 435.
[13] a) E. N. Maslen, A. G. Fox, M. A. O'Keefe, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992 Vol. C, Table 6.1.1.1, p. 477; b) D. C. Creagh, W. J. McAuley, *ibid*. Table 4.2.6.8, p. 219; c) D. C. Creagh, J. H. Hubbell, *ibid*. Table 4.2.4.3, p. 200.
[14] R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Chem. Phys.* **1965**, *42*, 3175.
[15] J. A. Ibers, W. C. Hamilton, *Acta Crystallogr.* **1964**, *17*, 781.
[16] teXsan: Single Crystal Structure Analysis Software, Version 1.10b, Molecular Structure Corporation, The Woodlands, Texas, 1999.
[17] H. D. Flack, *Acta Crystallogr.*, *Sect. A* **1983**, *39*, 876; G. Bernardinelli, H. D. Flack, *Acta Crystallogr., Sect. A* **1985**, *41*, 500.

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