C–C Couplings with Sulfur-Stabilized Carbanions, 8[+]

Formation of δ-Sultines (1,2-Oxathiane 2-Oxides) from Thiolane 1-Oxides

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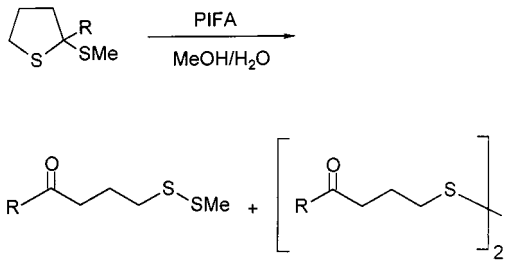
Keywords: Thiolane 1-oxides / Oxidations / δ-Sultines / [Bis(trifluoroacetoxy)iodo]benzene / Asymmetric synthesis / Carbanions

2-(Alkylthio)-2-benzylthiolane 1-oxides (**1a**, **b**) and 2-(alkylthio)-2-(α-hydroxybenzyl)thiolane 1-oxides (**1c**, **d**) are oxidized with [bis(trifluoroacetoxy)iodo]benzene (PIFA). Under ring enlargement the corresponding cyclic sulfinate esters (δ-sultines) **2** are formed. Only (1*R**,2*S**)-**1b** is reactive whereas (1*R**,2*R**)-**1b** is not attacked. This observation is explained with the formation of a cyclic intermediate **3**.

The oxidative hydrolysis of thioacetals by use of [bis(trifluoroacetoxy)iodo]benzene (PIFA) is a particularly versatile method to regenerate carbonyl compounds from e.g. 1,3-dithiane derivatives.[2] It has also been useful in our hands for the cleavage of semicyclic thioacetals, i.e. 2-(methylthio)thiolanes, which yield oxo disulfides[3] (Scheme 1). We have, therefore, studied the reaction of PIFA with the corresponding sulfoxides **1**,[1,4,5] which have turned out to be rather resistant to cleavage with ordinary reagents.[1][5]



Scheme 1

The sulfoxides **1** and 1.5 equivalents of PIFA were stirred at room temperature in the usual[3][6] solvent aqueous methanol. Unexpectedly, no disulfides were formed. Instead, oxidative ring enlargement occurred resulting in the formation of cyclic sulfinates **2** (δ-sultines), cf. Scheme 2. The yields were strongly dependent on the nature of the substituents R^1 and R^2 and, in particular, on the configuration of the sulfoxide as exemplified for the two diastereoisomers of **1b**. Only one stereoisomer was reactive; no product was formed from the other one. The surprising selectivity can be explained by the assumption that a chelate (**3**) between the nucleophilic sulfur and oxygen centres of **1b** and the hypervalent iodine is formed in the first step of the oxidation reaction (cf. Scheme 3).

This seems to be reasonable and is in accordance with Stork's[2] suggestion for the reaction between PIFA and thioacetals although the mechanism is not fully understood. The cationic chelate **3** is then cleaved by solvolysis and ultimately the sultine **2** is formed (Scheme 3).

Obviously, the five-membered ring of the intermediate chelate **3** can only be formed if the alkylthio substituent and the sulfoxide oxygen atom of **1b** are located in *cis* position. In fact, we assign this (1*R**,2*S**) configuration to the reactive stereoisomer on account of its ^{1}H-NMR spectrum. The signals of its benzylic protons, which occupy the *trans* position with respect to the oxygen atom, are observed at δ = 2.80 and δ = 3.21 whereas the $PhCH_2$ proton signal of the unreactive diastereoisomer appears at δ = 3.36, i.e. it is shifted downfield due to the anisotropy of the sulfoxide oxygen atom in the *cis* position. This effect has also been observed for the corresponding methylene protons of 2-(alkylthio)-2-(2-hydroxyalkyl)thiolane 1-oxides, *e.g.* (1*R**,2*R**)-**4** and (1*R**,2*S**)-**4**,[1][7] cf. Scheme 4.

The δ-sultines **2a**–**c** are formed as mixtures of diastereoisomers, although pure (1*R**,2*S**)-**1a** and (1*R**,2*S**)-**1b** are used as starting compounds. This can be explained by inversion of configuration at the sulfoxide sulfur atom which passes a bivalent state during the course of the oxidation reaction (cf. Scheme 3).

The sulfoxides **1c** and **1d** exhibit three centres of chirality. However, only two instead of the expected four diastereoisomers are formed. Both of them exhibit *trans* [(1*R**,2*R**)] configuration of the alkylthio and the sulfoxide group but differ in the relative configuration of the carbinol carbon atom C-1′. Due to the reaction mechanism, the missing two *cis* [(1*R**,2*S**)] isomers are not obtained.[4] The oxidation of **1c** and **1d** was performed with each the prevailing one of the two *trans* isomers, and in spite of the unfavourable configuration **2c** and **2d** were formed, although, not unexpectedly, the yields were low (cf. Scheme 2).

To achieve a reaction with (1*R**,2*R**)-**1b** as well as with the sterically hindered **1e** and also to enhance the yields of **2c** and **2d**, we have increased the amount of PIFA to a 2.5-

[+] Part 7: Ref.[4]

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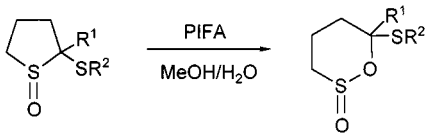
  1434–193X/99/0404–0943 $ 17.50+.50/0

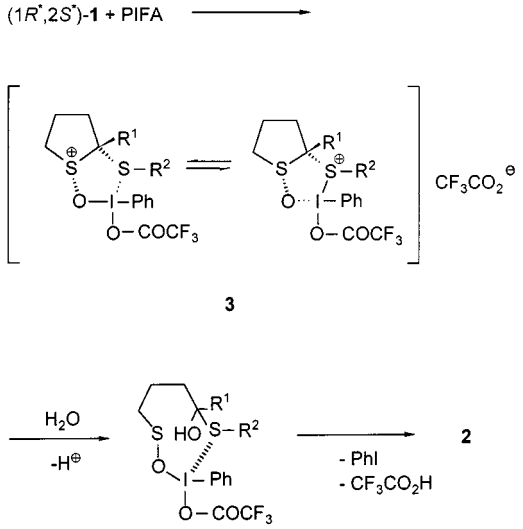


1a-e **2a-e**

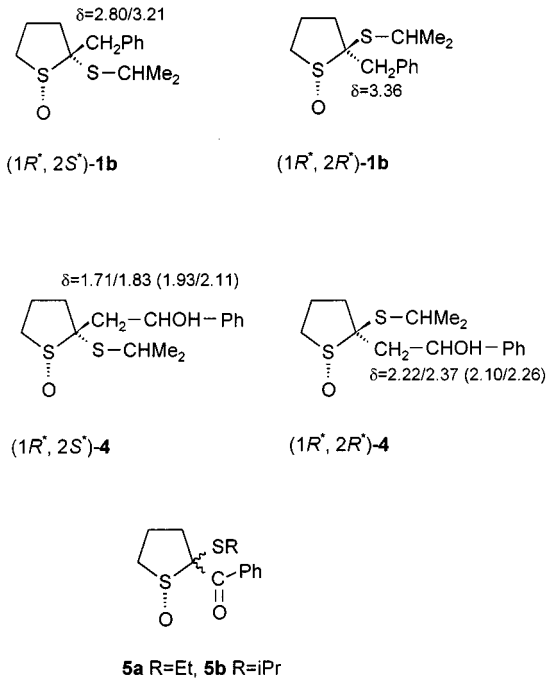
Sulfoxide Sultine	(1*R**,2*S**)-**1a** **2a**	(1*R**,*S**)-**1b** **2b**	(1*R**,2*R**)-**1b** **2b**	(1*R**,2*R**)-**1c** **2c**	(1*R**,2*R**)-**1d** **2d**	(1*R**,2*R**)-**1e** **2e**
R^1	$PhCH_2$	$PhCH_2$	$PhCH_2$	PhCHOH	PhCHOH	Me_2COH
R^2	Et	*i*Pr	*i*Pr	Et	*i*Pr	*i*Pr
yield [%]	85	70	0	22[a]	9[b]	0

[a] Reaction with a 2.6-fold excess of PIFA at reflux temp. yielded 17% of **2c** and 7% of **5a**. – [b] Besides 7% of **5b**.

Scheme 2. Yields (%) of δ-sultines



Scheme 3



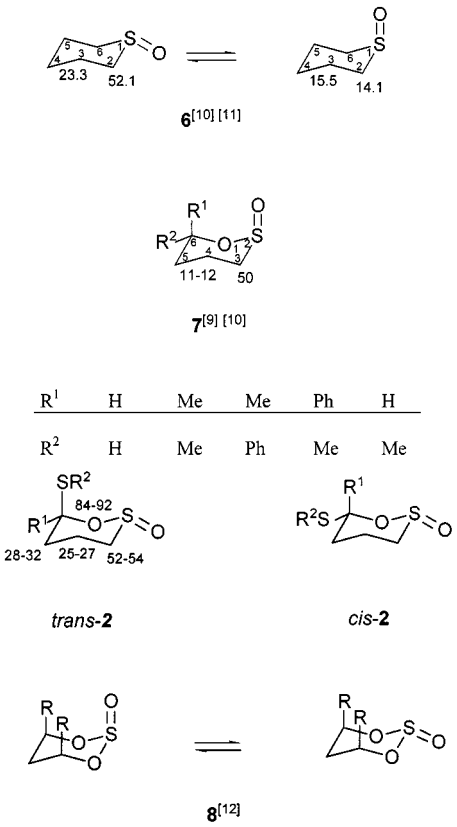
Scheme 4. Chemical shifts δ of methylene protons

fold molar excess. However, (1*R**,2*R**)-**1b** and **1e** remained unreactive. Interestingly, only each one of the two diastereoisomers of **2c** and **2d** were obtained under this condition. Possibly, this is due to a stereoselective oxidation brought about by the high excess of PIFA. In fact, the ketones **5**[8] are formed as by-products and this effect is even more pronounced if a higher reaction temperature is applied.

The diastereoisomers of **2a**–**c** can be separated by column chromatography. However, a definite assignment of their configurations is not straightforward. Two chair conformations with equatorial or axial orientation of the exocyclic oxygen atom are possible. Unsubstituted 1,2-oxathiane 2-oxide as well as derivates with methyl or phenyl substituents in the 6-position (**7**) have been shown to exist predominantly with axial oxygen atom on account of dipole compensation ("anomeric effect").[9][10] They exhibit a characteristic high-field shift of the C-4 NMR signal to δ = 11.5–12.8. Thiane 1-oxide (**6**) on the other hand can adopt both conformations[10][11] and the corresponding signals (of C-3 in this case) are observed at δ = 15.5 for the axial and δ = 23.3 for the equatorial sulfoxide. Since we found chemical shifts of δ = 24.8–27.4 for C-4 of the sultines **2**, we assign a chair conformation with the equatorial position of the sulfoxide to these compounds. Trimethylene sulfites (1,3,2-dioxathiane 2-oxides, **8**) with substituents in 4-(6-)position have also been found to contain considerable amounts of the diastereoisomers with equatorial conformation of the sulfoxide[12] (Scheme 5). Obviously, repulsive 1,3-interactions in **8** and especially in **2** destabilize conformations exhibiting axial oxygen substituents. We are, however, not able to assign the *cis* or *trans* configuration to the two diastereoisomers because neither their ^{1}H-NMR nor their ^{13}C-NMR spectra provide clear evidence.

Experimental Section

General: M.p.: Electrothermal melting point apparatus; corrected values. – IR: Genesis ATI-Mattson; KBr or film. – NMR: Bruker WM 400 (400 MHz and 100.6 MHz, for ^{1}H and ^{13}C respectively);



6[10] [11]

7[9] [10]

R^1	H	Me	Me	Ph	H
R^2	H	Me	Ph	Me	Me

trans-**2** *cis*-**2**

8[12]

Scheme 5. Conformations and selected ^{13}C-NMR chemical shifts δ [ppm] of thiane 1-oxide **6**, δ-sultines **7** and **2**, and trimethylene sulfites **8**

$CDCl_3$ as solvent, TMS as internal standard. The ^{13}C signals were assigned on the basis of DEPT spectra. − MS: Varian CH7 (EI). − HRMS: VG-Analytical 70-2050S. − Chromatography: SiO_2/ethyl acetate. − Elemental analyses: Microanalytical laboratory, Institute of Organic Chemistry, Univ. Hamburg, Germany. − (1*R**,2*R**)-2-(Ethylthio)-2-(1-hydroxy-1-phenylmethyl)thiolane 1-oxide (**1c**), (1*R**,2*R**)-2-(1-hydroxy-1-phenylmethyl)-2-(isopropylthio)thiolane 1-oxide (**1d**), and (1*R**,2*R**)-2-(2-hydroxypropan-2-yl)-2-(isopropylthio)thiolane 1-oxide (**1e**) were prepared as previously described.[4]

2-Benzyl-2-(ethylthio)thiolane 1-Oxide (1a) was prepared analogously (Method B)[4] from 2-(ethylthio)thiolane 1-oxide[4] (2.62g, 16.0 mmol) and benzyl bromide (2.74 g, 16.0 mmol). Yield: 3.27 g (80%) of a 1:1.7 mixture of (1*R**,2*R**)- and (1*R**,2*S**)-**1a**, which were separated by column chromatography.

(1*R,2*R**)-1a:** Yellowish crystals, m.p. 34−35°C, R_f = 0.35. − IR: $\tilde{\nu}$ = 3081, 3049, 3028, 2969, 2958, 2931, 2866, 2849, 1493, 1453, 1411, 1602, 1270, 1243, 1076, 1042 (S=O), 1013, 975, 937, 762, 705, 614 cm^{-1}. − ^1H NMR: δ = 1.24 (t, *J* = 7.51 Hz, 3 H, CH_3), 1.73 (ddd, ^2J = 14.05 Hz, ^3J = 2.10 Hz, ^3J = 6.80 Hz, 1 H, 3-H), 2.00−2.13 (m, 1 H, 4-H), 2.32−2.41 (m, 1 H, 4-H), 2.53 (ddd, ^2J = 14.05 Hz, ^3J = 8.07 Hz, ^3J = 11.10 Hz ,1 H, 3-H), 2.62−2.83 (m, 3 H, CH_2CH$_3$, 5-H), 3.29 (s, 2 H, CH_2Ph), 3.75 (ddd, ^2J = 14.01 Hz, ^3J = 4.29 Hz, ^3J = 9.73 Hz, 1 H, 5-H), 7.26−7.37 (m, 5 H, Ar-H). − ^{13}C NMR: δ = 14.12 (+, CH_3), 23.61 (−, *C*H$_2$CH$_3$), 24.71 (−, C-4), 35.88 (−, *C*H$_2$Ph), 36.50 (−, C-3), 54.39 (−, C-5), 79.13 (0, C-2), 127.02 (+, C_{ar}-4), 128.27 (+, 2 C_{ar}), 130.38 (+, 2 C_{ar}), 136.18 (0, C_{ar}-1). − MS (70 eV); *m/z* (%): 254 (2) [M^+], 236 (35), 193 (100) [$C_{11}H_{13}OS^+$], 176 (65), 175 (30), 147 (37), 129 (66) 115 (40), 91 (82) [$C_7H_7^+$], 85 (56), 71 (34), 69 (44), 55 (40). − $C_{13}H_{18}OS_2$ (254.4): calcd. C 61.40, H 7.14, S 25.17; found C 61.31, H 7.22, S 25.12.

(1*R,2*S**)-1a:** Yellowish crystals, m.p. 42°C, R_f = 0.30. − IR: $\tilde{\nu}$ = 3082, 3056, 3031, 2966, 2926, 2868, 1494, 1453, 1441, 1264, 1258, 1159, 1075, 1047 (S=O), 1022, 919, 757, 701, 639 cm^{-1}. − ^1H NMR: δ = 1.29 (t, *J* = 7.51 Hz, 3 H, CH_3), 1.91−2.05 (m, 2 H, 3-H, 4-H), 2.09−2.20 (m, 1 H, 3-H), 2.34−2.44 (m, 1 H, 4-H), 2.83 (d, ^2J = 14.44 Hz, 1 H, CH_2Ph), 2.84−2.98 (m, 3 H, CH_2CH$_3$, 5-H), 3.21 (d, 1 H, CH_2Ph, ^2J = 14.43 Hz), 3.22 (ddd, ^2J = 14.18 Hz, ^3J = 2.10 Hz, ^3J = 6.80 Hz, 1 H, 5-H,), 7.27−7.36 (m, 5 H, Ar-H). − ^{13}C NMR: δ = 13.55 (+, CH_3), 23.44 (−, C-4, *C*H$_2$CH$_3$), 33.83 (−, C-3), 38.92 (−, *C*H$_2$Ph), 52.14 (−, C-5), 79.20 (0, C-2), 126.95 (+, C_{ar}-4), 127.89 (+, 2 C_{ar}), 130.10 (+, 2 C_{ar}), 134.37 (0, C_{ar}-1). − MS (70 eV); *m/z* (%): 254 (2) [M^+], 253 (6) [M^+ − 1], 92 (9), 91 (100) [$C_7H_7^+$], 65 (4), 57 (5). − $C_{13}H_{18}OS_2$ (254.4): calcd. C 61.40, H 7.14, S 25.17; found C 61.14, H 7.20, S 25.28.

2-Benzyl-2-(isopropylthio)thiolane 1-Oxide (1b) was prepared as **1a** from 2-(isopropylthio)thiolane 1-oxide[4] (2.46 g, 13.8 mmol) and benzyl bromide (2.36 g, 13.8 mmol). Yield: 2.99 g (81%) of a 2.2:1 mixture of (1*R**,2*R**)- and (1*R**,2*S**)-**1b**, which were separated by column chromatography.

(1*R,2*R**)-1b:** Yellowish solid, m.p. 30−31°C, R_f = 0.56. − IR: $\tilde{\nu}$ = 3058, 3027, 2980, 2962, 2952, 2943, 2929, 2920, 2864, 1601, 1494, 1452, 1406, 1383, 1364, 1304, 1255, 1243, 1156, 1075, 1042 (S=O), 937, 762, 705, 614 cm^{-1}. − ^1H NMR: δ = 1.35 (d, *J* = 6.87 Hz, 3 H, CH_3), 1.36 (d, *J* = 6.61 Hz, 3 H, CH_3), 1.73 (ddd, ^2J = 14.10 Hz, ^3J = 2.02 Hz, ^3J = 6.98 Hz, 1 H, 3-H), 2.00−2.13 (m, 1 H, 4-H), 2.29−2.39 (m, 1 H, 4-H), 2.53 (ddd, ^2J = 14.11 Hz, ^3J = 8.33 Hz, ^3J = 11.00 Hz, 1 H, 3-H), 2.78 (ddd, ^2J = 14.12 Hz, ^3J = 6.26 Hz, ^3J = 8.87 Hz, 1 H, 5-H), 3.22 (sept, *J* = 6.82 Hz, 1 H, CH(CH$_3$)$_2$), 3.36 (s, 2 H, CH_2Ph), 3.72 (ddd, ^2J = 14.18 Hz, ^3J = 4.39 Hz, ^3J = 9.92 Hz, 1 H, 5-H), 7.25−7.35 (m, 3 H, Ar-H), 7.39−7.43 (m, 2 H, Ar-H). − ^{13}C NMR: δ = 24.41 (+, CH_3), 24.57 (−, C-4), 26.93 (+, CH_3), 34.84 [+, *C*H(CH$_3$)$_2$], 35.91 (−, *C*H$_2$Ph), 36.96 (−, C-3), 53.65 (−, C-5), 80.06 (0, C-2), 126.98 (+, C_{ar}-4), 128.26 (+, 2 C_{ar}), 130.46 (+, 2 C_{ar}), 136.50 (0, C_{ar}-1). − MS (70 eV); *m/z* (%): 268 (2) [M^+], 250 (8), 193 (100) [$C_{11}H_{13}OS^+$], 176 (11), 147 (11), 135 (34), 117 (14), 115 (14), 91 (43) [$C_7H_7^+$], 77 (19) [$C_6H_5^+$]. − $C_{14}H_{20}OS_2$ (268.4): calcd. 62.64 C, 7.51 H, 23.89 S; found 62.20 C, 7.58 H, 23.70 S.

(1*R,2*S**)-1b:** White solid, m.p. 73°C, R_f = 0.20. − IR: $\tilde{\nu}$ = 3051, 3030, 2969, 2936, 2922, 2903, 2865, 1600, 1494, 1457, 1240, 1059, 1081, 1044 (S=O), 1018, 750, 705 cm^{-1}. − ^1H NMR: δ = 1.39 (d, *J* = 6.93 Hz, 3 H, CH_3), 1.42 (d, *J* = 6.74 Hz, 3 H, CH_3), 1.85−2.02 (m, 2 H, 3-H, 4-H), 2.18 (dt, ^2J_d = 13.52 Hz, ^3J_t = 8.15 Hz, 1 H, 3-H,), 2.29−2.39 (m, 1 H, 4-H), 2.80 (d, 1 H, CH_2Ph, ^2J = 14.69 Hz), 2.86 (ddd, ^2J = 14.07 Hz, ^3J = 6.44 Hz, ^3J = 8.92 Hz, 1 H, 5-H), 3.21 (d, ^2J = 14.68 Hz, 1 H, CH_2Ph), 3.23 (ddd, ^2J = 14.05 Hz, ^3J = 5.12 Hz, ^3J = 9.00 Hz, 1 H, 5-H), 3.43 [sept, *J* = 6.84 Hz, 1 H, CH(CH$_3$)$_2$], 7.27−7.37 (m, 5 H, Ar-H). − ^{13}C NMR: δ = 23.09 (−, C-4), 23.98 (+, CH_3), 25.33 (+, CH_3), 33.98 (−, C-3), 34.14 (+, *C*H(CH$_3$)$_2$), 38.58 (−, *C*H$_2$Ph), 52.27 (−, C-5), 79.86 (0, C-2), 126.95 (+,C_{ar}-4), 127.93 (+, 2 C_{ar}), 130.06 (+, 2 C_{ar}), 134.32 (0, C_{ar}-1). − MS (70 eV); *m/z* (%): 268 (6) [M^+], 193 (100) [$C_{11}H_{13}OS^+$], 176 (31), 129 (25), 91 (36) [$C_7H_7^+$], 84 (24), 69 (20), 55 (20). − $C_{14}H_{20}OS_2$ (268.4): calcd. 62.64 C, 7.51 H, 23.89 S; found 62.50 C, 7.63 H, S 23.89.

Oxidation of 1a−e with [1,1-Bis(trifluoroacetoxy)iodo]benzene (PIFA): A solution of **1** and PIFA (Fluka) in 1 mL 10% aqueous methanol was stirred at room temp. for 10 min and then poured into cold satd. $NaHCO_3$ solution. The aqueous phase was extracted

with CH_2Cl_2, the extract was dried with Na_2SO_4 and the CH_2Cl_2 removed. The crude δ-sultines **2** were purified by column chromatography.

6-Benzyl-6-(ethylthio)-1,2-oxathiane 2-Oxide (2a): Yield: 91 mg (85%), 1:1.4 mixture of diastereoisomers, from 101 mg (0.40 mmol) of (1*R**,2*S**)-**1a** and 253 mg (0.59 mmol) of PIFA.

Diastereoisomer 1: Yellowish solid, m.p. 33°C, R_f = 0.10. − IR : ṽ = 3027, 2954, 2930, 2853, 1728, 1475, 1455, 1240, 1052 (S=O), 1017, 761, 706 cm^{-1}. − ^1H NMR: δ = 1.51 (t, 3 H, CH_3, J = 7.54 Hz), 1.84−1.91 (m, 1 H, 5-H), 1.93−2.00 (m, 1 H, 4-H), 2.38−2.46 (m, 1 H, 3-H), 2.59−2.76 (m, 2 H, 4-H, 5-H), 2.95−3.01 (m, 1 H, 3-H), 2.99 (dq, ^2J_d = 12.37 Hz, ^3J_q = 7.44 Hz, 1 H, CH_2CH$_3$), 3.36 (d, ^2J = 14.05 Hz, 1 H, CH_2Ph), 3.38 (dq, ^2J_d = 12.33 Hz, ^3J_q = 7.66 Hz, 1 H, CH_2CH$_3$), 3.56 (d, ^{2}J = 14.05 Hz, 1 H, CH_2Ph), 7.20−7.23 (m, 2 H, Ar-H), 7.27−7.35 (m, 3 H, Ar-H). − ^{13}C NMR: δ = 8.73 (+, CH_3), 24.47 (−, C-4), 32.08 (−, CH$_2$Ph), 32.22 (−, C-5), 43.57 (−, CH$_2$CH$_3$), 53.64 (−, C-3), 84.19 (0, C-6), 127.65 (+, C_{ar}-4), 129.08 (+, 2 C_{ar}), 130.69 (+, 2 C_{ar}), 133.99 (0, C_{ar}-1). − MS (70 eV); *m/z* (%): 271 (0.2) [M^+ + 1], 193 (60) [$C_{11}H_{13}OS^+$], 147 (28), 131 (24), 129 (40), 128 (30), 117 (30), 115 (38), 91 (100) [$C_7H_7^+$], 77 (24) [$C_6H_5^+$], 65 (23), 63 (41).

Diastereoisomer 2: Yellowish solid, m.p. 88°C, R_f = 0.05. − IR: ṽ = 3419 (H_2O), 3082, 3056, 3031, 2966, 2926, 2868, 1494, 1453, 1441, 1264, 1258, 1159, 1075, 1047 (S=O), 1022, 919, 757, 701, 639 cm^{-1}. − ^1H NMR: δ = 1.48 (t, J = 7.53 Hz, 3 H, CH_3), 1.98−2.09 (m, 2 H, 3-H, 5-H), 2.10−2.25 (m, 1 H, 4-H), 2.51−2.63 (m, 2 H, 4-H, 5-H), 2.77−2.83 (m, 1 H, 3-H), 2.81 (dq, ^2J_d = 12.42 Hz, ^3J_q = 7.39 Hz, 1 H, CH_2CH$_3$), 2.96 (dq, ^2J_d = 12.49 Hz, ^3J_q = 7.73 Hz, 1 H, CH_2CH$_3$), 3.07 (d, ^2J = 14.11 Hz, 1 H, CH_2Ph), 3.70 (d, ^2J = 14.05 Hz, 1 H, CH_2Ph), 7.28−7.26 (m, 5 H, Ar-H). − ^{13}C NMR: δ = 8.76 (+, CH_3), 26.92 (−, C-4), 30.70 (−, C-5), 36.29 (−, CH$_2$Ph), 42.66 (−, CH$_2$CH$_3$), 52.82 (−, C-3), 88.29 (0, C-6), 128.14 (+, C_{ar}-4), 128.77 (+, 2 C_{ar}), 130.95 (+, 2 C_{ar}), 133.60 (0, C_{ar}-1). − MS (70 eV); *m/z* (%): 271 (0.2) [M^+ + 1], 193 (60) [$C_{11}H_{13}OS^+$], 176 (22), 147 (28), 129 (38), 128 (32), 117 (32), 115 (42), 91 (100) [$C_7H_7^+$], 77 (32) [$C_6H_5^+$], 65 (24), 63 (48), 50 (32).

6-Benzyl-6-(isopropylthio)-1,2-oxathiane 2-Oxide (2b): Yield 111 mg (70%), 1:1 mixture of diastereoisomers, from 150 mg (0.56 mmol) of (1*R**,2*S**)-**1b** and 363 mg (0.84 mmol) of PIFA.

Diastereoisomer 1: Colourless liquid, R_f = 0.19. − ^1H NMR: δ = 1.37 (d, J = 6.80 Hz, 3 H, CH_3,), 1.49 (d, J = 7.05 Hz, 3 H, CH_3,), 1.83−1.96 (m, 2 H, 4-H, 5-H), 2.33 (ddd, ^2J = 13.29 Hz, ^3J = 6.43 Hz, ^3J = 10.54 Hz, 1 H, 3-H), 2.58−2.71 (m, 1 H, 4-H), 2.75−2.83 (m, 1 H, 5-H), 2.92−2.99 (m, 1 H, 3-H), 3.34 (d, ^2J = 13.99 Hz, 1 H, CH_2Ph,), 3.49 (d, ^2J = 13.93 Hz, 1 H, CH_2Ph), 3.67 [sept, 1 H, J = 6.95 Hz, CH(CH$_3$)$_2$], 7.18−7.22 (m, 2 H, Ar-H), 7.24−7.36 (m, 3 H, Ar-H). − ^{13}C NMR: δ = 15.05 (+, CH_3), 19.83 (+, CH_3), 24.85 (−, C-4), 32.26 (−, C-5), 33.17 (−, CH$_2$Ph), 48.68 (+, CH(CH$_3$)$_2$), 54.01 (−, C-3), 86.97 (0, C-6), 127.64 (+, C_{ar}-4), 129.07 (+, 2 C_{ar}), 130.63 (+, 2 C_{ar}), 134.10 (0, C_{ar}-1) MS (70 eV); *m/z* (%): 285 (0.02) [M^+ + 1], 284 (0.02) [M^+], 242 (4) [$C_{11}H_{14}O_2S_2^+$], 193 (50) [$C_7H_{13}O_2S_2^+$], 192 (28), 176 (20), 175 (25), 147 (25), 143 (20), 129 (44), 128 (42), 117 (26), 115 (44), 92 (28), 91 (100) [$C_7H_7^+$], 77 (19) [$C_6H_5^+$], 65 (24).

Diastereoisomer 2: White solid, m.p. 102°C, R_f = 0.10. − IR: ṽ = 3222 (H_2O), 3048, 2958, 2916, 2875, 2863, 1493, 1457, 1071, 1071, 1049, 1033, 1025 (S=O), 755, 700 cm^{-1}. − ^1H NMR: δ = 1.379 (d, J = 7.00 Hz, 3 H, CH_3), 1.384 (d, J = 6.87 Hz, 3 H, CH_3), 1.79−1.87 (m, 1 H, 3-H), 2.05−2.20 (m, 2 H, 4-H, 5-H), 2.44−2.52 (m, 1 H, 5-H), 2.57−2.76 (m, 2 H, 3-H, 4-H), 3.00 (d, 1 H, ^2J = 13.92 Hz, CH_2Ph), 3.25 (sept, J = 6.95 Hz, 1 H, CH(CH$_3$)$_2$), 3.76 (d, ^2J = 13.92 Hz, 1 H, CH_2Ph), 7.25−7.36 (m, 5 H, Ar-H). − ^{13}C NMR: δ = 15.94 (+, CH_3), 19.98 (+, CH_3), 27.20 (−, C-4), 30.87 (−, C-5), 38.71 (−, CH$_2$Ph), 47.85 (+, CH(CH$_3$)$_2$), 52.05 (−, C-3), 90.46 (0, C-6), 127.93 (+, C_{ar}-4), 128.83 (+, 2 C_{ar}), 130.76 (+, 2 C_{ar}), 133.67 (0, C_{ar}-1). − MS (70 eV); *m/z* (%): 242 (0.6) [$C_{11}H_{14}O_2S_2^+$], 193 (21) [$C_7H_{13}O_2S_2^+$], 192 (64), 176 (31), 175 (39), 147 (28), 129 (56), 128 (742), 124 (27), 117 (52), 115 (84), 92 (46), 91 (100) [$C_7H_7^+$], 77 (37) [$C_6H_5^+$], 65 (32), 59 (24), 45 (26). − MS (CI, NH_3); *m/z* (%): 285 (3) [M^+ + 1], 193 (100) [$C_7H_{13}O_2S_2^+$], 91 (5) [$C_7H_7^+$].

Reaction of (1*R**,2*R**)-**1b,** even with a 2.6-fold excess of PIFA did not yield any **2b**.

6-(Ethylthio)-6-(1-hydroxy-1-phenylmethyl)-1,2-oxathiane 2-Oxide (2c): Yield 36 mg (22%), 1:1.4 mixture of diastereoisomers, from 152 mg (0.56 mmol) (1*R**,2*R**)-**1c** and 363 mg (0.85 mmol) of PIFA.

Diastereoisomer 1: Yellow solid, m.p. 98°C, R_f = 0.17. − IR: ṽ = 3293 (OH), 2960, 2947, 2921, 2875, 2850, 1455, 1402, 1096, 1062, 1048, 1035, 1014, 1002 (S=O), 969, 738, 705 cm^{-1}. − ^1H NMR: δ = 1.38 (t, J = 7.51 Hz, 3 H, CH_3), 2.43−2.53 (m, 2 H, 4-H, 5-H), 2.61−2.73 (m, 1 H, 4-H), 3.10−3.26 (m, 4 H, CH_2CH$_3$, 3-H), 3.42−3.49 (m, 1 H, 5-H), 5.44 (s, 1 H, CHOH), 7.35−7.43 (m, 5 H, Ar-H). − ^{13}C NMR: δ = 8.31 (+, CH_3), 27.37 (−, C-4), 29.86 (−, C-5), 43.45 (−, CH$_2$CH$_3$), 55.38 (−, C-3), 72.10 (+, CHOH), 89.33 (0, C-6), 127.79 (+, 2 C_{ar}), 128.90 (+, 2 C_{ar}), 129.25 (+, C_{ar}-4), 136.98 (0, C_{ar}-1). − MS (70 eV); *m/z* (%): 286 (0.03) [M^+], 268 (2) [$C_{13}H_{16}O_2S_2^+$], 209 (44) [$C_7H_{13}O_3S_2^+$], 147 (24), 129 (24), 106 (36), 105 (100), 91 (23), 87 (26), 85 (22), 77 (86) [$C_6H_5^+$], 63 (23), 51 (22).

Diastereoisomer 2: Yellowish oil, R_f = 0.07. − IR: ṽ = 3345 (OH), 3005, 2931, 285, 2855, 1718, 1657, 1452, 1217, 1051 (S=O), 1037, 1017, 755, 707, 666 cm^{-1}. − ^1H NMR: δ = 1.09 (t, J = 7.76 Hz, 3 H, CH_3), 1.10−1.23 (m, 1 H, CH_2CH$_3$), 1.93 (ddd, ^2J = 13.72 Hz, ^3J = 6.54 Hz, ^3J = 8.76 Hz, 1 H, 4-H), 2.16 (dq, ^2J = 11.81 Hz, ^3J = 7.07 Hz, 1 H, CH_2CH$_3$,), 2.35−2.44 (m, 1 H, 5-H), 2.68−2.79 (m, 1 H, 5-H), 3.05 (ddd, ^2J = 13.78 Hz, ^3J = 4.82 Hz, ^3J = 6.56 Hz, 1 H, 4-H), 3.07−3.15 (m, 2 H, 3-H), 5.76 (s, 1 H, CHOH), 7.47−7.51 (m, 5 H, Ar-H). − ^{13}C NMR: δ = 8.00 (+, CH_3), 24.91 (−, C-4), 27.86 (−, C-5), 42.33 (−, CH$_2$CH$_3$), 54.20 (−, C-3), 72.32 (+, CHOH), 91.89 (0, C-6), 127.09 (+, 2 C_{ar}), 128.89 (+, 2 C_{ar}), 129.37 (+, C_{ar}-4), 137.77 (0, C_{ar}-1). − MS (70 eV); *m/z* (%): 268 (2) [$C_{13}H_{16}O_2S_2^+$], 219 (10), 209 (5) [$C_7H_{13}O_3S_2^+$], 147 (10), 106 (24), 105 (100), 85 (20), 77 (67) [$C_6H_5^+$], 71 (15), 60 (15), 57 (25).

Heating of 100 mg (0.37 mmol) of **1c** with 398 mg (0.96 mmol) of PIFA in 2 mL of 10% aqueous methanol to reflux for 2 h gave 18 mg (17%) of **2c** (Diastereoisomer 1) and 7 mg (7%) of 2-benzoyl-2-(ethylthio)thiolane 1-oxide (**5a**); light yellow oil, R_f = 0.38. − IR: ṽ = 2982, 2935, 2872, 2831, 1729 (C=O), 1658, 1596, 1448, 1259, 1236, 1219, 1053, 1021 (S=O), 754, 665, 576, 468, 452, 439 cm^{-1}. − ^1H NMR: δ = 1.20 (t, J = 7.63 Hz, 3 H, CH_3), 1.79−1.90 (m, 1 H, 4-H), 2.39−2.60 (m, 3 H, 4-H, CH_2), 2.70−2.79 (m, 2 H, 3-H), 2.89−2.97 (m, 1 H, 5-H), 3.18−3.26 (m, 1 H, 5-H), 7.47−7.52 (m, 2 H, Ar-H), 7.61−7.66 (m, 1 H, Ar-H), 8.33−8.37 (m, 2 H, Ar-H). − ^{13}C NMR: δ = 13.90 (+, CH_3), 24.49 (−, C-4), 26.03 (+, CH_2), 35.68 (−, C-3), 51.87 (−, C-5), 88.32 (0, C-2), 128.85 (+, 2 C_{ar}), 129.66 (+, 2 C_{ar}), 133.74 (0, C_{ar}-1), 134.13 (+, C_{ar}-4), 197.60 (0, CO). − MS (70 eV); *m/z* (%): 268 (2) [M^+], 219 (12), 207 (10) [$C_{11}H_{11}O_2S^+$], 157 (10), 147 (11), 115 (11), 105 (100), 85 (11), 77 (97) [$C_6H_5^+$], 59 (11), 51 (22). − Spectra identical with those of **5a** obtained from 2-(ethylthio)thiolane 1-oxide and benzoyl chloride.[1][8]

6-(1-Hydroxy-1-phenylmethyl)-6-(isopropylthio)-1,2-oxathiane 2-Oxide (2d): Yield 14 mg (9%) from 145 mg (0.51 mmol) of (1*R**,2*R**)-**1d** and 553 mg (1.29 mmol) of PIFA in 2 mL of 10% aqueous methanol. − Yellow oil, R_f = 0.41. − ^{1}H NMR: δ = 1.14 (d, *J* = 7.12 Hz, 3 H, CH_3), 1.38 (d, *J* = 6.74 Hz, 3 H, CH_3,), 2.42−2.50 (m, 1 H, 4-H), 2.53−2.69 (m, 2 H, 4-H, 5-H), 3.12−3.17 (m, 2 H, 3-H), 3.44 [sept, *J* = 6.91 Hz, 1 H, C*H*$(CH_3)_2$], 3.45−3.50 (m, 1 H, 5-H), 5.47 (s, 1 H, C*H*OH), 7.33−7.45 (m, 5 H, Ar-H). − ^{13}C NMR: δ = 15.07 (+, CH_3), 19.95 (+, CH_3), 27.03 (−, C-4), 31.08 (−, C-5), 48.14 (+, *C*H$(CH_3)_2$), 55.18 (−, C-3), 72.73 (+, CHOH), 90.03 (0, C-2), 128.46 (+, C_{ar}), 128.75 (+, C_{ar}), 129.23 (+, C_{ar}), 137.15 (0, C_{ar}-1).

Besides **2d**, 10 mg (7%) of **5b** was obtained; yellow oil, R_f = 0.75. − ^{1}H NMR: δ = 1.14 (d, *J* = 6.81 Hz, 3 H, CH_3), 1.39 (d, *J* = 6.68 Hz, 3 H, CH_3), 1.71−1.84 (m, 1 H, 4-H), 2.35−2.45 (m, 1 H, 4-H), 2.56 (ddd, ^2J = 13.80 Hz, ^3J = 7.79 Hz, ^3J = 10.56 Hz, 1 H, 3-H), 2.76 (ddd, ^2J = 13.80 Hz, ^3J = 2.83 Hz, ^3J = 6.58 Hz, 1 H, 3-H), 2.91 (ddd, ^2J = 14.21 Hz, ^3J = 5.94 Hz, ^3J = 8.49 Hz, 1 H, 5-H), 3.00 [sept, *J* = 6.77 Hz, 1 H, C*H*$(CH_3)_2$], 3.25 (ddd, ^2J = 14.04 Hz, ^3J = 5.10 Hz, ^3J = 9.81 Hz, 1 H, 5-H,), 7.47−7.52 (m, 2 H, Ar-H), 7.60−7.75 (m, 1 H, Ar-H), 8.41−8.41 (m, 2 H, Ar-H). − ^{13}C NMR: δ = 23.59 (+, CH_3), 24.01 (−, C-4), 24.32 (+, CH_3), 36.27 (−, C-3), 37.11 [+, *C*H$(CH_3)_2$], 52.20 (−, C-5), 88.25 (0, C-2), 128.65 (+, 2 C_{ar}), 129.80 (+, 2 C_{ar}), 133.89 (0, C_{ar}-1), 134.13 (+, C_{ar}-4), 198.07 (0, CO).

Reaction of (1*R**,2*R**)-**1e** with PIFA did not yield any product.

Acknowledgments

This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

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Received September 15, 1998
[O98419]