Stereochemical Studies on the Halogenation of Sulfoxides. II. The Bromination of Cyclic Sulfoxides[1]

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The cyclic sulfoxides, thiane 1-oxide, 4-chlorothiane 1-oxides, and 4-phenylthiane 1-oxides, were brominated with a mixture of bromine and *N*-bromosuccinimide in the presence of pyridine. The stereoformulas of the products, together with those of the isomers with an inverted sulfoxide configuration, were determined by means of the IR and NMR spectral data and by a comparison of the R_f-values in the tlc. As a result, it has been revealed that the bromination reaction gives products in which a bromine atom is introduced stereospecifically at a *trans*-position to the sulfinyl lone pair, in a manner similar to that of the chlorination reaction reported previously. The same mechanism as in the chlorination is proposed for the main reaction course.

The α-halogenation of sulfoxides with the halogenating agents in the presence of base is known to be a stereoselective reaction.[2,3] In the preceding paper[4] we have reported on the chlorination of the cyclic sulfoxides with *t*-butyl hypochlorite, sulfuryl chloride, and chlorine in the presence of potassium acetate or pyridine. In the present paper we would like to describe our stereochemical study on the bromination of the cyclic sulfoxides,[4] thiane 1-oxide, *cis*- or *trans*-4-chlorothiane 1-oxide, and *cis*- or *trans*-4-phenylthiane 1-oxide, with a mixture of bromine and *N*-bromosuccinimide[5] in the presence of pyridine.

Results and Discussion

Bromination of Thiane 1-Oxide. The bromination of six-membered thiane 1-oxide (**1**) with a mixture of 0.5 equiv of bromine and 1.0 equiv of *N*-bromosuccinimide[5] in the presence of pyridine in dichloromethane produced, stereospecifically, *cis*-2-bromothiane 1-oxide(**2**) (mp 61—62°C) (Fig. 1) in an 80% yield. The inversion of the sulfoxide configuration of **2** with triethyloxonium tetrafluoroborate (Et_3OBF_4)[6] furnished *trans*-2-bromothiane 1-oxide(**3**) (mp 59.5—60°C) in a 68% yield.

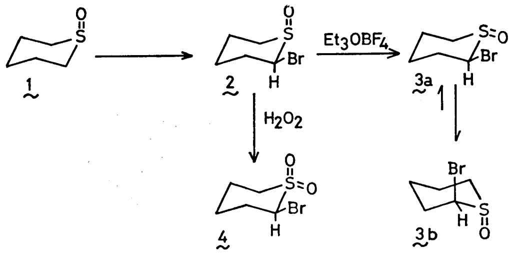

Fig 1.

The stereoformulas of **2** and **3** were determined in the same way as the corresponding chloro-derivatives described in the preceding paper:[4] the aromatic solvent-induced shifts (ASIS; $\Delta=\delta_{CCl_4}-\delta_{C_6H_6}$) are also a useful method in determining the stereoformulas of sulfoxides. Since a proton *trans* to the sulfinyl oxygen is more shielded and has a larger Δ-value than a proton *cis* to the sulfinyl oxygen, the product obtained by bromination, which has a larger Δ-value (Δ=0.64)(Table 1), should possess a *cis*-form (**2**), while the inverted isomer, with a smaller Δ-value (Δ=0.43), should possess a *trans*-form (**3**). This assignment was supported by the following facts: the H–C_2 of **3** was observed as axial in the polar solvents (CD_3OD, D_2O, CF_3COOH, and CD_3SOCD_3) and as equatorial rather than axial in the nonpolar solvents (CCl_4, $CDCl_3$, and C_6H_6), whereas the H–C_2 of **2** was always observed as axial, regardless of whether the solvent was polar or not(Table 1). This observation can be explained as follows. The product (**2**) has a thermodynamically stable *cis*-form possessing a preferable axial sulfinyl oxygen and equatorial bromine. On the other hand, since **3** has an unstable *trans*-form, its conformation changes with the solvent polarity;

TABLE 1. NMR SPECTRAL DATA OF H–C_2 OF 2-BROMOTHIANE 1-OXIDES(**2** AND **3**). $\Delta=\delta_{CCl_4}-\delta_{C_6H_6}$

Solvent	**2**	**3**
CCl_4	5.14 q(ax) J=3.5, 9	4.78 m(eq)
C_6H_6	4.50 oct(ax) J=1, 3, 9.5	4.35 m(eq)
$CDCl_3$	5.09 oct(ax) J=1, 3.5, 8	4.76 m(eq)
CD_3OD	—	4.93 oct(ax) J=1, 3.2, 7.4
CD_3CN	5.13 oct(ax) J=1, 3.5, 9.5	—
CD_3SOCD_3	—	5.12 q(ax) J=3.5, 7.5
D_2O	5.84 oct(ax) J=0.5, 4, 8.5	5.43 q(ax) J=3.5, 8.3
CF_3COOH	5.37 oct(ax) J=1.6, 3.4, 7	5.09 q(ax) J=3, 7.2
Δ	0.64	0.43

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[1] G. Tsuchihashi, S. Iriuchijima, and M. Ishibashi, Abstracts of the Third International Congress of Heterocyclic Chemistry: B, Sendai, Japan(1971), p. 624.

[2] M. Cinquini, S. Colonna, and F. Montanari, *Chem. Commun.*, **1969**, 607. M. Cinquini and S. Colonna, *Boll. Sci. Fac. Chim. Ind. Bologna*, **27**, 201 (1969).

[3] S. Iriuchijima and G. Tsuchihashi, *Tetrahedron Lett.*, **1969**, 5259.

[4] S. Iriuchijima, M. Ishibashi, and G. Tsuchihashi, This Bulletin, **46**, 921 (1973).

[5] S. Iriuchijima and G. Tsuchihashi, *Synthesis*, **1970**, 588.

[6] C. R. Johnson and D. McCants, Jr., *J. Amer. Chem. Soc.*, **87**, 5404 (1965).

Table 2. NMR spectral data of H-C_2 and H-C_4 of 2-bromo-4-chlorothiane 1-oxides(**6**, **7**, **9**, and **10**)

	6		**7**		**9**		**10**	
	H-C_2	H-C_4	H-C_2	H-C_4	H-C_2	H-C_4	H-C_2	H-C_4
δ_{CCl_4}	5.10 ax	4.47 eq	4.87 eq	4.17 ax	4.51 ax	3.80 ax	4.90 ax	4.16 ax
$\delta_{C_6H_6}$	4.57	3.63	4.17	—	3.56	—	4.20	3.28
Δ	0.53	—	0.70	—	0.95	—	0.70	—

the polar conformation, **3a**, is favored in the polar solvents, while the less polar conformation, **3b**, dominates in the non-polar solvents. Moreover, the fact that, in thin-layer chromatography, **3** was found at a higher position than **2** indicates that **3** has a less polar structure than **2**. The possibility that **3**, which might be formed by the bromination of **1**, was isomerized to the stable isomer (**2**) during the reaction was excluded by the fact that **2** was not produced when **3** was kept under the bromination conditions for 3 hr.

The halogenation of **1** in the presence of base[7] proved to give, stereospecifically, the *cis*-halogenated product in both chlorination[4] and bromination.

The hydrogen peroxide oxidation of **2** in acetic acid gave 2-bromothiane 1,1-dioxide (**4**) (mp 89—90°C), in a 95% yield.

Bromination of 4-Chlorothiane 1-Oxide. The bromination of *trans*-4-chlorothiane 1-oxide(**5**) afforded, stereospecifically, 2e-bromo-4a-chlorothiane 1a-oxide(**6**) (Fig. 2) (mp 48—49°C) in an 81% yield. The bromination of *cis*-4-chlorothiane 1-oxide (**8**), however, furnished, in an 85% yield, a 20 : 80 mixture of **6** and 2e-bromo-4e-chlorothiane 1a-oxide (**9**) (mp 102—103°C). This fact indicates that **8** is brominated, mainly, not *via* **5** but *via* the ring inversion, unlike as in the chlorination with *t*-butyl hypochlorite in the presence of potassium acetate.[4] The competitive bromination of **5** and **8** showed that **8** is brominated approximately five times faster than **5**. This is a somewhat unexpected result, which remains unexplained.

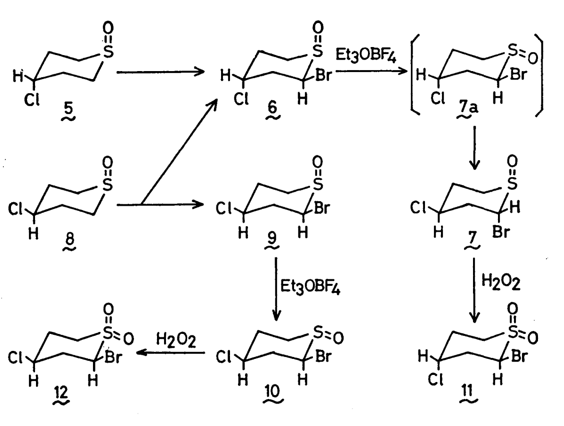

Fig. 2.

The products, **6** and **9**, were transformed with Et_3OBF_4 to 2a-bromo-4e-chlorothiane 1a-oxide (**7**) (mp 73.5—75°C) in an 86% yield and 2e-bromo-4e-chlorothiane 1e-oxide (**10**) (mp 93—94.5°C) in an 85% yield respectively.

The stereochemical structures of **6**, **7**, **9**, and **10** were established by means of the NMR coupling constants of H–C_2 and H–C_4, ASIS shown in Table 2 (the isomer **9** is expected to have the largest Δ-value), and the behavior on a thin-layer plate; the compound **7** was observed higher, than **6** and **9** which were themselves higher than **10**. According to the axial-equatorial sulfinyl oxygen rule,[8] the compound **9**, which possesses an axial oxygen, is expected to be higher on a thin-layer plate than **10**, which possesses an equatorial one.

The oxidation of **7** and **10** with hydrogen peroxide in acetic acid yielded *trans*-2-bromo-4-chlorothiane 1,1-dioxide (**11**) (mp 105—108°C) in a 93% yield and *cis*-2-bromo-4-chlorothiane 1,1-dioxide (**12**) (mp 124—125°C) in a 93.5% yield respectively.

Bromination of 4-Phenylthiane 1-Oxides. The bromination of conformationally rigid *trans*-4-phenylthiane 1-oxide (**13**) with a mixture of bromine (0.5 equiv) and NBS(1.0 equiv) for 0.5 hr furnished, in an 86% yield, a 63 : 37 mixture of 2a-bromo-4e-phenylthiane 1e-oxide (**14**) (mp 143—144°C) and 2e-bromo-4e-phenylthiane 1a-oxide (**15**) (mp 132—133°C), while *cis*-4-phenylthiane 1-oxide (**18**) with bromine (0.5 equiv) and NBS (2.2 equiv) for 23 hr afforded, in only a 48.5% yield, a 81 : 19 mixture of **14** and **15** (Fig. 3), with a 44% recovery of **18**. This fact, indicating that **13** is much more easily brominated than **18**, is in agreement with the result of the competitive bromination that **13** is brominated approximately five times faster than **18**. The bromination of both **13** and **18** produced an all-*cis* product

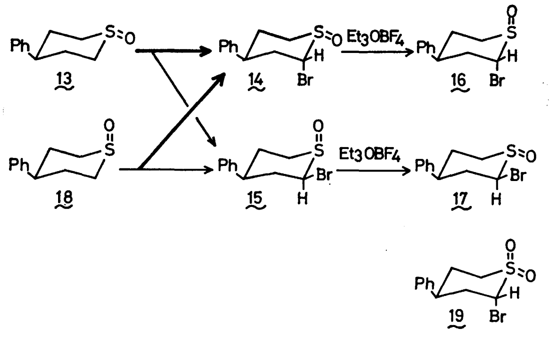

Fig. 3.

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[7] In the absence of base, non-stereoselectivity was observed. K.-C. Tin and T. Durst, *Tetrahedron Lett.*, **1970**, 4643.

[8] A sulfoxide which possesses an axial oxygen is observed higher on a thin-layer plate than a sulfoxide which possesses an equatorial one, when the other part of their structures is the same.[4]

Table 3. NMR spectral data of H-C_2 of 2-bromo-4-phenylthiane 1-oxides(**14**, **15**, **16**, and **17**)

	14	**15**	**16**	**17**
δ_{CCl_4}	5.23 eq	4.71 ax	4.86 ex	4.61 ax
$\delta_{C_6H_6}$	4.80	4.16	4.42	4.30
Δ	0.43	0.55	0.44	0.31

(**15**) as a minor component, while the corresponding chloro-derivative was never detected in the chlorination.[4]

The products, **14** and **15**, were isomerized with Et_3OBF_4 to 2a-bromo-4e-phenylthiane 1a-oxide (**16**) (mp 93°C) in an 83% yield and 2e-bromo-4e-phenylthiane 1e-oxide (**17**) (mp 133—143°C) in a 59% yield respectively. The assignment of the stereoformulas of **14**, **15**, **16**, and **17**, is based on the NMR spectral data shown in Table 3 (the isomer **15** is expected to have the largest Δ-value) and the comparison of the R_f-values in the tlc: the isomer **16** was observed higher than **15**, which was itself higher than **14** and **17** on a thin-layer plate; according to the rule (see above), the isomer **16** which possesses an axial sulfinyl oxygen is expected to be higher than **14** which possesses an equatorial oxygen, and **15** is expected to be higher than **17** as well.

The inverted isomer **16** was not isomerized to **14** when it was placed in the bromination condition. Moreover, since the both compounds **14** and **16** were recovered unchanged after treatment with concentrated hydrochloric acid(1 vol) in dioxane(2 vol),[9] they are configurationally-stable compounds.

The oxidation of **14** gave *trans*-2-bromo-4-phenylthiane 1,1-dioxide(**19**) (mp 149—151°C) in an 82.5% yield.

*Mechanism of the Bromination with Bromine/*N*-Bromosuccinimide in the Presence of Pyridine.* The bromination of the thiane 1-oxides(**1**, **5**, **8**, **13**, and **18**) with bromine/NBS in the presence of pyridine proved to give products in which bromine was introduced at a *trans*-position to the sulfinyl lone pair, mainly in the same manner as in the chlorination.[4] Consequently, the mechanism postulated for the chlorination[4] is also applicable to the bromination reaction as shown in Fig. 4; the bromo-oxosulfonium ion (**21**), which is formed by the attack of a positive bromine of a bromine molecule on the sulfinyl lone pair, gives the ylid (**22**) by the action of the bromide ion, and then **22** gives rise to the hypothetical intermediate (**23**) by the elimination of the bromide ion. The final step is the addition of the bromide ion to **23**, producing the α-bromosulfoxides (**24**), in which the bromine atom and sulfinyl lone pair are in a *trans* relationship.

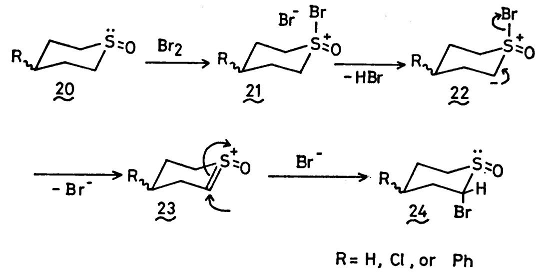

Fig. 4.

Experimental

Unless otherwise stated, the NMR spectra were measured with a Varian HA-100 spectrometer (100 MHz) and/or a Hitachi R/20B spectrometer (60 MHz) in a concentration of 40—50 mg in 0.4 ml of $CDCl_3$, while the IR spectra were recorded with Nujol mull using a Hitachi EPI-G3 spectrometer. In the NMR spectral data, *J*(coupling constant) is expressed in Hz, and HHW means a half-height width or the sum of the coupling constants. In the crystallization solvents, B, C, and H stand for benzene, cyclohexane, and hexane respectively, and the expressions B/C/H, *etc.* mean that the crystallization was carried out by dissolution in benzene, followed by the successive addition of cyclohexane and hexane.

*Bromination of Thiane 1-Oxide (**1**) to* cis*-2-Bromothiane 1-Oxide (**2**).* A solution of Br_2(0.6 g, 3.75 mmol) in 5 ml of CH_2Cl_2 and *N*-Bromosuccinimide (NBS) (1.34 g, 7.5 mmol) was added to a stirred solution of **1** (0.89 g, 7.55 mmol) and pyridine (0.61 ml, 7.6 mmol) in 30 ml of CH_2Cl_2. After stirring at room temperature for 1 hr, 30 ml of water, 10 ml of a 1M aqueous Na_2CO_3 solution, and 10 ml of a 1M Na_2SO_3 solution were added; the mixture was then extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4 and then concentrated to an oily residue which was subsequently chromatographed on silica gel with benzene. Elution with benzene containing 2—5% ethyl acetate afforded 1.20 g (0.608 mmol; 80.5%) of the white crystals (**2**). Recrystallization from B/C/H gave mp 61—62°C. IR: 697, 946, 953, 1002, 1040 (S=O), 1058, 1068 cm^{-1}. IR (5% in CS_2): 700, 1078 (S=O) cm^{-1}. NMR: 1.2—3.4(8H), 5.09 (1H, octet, *J*=1, 3.5, 8). NMR (CCl_4): 1.3—3.1 (8H), 5.14(1H, q, *J*=3.5, 9). NMR(C_6H_6): 0.6—2.8 (8H), 4.50(1H, octet, *J*=1, 3, 9.5). NMR(CD_3CN): 5.13 (1H, octet, *J*=1, 3.5, 9.5). NMR(HCOOH): 1.5—3.5(8H), 5.40(1H, octet, *J*=1, 3.8, 8). NMR(D_2O): 2.0—3.7(8H), 5.84(1H, octet, *J*=0.5, 4, 8.5). NMR(CF_3COOH): 1.5—3.55(8H), 5.37(1H, octet, *J*=1.6, 3.4, 7). Mass: *m/e* 196(M^+), 117(base peak). Found: C, 30.59; H, 4.58; Br, 40.49%. Calcd for C_5H_9BrOS: C, 30.47; H, 4.60; Br, 40.54%.

*Transformation of **2** to* trans*-2-Bromothiane 1-Oxide(**3**).* To a stirred solution of **2** (0.885 g; 4.5 mmol) in CH_2Cl_2 (5 ml) *ca.* 1.5 g (7.9 mmol) of triethyloxonium tetrafluoroborate (Et_3OBF_4) was added. After the mixture had been stirred at room temperature for 1 hr, 40 ml of anhydrous ether was added at 0°C to give the oily ethoxysulfonium salt as a precipitation. After standing for 2 hr, the solvents were removed by decantation, and to the residue was added 20 ml of a 0.5M NaOH solution. The mixture was then extracted with CH_2Cl_2. The solvent was dried over Na_2SO_4 and evaporated to the residue, which was then chromatographed on silica gel with benzene. Elution with benzene containing 2% ethyl acetate yielded 0.60 g (3.06 mmol; 67.8 %) of a colorless oil (**3**) which was crystallized on standing. Recrystallizations from B/C/H at 0°C gave mp 59.5—60°C. **3** was detected with iodine higher than **2** on a thin-layer plate, using ethyl acetate: 95% ethanol (95 : 5). IR: 1016, 1023, 1050(S=O) cm^{-1}. IR(2% in CS_2): 1059 cm^{-1}.

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[9] K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **86**, 1452 (1964).

IR(CCl$_4$): 1058 cm^{-1}. NMR: 1.4—3.6(8H), 4.76(1H, m, HHW=10.5). NMR(CCl$_4$): 1.4—3.45(8H), 4.78(1H, m, HHW=9). NMR(CS$_2$): 1.35—3.45(8H), 4.70(1H, m, HHW=9). NMR(C$_6$H$_6$): 0.7—2.95(8H), 4.35(1H, m, HHW=10). NMR(Et$_3$N): 4.98 (1H, m, HHW=10). NMR(Et$_2$O): 4.88(1H, m, HHW=8.5). NMR(pyridine): 1.1—3.5(8H), 5.08(1H, octet, J=1, 3.2, 6.3). NMR(CF$_3$COOH): 1.5—4.0(8H), 5.09(1H, q, J=3, 7.2). NMR (CD$_3$SOCD$_3$): 1.3—3.5, 5.12(1H, q, J=3.5, 7.5). NMR(CD$_3$OD): 1.4—3.5, 4.93(1H, octet, J=1, 3.2, 7.4). NMR(CD$_3$COCD$_3$): 1.45—3.4, 4.91(1H, octet, J=1.2, 3, 7). NMR(D$_2$O): 1.9—4.12, 5.43 (1H, q, J=3.5, 8.3). Mass: *m/e* 196(M$^+$), 117(base peak). Found: C, 30.48; H, 4.59; Br, 40.27%. Calcd for C$_5$H$_9$BrOS: C, 30.47; H, 4.60; Br, 40.54%.

*Oxidation of **2** to 2-Bromothiane 1,1-Dioxide (**4**).* A solution of **2** (0.89 g; 4.51 mmol) and 30% H$_2$O$_2$(1 ml; 10 mmol) in acetic acid (10 ml) was kept at 45°C for 15 hr. The subsequent addition of water (40 ml) gave crystals which were then filtered off and recrystallized from B/C/H to yield 0.92 g (4.3 mmol; 95%) of **4**. Recrystallization from the same solvents gave mp 89—90°C. IR: 1122, 1155, 1279, 1309 cm^{-1}. NMR: 1.3—3.8 (8H), 4.82(1H, octet, J=2, 4, 8). Mass: *m/e* 212 (M$^+$), 41(base peak). Found: C, 28.19; H, 4.28; Br, 37.46%. Calcd for C$_5$H$_9$BrO$_2$S: C, 28.18; H, 4.26; Br, 37.50%.

Bromination of trans-*4-Chlorothiane 1-Oxide(**5**) to 2e-Bromo-4e-chlorothiane 1a-Oxide (**6**).* To a stirred solution of **5** (347 mg; 2.28 mmol) and pyridine (0.2 ml; 2.5 mmol) in CH$_2$Cl$_2$ (20 ml) were added NBS (405 mg; 2.28 mmol) and a solution of Br$_2$(0.18 g; 1.14 mmol) in CH$_2$Cl$_2$ (5 ml). The mixture was then stirred at room temperature for 22 hr. The usual work-up gave a residue, which was subsequently chromatographed on silica gel with benzene. Elution with benzene containing 4% ethyl acetate afforded 0.43 g (1.86 mmol; 81.5%) of the white crystals (**6**), which were then recrystallized from B/C at 0°C to give mp 48—49°C. IR: 965, 1031(S=O) cm^{-1}. IR (2% in CS$_2$): 982, 1073 (S=O) cm^{-1}. NMR: 1.7—3.35 (6H), 4.48 (1H, m, HHW=9), 5.13 (1H, q, J=3.6, 11). NMR (CCl$_4$): 1.82—3.40 (6H), 4.47 (1H, m, HHW=9), 5.10 (1H, q, J=3.3, 11.5). NMR (C$_6$H$_6$): 1.03—1.45 (1H), 1.78—2.4 (4H), 2.54—2.85 (1H), 3.63 (1H, m, HHW=9), 4.57 (1H, q, J=3.2, 11.2). NMR (CF$_3$COOH): 1.92—3.67 (6H), 4.53 (1H, m, HHW=9.5), 5.38 (1H, m, HHW=19). Mass: *m/e* 230 (M$^+$), 151 (base peak). Found: C, 26.43; H, 3.59; S, 13.76%. Calcd for C$_5$H$_8$BrClOS: C, 25.94; H, 3.48; S, 13.85%.

45 mg (13.0%) of **5** was recovered by elution with benzene: ethyl acetate (9 : 1).

*Transformation of **6** to 2a-Bromo-4e-chlorothiane 1a-Oxide (**7**).* To a stirred solution of **6** (365 mg; 1.58 mmol) in CH$_2$Cl$_2$ (5 ml) was added 0.45 g (2.37 mmol) of Et$_3$OBF$_4$, and the mixture was then stirred at room temperature for 1 hr. The addition of anhydrous ether (40 ml) gave rise to a white solid as a precipitation. The solvent was removed by decantation, and to the residue a 0.2M NaOH solution (25 ml) was added. The mixture was extracted with CH$_2$Cl$_2$. The evaporation of the solvent afforded an oil which was subsequently crystallized from B/C/H at −20°C to give 315 mg (86.6%) of **7**. Recrystallizations gave mp 73.5—75°C. IR: 762, 832, 870, 921, 1012, 1023, 1054 (S=O) cm^{-1}. IR (5% in CS$_2$): 970, 1022, 1064 (S=O) cm^{-1}. NMR: 2.0—3.44 (6H), 4.24 (1H, nonet, J=4, 4, 10, 10), 4.88 (1H, m, HHW=10). NMR (CCl$_4$): 1.95—3.38 (6H), 4.17 (1H, nonet, J=4, 4, 11, 11), 4.87 (1H, m, HHW=9.5). NMR (C$_6$H$_6$): 3.66 (1H, m, HHW=29.5), 4.17 (1H, m, HHW=9.5). NMR (CF$_3$COOH): 2.1—3.77 (6H), 4.33 (1H, septet, J=*ca.* 4, 4, 8, 8), 5.29 (1H, q, J=3.4, 7.4). NMR (CD$_3$OD): 2.0—3.72 (6H), 4.39 (1H, septet, J=*ca.* 4.3, 4.3, 8.6, 8.6), 5.19 (1H, m, HHW=10). NMR (CD$_3$CN): 1.85—3.60 (6H), 4.37 (1H, septet, J=4.3, 4.3, 8.6, 8.6), 5.02 (1H, m, HHW=10.5). Mass: *m/e* 230 (M$^+$). Found: C, 25.93; H, 3.56; S, 13.95%. Calcd for C$_5$H$_8$BrClOS: C, 25.94; H, 3.48; S, 13.85%.

Bromination of cis-*4-Chlorothiane 1-Oxide (**8**).* To a stirred solution of **8** (0.42 g, 2.75 mmol) and pyridine (0.33 ml, 4.1 mmol) in CH$_2$Cl$_2$ (10 ml) were added bromine (0.22 g, 1.38 mmol) and *N*-bromosuccinimide (0.49 g, 2.75 mmol). The mixture was stirred at room temperature for 6 hr. The NMR spectrum of the extract after the usual work-up showed it to be a 80 : 20 mixture of 2e-bromo-4e-chlorothiane 1a-oxide (**9**) and **6**. Crystallization from CHCl$_3$/B/C/H at 0°C gave 0.39 g (1.684 mmol; 61.2%) of **9**. The chromatography of the mother liquor gave 46 mg of **6** and 104 mg of a mixture of **6** and **9**, by elution with benzene containing 2% ethyl acetate. **6** was identified by mp, IR, and NMR. The total yield of **6** and **9** became 84.7%. Recrystallization of **9** from B/C gave mp 102—103°C (decompn.). IR: 681, 925, 1010, 1042, 1059 (S=O) cm^{-1}. IR (0.6% in CS$_2$): 917, 1079, 1086 (S=O) cm^{-1}. NMR: 1.95—3.38 (6H), 3.91 (1H, m, axial H), 4.68 (1H, q, J=4, 12). NMR (15 mg in 0.4 ml C$_6$H$_6$): 3.56 (1H, q, J=3, 12), NMR (CF$_3$COOH): 2.25—3.35 (5H), 3.61 (1H, sextet, J=3.5, 3.5, 15), 4.01 (1H, m, HHW=30, axial H), 4.90 (1H, q, J=7.2, 8.8). NMR (5 mg in 0.4 ml CCl$_4$+0.1 ml CDCl$_3$): 3.80 (1H, m, axial H), 4.51 (1H, q, J=4, 12). Mass: *m/e* 230 (M$^+$), 151 (base peak). Found: C, 26.04; H, 3.64; S, 13.74%. Calcd for C$_5$H$_8$BrClOS: C, 25.94; H, 3.48; S, 13.85%.

*Transformation of **9** to 2e-Bromo-4e-chlorothiane 1e-Oxide (**10**).* A solution of **9** (0.33 g, 1.43 mmol) and 0.42 g (2.2 mmol) of Et$_3$OBF$_4$ in CH$_2$Cl$_2$ (5 ml) was stirred at room temperature for 1 hr. The usual work-up and chromatography gave 282 mg (85.5%) of **10**, eluted with benzene containing 2% ethyl acetate. Recrystallization from B/C/H gave mp 93—94.5°C. IR: 490, 643, 674, 850, 931, 1051 (S=O) cm^{-1}. IR (1% in CS$_2$): 988, 1063 (S=O), 1078 cm^{-1}. NMR: 1.87—3.19 (5H), 3.53 (1H, octet, J=3, 7, 13), 4.12 (1H, nonet, J=4, 4, 9.5, 9.5), 4.65 (1H, q, J=3.6, 10). NMR (25 mg in CCl$_4$ 0.4 ml): 1.82—3.14 (5H), 3.40 (1H, octet, J=3, 7, 12.5), 4.16 (1H, nonet, J=4, 4, 9.5, 9.5), 4.90 (1H, q, J=4, 10.5). NMR (C$_6$H$_6$): 1.11—2.52 (5H), 2.71 (1H, octet, J=3, 6, 13), 3.28 (1H, nonet, J=4, 4, 10, 10), 4.20 (1H, q, J=4, 11). NMR (CF$_3$COOH): 1.95—3.40 (5H), 3.80 (1H, octet, J=3, 5.7, 13), 4.11 (1H, nonet, J=4, 4, 10.5, 10.5), 5.02 (1H, q, J=3.8, 11.5). Mass: *m/e* 230 (M$^+$). Found: C, 26.12; H, 3.56; S, 13.84%. Calcd for C$_5$H$_8$BrClOS: C, 25.94; H, 3.48; S, 13.85%.

*Oxidation of **7** to* trans-*2-Bromo-4-chlorothiane 1,1-Dioxide(**11**).* A solution of **7** (0.26 g, 1.12 mmol) and 30% hydrogen peroxide (0.3 ml, 2.94 mmol) in 3 ml of acetic acid was kept at 45°C for 15 hr. The subsequent evaporation and crystallization from B/C gave 257 mg (1.04 mmol; 92.7%) of **11**. Recrystallization from B/C gave mp 105—108°C. IR: 485, 718, 1004, 1119, 1143, 1155, 1288, 1313 cm^{-1}. NMR: 2.1—3.1 (4H), 3.15—3.85 (2H), 4.47 (1H, quintet, J=*ca.* 4, 4, 4, 4), 5.08 (1H, q, J=6, 8.2). Mass: *m/e* 246 (M$^+$), 131 (base peak). Found: C, 24.32; H, 3.50; S, 13.10%. Calcd for C$_5$H$_8$BrClO$_2$S: C, 24.26; H, 3.26; S, 12.95%.

*Oxidation of **10** to* cis-*2-Bromo-4-chlorothiane 1,1-Dioxide(**12**).* A solution of **10** (83 mg, 0.354 mmol) and 30% H$_2$O$_2$ (0.1 ml, 1 mmol) in 3 ml of acetic acid was kept at 45°C for 15 hr. The subsequent evaporation of the solvent afforded white crystals, which were recrystallized from B/C/H to give 82 mg (0.33 mmol; 93%) of **12**. The recrystallization gave mp 124—125°C. IR: 1139, 1280, 1320 cm^{-1}. NMR: 2.05—3.70 (6H), 4.14 (1H, m, HHW=30.5), 4.83 (1H, q, J=5.1, 11.1). Mass: m/e 246 (M$^+$). Found: C, 24.23; H, 3.29; S, 12.89%. Calcd for $C_5H_8BrClO_2S$: C, 24.26; H, 3.26; S, 12.95%.

Bromination of trans-*4-Phenylthiane 1-Oxide (**13**).* To a stirred solution of **13** (0.36 g, 1.85 mmol) and pyridine (0.23 ml, 2.8 mmol) in 10 ml of CH_2Cl_2 were added Br_2 (0.15 g, 0.94 mmol) and NBS (0.48 g, 2.7 mmol). The mixture was stirred at room temperature for 30 min. The NMR spectrum of the crystalline residue, obtained by the usual work-up, showed it to be 63 : 37 mixture of 2a-bromo-4e-phenylthiane 1e-oxide (**14**) and 2e-bromo-4e-phenylthiane 1a-oxide (**15**). Crystallization from B/CCl_4 followed by recrystallization from B/C/H gave 0.12 g (0.44 mmol; 23.7%) of **14**. Recrystallizations from B/C/H gave mp 143—144°C. IR: 710, 771, 1065 cm^{-1}. NMR: 1.7—3.4 (7H), 5.39 (1H, m, HHW=9), 7.20 (5H, m). NMR (C_6H_6): 1.0—3.2 (7H), 4.80 (1H, m, HHW=9). NMR (3 mg in 0.4 ml CCl_4): 5.23 (1H, m, HHW=8). Mass: m/e 272 (M$^+$), 193 (base peak). Found: C, 48.30; H, 4.77; S, 11.78%. Calcd for $C_{11}H_{13}BrOS$: C, 48.36; H, 4.80; S, 11.74%.

The combined mother liquors were chromatographed with benzene. Elution with benzene containing 1% ethyl acetate furnished 0.157 g (0.574 mmol; 31%) of **15**, and then 0.158 g (0.578 mmol; 31.2%) of **14**. Recrystallizations of the former (**15**) from B/C gave mp 132—133.5°C. IR: 699, 751, 921, 1011, 1037, 1055 cm^{-1}. NMR: 1.7—3.35 (7H), 4.77 (1H, q, J=3.5, 12.2), 7.20 (5H, m). NMR (C_6H_6): 0.8—3.4 (7H), 4.16 (1H, q, J=3.2, 12). NMR (6 mg in 0.4 ml CCl_4): 4.71 (1H, q, J=3.5, 12). Mass: m/e 272 (M$^+$). Found: C, 47.84; H, 4.84; S, 11.75%. Calcd for $C_{11}H_{13}BrOS$: C, 48.36; H, 4.80; S, 11.74%.

Bromination of cis-*4-Phenylthiane 1-Oxide (**18**).* *(a) With 1.0 equiv of NBS*: A solution of **18** (0.25 g, 1.29 mmol), pyridine (0.21 ml, 2.6 mmol), Br_2 (0.1 g, 0.64 mmol), and NBS (0.23 g, 1.29 mmol) in 10 ml of CH_2Cl_2 was stirred for 3 hr at room temperature. Chromatography after the usual work-up gave 128 mg (0.47 mmol; 36.0%) of a 77 : 23 mixture of **14** and **15**, eluted with benzene containing 1—2% ethyl acetate, and 0.15 g (60%) of **18** containing *ca.* 5% of **13** eluted with benzene–ethyl acetate (1 : 1).

(b) With 2.2 equiv of NBS: To a stirred solution of **18** (0.42 g, 2.16 mmol) and pyridine (0.26 ml, 3.24 mmol) in 10 ml of CH_2Cl_2, were added Br_2(0.17 g, 1.06 mmol) and NBS (0.46 g, 2.58 mmol). After the mixture had then been stirred at room temperature for 18 hr, more NBS (385 mg, 2.16 mmol) and pyridine (0.26 ml, 3.24 mmol) were added and the reaction was continued for 5 hr. The NMR spectrum of the extract from the usual work-up showed that a 81 : 19 mixture of **14** and **15** was obtained. Chromatography gave 45 mg (0.165 mmol; 7.6%) of **15**, with benzene containing 1% ethyl acetate, and then 0.245 g (0.90 mmol; 41.5%) of **14**, with 1—4% ethyl acetate. **14** and **15** were identified by mp, IR, NMR, and tlc. 185 mg (44.0%) of **18** was recovered by the elution of benzene containing 5% methanol.

*Transformation of **14** to 2a-Bromo-4e-phenylthiane 1a-Oxide (**16**).* A solution of **14** (0.38 g, 1.39 mmol) and 0.53 g (2.8 mmol) of Et_3OBF_4 in 5 ml of CH_2Cl_2 was stirred at room temperature for 30 min. The addition of ether at 0°C gave a crystalline ethoxysulfonium salt, which was decomposed with 20 ml of a 0.2M NaOH solution and extracted with CH_2Cl_2. The chromatography of the extract afforded 315 mg (1.15 mmol; 82.8%) of **16** with 1% ethyl acetate in benzene. Recrystallizations from B/H gave mp 93°C. IR: 703, 750, 1016, 1049 cm^{-1} (S=O) cm^{-1}. NMR: 1.65—3.50 (7H), 4.91 (1H,m, HHW=7), 7.23 (5H, m). NMR (C_6H_6): 0.95—3.15 (7H), 4.42 (1H, m, HHW=7.5). NMR (CCl_4): 1.55—3.41 (7H), 4.86 (1H, m, HHW=7), 7.18 (5H, s), NMR (CF_3COOH): 1.7—4.0 (7H), 5.29 (1H, m, HHW =7). Found: C, 48.51; H, 4.92; S, 11.67%. Calcd for $C_{11}H_{13}BrOS$: C, 48.36; H, 4.80; S, 11.74%.

*Transformation of **15** to 2e-Bromo-4e-phenylthiane 1e-Oxide (**17**).* A solution of **15** (205 mg, 0.75 mmol) and Et_3O-BF_4 (285 mg, 1.5 mmol) in 3 ml of CH_2Cl_2 was stirred at room temperature for 1 hr. The usual work-up furnished a crystalline extract, which was subsequently recrystallized from B/H to give 0.12 g (59%) of **17**. Several recrystallizations from B/H gave mp 133—143°C (decompn.). IR: 703, 750, 1016, 1049 (S=O) cm^{-1}. NMR: 1.8—3.2 (6H), 3.60 (1H, sextet, J=3.6, 3.6, 13), 4.74 (1H, q, J=4, 11.3), NMR (3 mg in 0.4 ml CCl_4+0.05 ml $CDCl_3$): 4.61 (1H, q, J=4, 12). NMR (5 mg in 0.4 ml C_6H_6): 4.30 (1H, q, J=4, 12). Found: C, 47.76; H, 4.87; S, 11.66%. Calcd for $C_{11}H_{13}BrOS$: C, 48.36; H, 4.80; S, 11.74%.

*Oxidation of **14** to* trans-*2-Bromo-4-phenylthiane 1,1-Dioxide (**19**).* A solution of **14** (0.24 g, 0.88 mmol) and 0.2 ml (2.0 mmol) of 30% H_2O_2 in 5 ml of acetic acid was kept at 50°C for 15 hr. The subsequent evaporation of the solvent followed by passage through silica gel with benzene, gave 0.21 g (0.725 mmol; 82.5%) of **19**. Recrystallization from B/H gave mp 149—151°C (sintered at 144°C). IR: 1110, 1287, 1314 cm^{-1}. NMR: 1.93—3.87 (7H), 4.85 (1H, q, J=3.2, 6.4), 7.22 (5H, m). Mass: m/e 288 (M$^+$), 209 (base peak). Found: C, 45.80; H, 4.60; S, 11.14%. Calcd for $C_{11}H_{13}BrO_2S$: C, 45.68; H, 4.53; S, 11.09%.

*Competitive Bromination of **13** and **18**.* A solution of **13** (197 mg), **18** (180 mg), pyridine (0.12 ml, 1.5 mmol), Br_2 (80 mg, 0.5 mmol), and NBS (0.18 g, 1 mmol) in 10 ml of CH_2Cl_2 was stirred at room temperature for 40 min. The NMR spectrum of the residue, which had been obtained by the usual work-up, showed that **14** and **15** were obtained in a 65 : 35 ratio. Chromatography gave 53 mg of **15** and 125 mg of **14**, together with 243 mg of a 37 : 63 mixture of **13** and **18**. Accordingly, in this bromination reaction, 107 mg of **13** was consumed, while only 27 mg of **18** was used, showing that **13** is brominated approximately five times faster than **18**.

*Treatment of 2-Bromo-4-phenylthiane 1-Oxides (**14** and **16**) with Concentrated Hydrochloric Acid (1 vol) in Dioxane (**2** vol).*

*(a) **14***: To a stirred solution of **14** (117 mg) in 4 ml of dioxane, 2 ml of concentrated HCl were added. The mixture was then stirred at room temperature for 24 hr. After the usual work-up, **14** was recovered unchanged, as was confirmed by the NMR and mass spectra and by tlc.

*(b) **16***: A solution of **16** (53 mg) in 6 ml of the reagent was stirred at room temperature for 2 hr. After the usual work-up, **16** was recovered quantitatively, as estimated by means of the NMR spectrum and tlc.