Stereochemical Studies on the Halogenation of Sulfoxides. I. The Chlorination of Cyclic Sulfoxides[1]

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The cyclic sulfoxides, thiane 1-oxide, *cis*- or *trans*-4-chlorothiane 1-oxide, and *cis*- or *trans*-4-phenylthiane 1-oxide, were chlorinated with *t*-butyl hypochlorite, sulfuryl chloride, and chlorine in the presence of potassium acetate or pyridine. The stereoformulas of the products, together with those of the isomers having an inverted sulfoxide configuration, were determined by means of the IR and NMR spectral data and the R_f-values in the tlc. Consequently, it has been found that chlorination occurs when the sulfinyl oxygen is equatorial and that chlorine is always introduced at a *trans*-position to the sulfinyl lone pair to give rise to the *cis*-products. A mechanism accommodating these results is proposed. The conformation of the substituted thiane 1-oxide rings is also discussed.

The configurational stability of sulfoxides has been confirmed by the resolution of three sulfoxides,[2] and examples of geometrical isomerism attributable to the sulfinyl group has been reported.[3] Recently, a simple synthetic method of the optically active sulfoxides has been established,[4] and there has been much interest in the stereochemical aspects of sulfoxides.[5]

The α-halogenation of sulfoxides with halogenating agents in the presence of base is known to be a stereoselective reaction. For example, in the halogenation of benzyl methyl sulfoxide with iodobenzene dichloride or bromine in the presence of pyridine, it has been shown that the proton diastereotopic to the proton which is preferentially exchanged by deuterium in the presence of NaOD in D_2O is replaced with halogen stereospecifically.[6] The stereoselectivity was also observed in the chlorination of benzyl phenyl sulfoxide with *t*-butyl hypochlorite.[7]

In this and the following papers we would like to report on our stereochemical studies of the halogenation of the cyclic sulfoxides, designed to ascertain the stereochemical course of the reaction. The cyclic sulfoxides used were thiane 1-oxide, *cis*- or *trans*-4-chlorothiane 1-oxide,[8] and *cis*- or *trans*-4-phenylthiane 1-oxide.[9] The chlorination with *t*-butyl hypochlorite,[7] sulfuryl chloride,[10] and chlorine[11] in the presence of potassium acetate or pyridine will be described here, while the bromination with bromine/*N*-bromosuccinimide in the presence of pyridine[12] will be reported in the following paper.[13]

Results and Discussion

The Chlorination of Thiane 1-Oxide with t-*Butyl Hypochlorite.* The chlorination of six-membered thiane 1-oxide (**1**) with *t*-butyl hypochlorite in the presence of anhydrous potassium acetate in dichloromethane produced, stereospecifically, *cis*-2-chlorothiane 1-oxide (**2**) (Fig. 1) (mp 65.5—66.5°C) in an 88% yield. The inversion of the sulfoxide configuration of **2** with triethyloxonium tetrafluoroborate(Et_3OBF_4)[14] furnished *trans*-2-chlorothiane 1-oxide (**3**) (mp 43—44 °C) in a 74% yield.

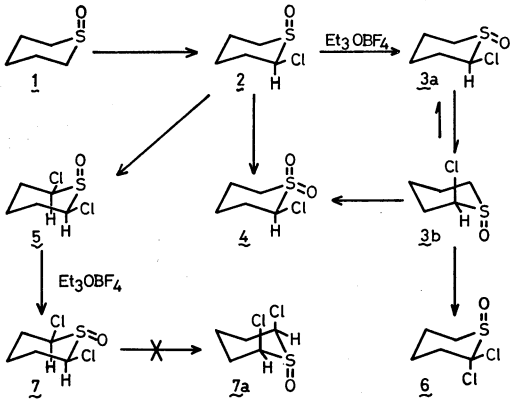

Fig. 1.

The stereoformulas of **2** and **3** were determined as follows. Aromatic solvent-induced shifts(ASIS; $\Delta = \delta_{CCl_4} - \delta_{C_6H_6}$), known as a useful method in deriving stereochemistry, are also applicable to the sulfoxides, as has been shown in the cases of penicillin sulfoxides,[15]

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2) P. W. B. Harrison, J. Kenyon, and H. Phillips, *J. Chem. Soc.*, **1926**, 2079.
3) E. V. Bell and G. M. Bennett, *ibid.*, **1927**, 1798.
4) K. K. Andersen, *J. Org. Chem.*, **29**, 1953 (1964).
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6) M. Cinquini, S. Colonna, and F. Montanari, *ibid.*, **1969**, 607 and M. Cinquini and S. Colonna, *Boll. sci. Fac. Chim. ind. Bologna*, **27**, 201 (1969).
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8) J. C. Martin and J. J. Uebel, *J. Amer. Chem. Soc.*, **86**, 2936 (1964).
9) B. J. Hutchinson, K. K. Andersen, and A. R. Katritzky, *ibid.*, **91**, 3839 (1969).
10) G. Tsuchihashi, K. Ogura, S. Iriuchijima, and S. Tomisawa, *Synthesis*, **1971**, 89.
11) G. Tsuchihashi and S. Iriuchijima, This Bulletin, **43**, 2271 (1970).
12) S. Iriuchijima and G. Tsuchihashi, *Synthesis*, **1970**, 588.
13) S. Iriuchijima and G. Tsuchihashi, This Bulletin, **46**, 929 (1973).
14) C. R. Johnson and D. McCants, Jr., *J. Amer. Chem. Soc.*, **87**, 5404 (1965).
15) R. D. G. Cooper, P. V. DeMarco, J. C. Cheng, and N. D. Jones, *ibid.*, **91**, 1408 (1969); R. D. G. Cooper, P. V. DeMarco, D. O. Spry, *ibid.*, **91**, 1528 (1969); D. H. R. Barton, F. Comer, and P. G. Sammes, *ibid.*, **91**, 1529 (1969).

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

Solvent	**2**	**3**
CCl_4	4.88 q(ax) J=3.2, 9.3	4.72 m(eq)
C_6H_6	4.23 q(ax) J=3.1, 9.6	4.29 m(eq)
$CDCl_3$	4.91 oct(ax) J=1, 3, 8	4.69 m(eq)
CD_3CN	4.95 oct(ax) J=1, 3.3, 10	—
D_2O	5.71 oct(ax) J=1, 4, 8.3	5.36 q(ax) J=3.4, 8.7
CF_3COOH	5.33 oct(ax) J=1.5, 2.7, 6.6	5.02 q(ax) J=3, 7.5
CD_3OD	—	4.84 oct(ax) J=1, 3, 7.5
Δ	0.65	0.43

biotin sulfoxides,[16] and thiolane 1-oxide.[17] According to ASIS for the sulfoxides, the proton *trans* to the sulfinyl oxygen is more shielded and has a larger Δ-value than the proton *cis* to the sulfinyl oxygen, because aromatic systems like benzene coordinate at electron-deficient sites, avoiding a strongly negative sulfinyl oxygen atom (and probably a negative halogen atom, also). Therefore, the chlorinated product with a larger Δ-value(Δ=0.65) (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 is supported by the facts that the IR C–Cl stretching frequency of **2** is observed at 763 cm^{-1}(C–Cl_{eq}) while that of **3** is observed at 696 cm^{-1}(C–Cl_{ax})[18] in carbon disulfide, and that **3** is detected higher than **2** on a thin-layer plate of silica gel, indicating that **3** is a less polar substance than **2**. Moreover, in the polar solvents (CD_3CN, D_2O, and CF_3COOH), the H–C_2 of **3** was observed as axial, while in the non-polar solvents(CCl_4, $CDCl_3$, and C_6H_6), it was observed as equatorial rather than axial, whereas the H–C_2 of **2** was always observed as axial regardless of whether the solvent was polar or not (Table 1). This phenomenon can be well explained by saying that **2** has a stable *cis*-form possessing a preferable axial sulfinyl oxygen[8,19] and equatorial chlorine. On the other hand, since **3** has an unstable *trans*-form, its conformation changes with the solvent polarity; the polar conformation **3a** is favored in the polar solvents, while the less polar conformation **3b** dominates in the non-polar solvents. The possibility that **3**, which might be formed by the chlorination of **1**, was isomerized to the thermodynamically stable isomer(**2**) during the reaction was excluded by the fact that **2** was not produced at all when **3** was kept in the chlorination condition with 0.5 equivalent of *t*-butyl hypochlorite. After treatment with concentrated hydrochloric acid (1 volume) in dioxane (2 volumes), which is known to cause the complete racemization of sulfoxides,[20] **3** was recovered unchanged, whereas *cis*-4-chlorothiane 1-oxide(**10**) or *trans*-isomer(**8**) was equilibrated to a 47.5 : 52.5 mixture of **10** and **8**.[21] Therefore, **3** is a configurationally stable compound, and it is evident that **2** is directly formed by the chlorination of **1**.

The hydrogen peroxide oxidation of both **2** and **3** in acetic acid gave 2-chlorothiane 1,1-dioxide(**4**) (mp 68—69.5°C).

Further chlorination of **2** and **3** gave results which are quite informative of the reaction mechanism. The chlorination of **2** gave a mixture from which 2e,6e-dichlorothiane 1a-oxide(**5**) (mp 134—135°C), was subsequently isolated in a 37% yield as the major product, whereas the chlorination of **3** produced 2,2-dichlorothiane 1-oxide(**6**) (mp 34.5—36°C) in a 67% yield. The transformation of **5** with Et_3OBF_4 afforded 2e,6e-dichlorothiane 1e-oxide(**7**) (mp 129—130°C) in a 60% yield. The stereochemistry of **5** and **7** has been established on the basis of the NMR coupling constants, ASIS(Table 2), and tlc; **5** is detected higher than **7** on a thin-layer plate. According to the general rule which we found in a series of studies, a sulfoxide having an axial sulfinyl oxygen is observed higher on a thin-layer plate than the isomer having an equatorial oxygen if the other parts of the structures are the same.

TABLE 2. NMR SPECTRAL DATA OF H-C_2(AND H-C_6) OF 2,6-DICHLOROTHIANE 1-OXIDES (**5** AND **7**), 2-CHLORO-4-PHENYLTHIANE 1-OXIDES(**17** AND **18**), AND 2,6-DICHLORO-4-PHENYLTHIANE 1-OXIDES(**20** AND **21**). $\Delta=\delta_{CCl_4}-\delta_{C_6H_6}$.

	5	**7**	**17**	**18**	**20**	**21**
δ_{CCl_4}	4.45 ax	4.97 ax	5.14 eq	4.75 eq	4.52 ax	4.80 eq
$\delta_{C_6H_6}$	3.82	4.49	4.65	4.20	3.81	4.28
Δ	0.63	0.48	0.49	0.55	0.71	0.52

The Chlorination of 4-Chlorothiane 1-Oxides and 4-Phenylthiane 1-Oxides with t-Butyl Hypochlorite. The chlorination of *trans*-4-chlorothaine 1-oxide(**8**) gave, stereospecifically, 2e,4a-dichlorothiane 1a-oxide(**9**) (mp 72.5—74°C) in a 70% yield, while *cis*-4-chlorothiane 1-oxide(**10**) furnished, in a 66% yield, a 67 : 33 mixture of **9** and 2e,4e-dichlorothiane 1a-oxide(**11**) (mp 110—111.5°C) (Fig. 2). The inversion of **9** with Et_3OBF_4 gave 2a,4e-dichlorothiane 1a-oxide (**12**) (mp 92—93.5°C) in an 83% yield. The stereochemical structures of **9**, **11**, and **12** were established by means of the NMR coupling constants of H–C_2 and H–C_4, ASIS (Table 3), and by comparison with the corresponding bromo-derivatives.[13]

The oxidation of a mixture of **9** and **12** produced *trans*-2,4-dichlorothiane 1,1-dioxide(**13**) (mp 131.5—

16) R. Lett and A. Marquet, *Tetrahedron Lett.*, **1971**, 2855.
17) E. T. Strom, B. S. Snowden, Jr., and P. A. Toldan, *Chem. Commun.*, **1969**, 50.
18) K. Kojima and K. Sakashita, This Bulletin, **31**, 796 (1958).
19) J. B. Lambert and R. G. Keske, *J. Org. Chem.*, **31**, 3429 (1966).
20) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **86**, 1452 (1964).
21) On the contrary to C. R. Johnson and D. McCants, Jr., *ibid.* **87**, 1109 (1965), in which a 65 : 35 mixture of **10** and **8** was obtained.

Table 3. NMR spectral data of H-C_2 and H-C_4 of 2,4-dichlorothiane 1-oxides(**9**, **11**, and **12**)

	9		**11**		**12**	
δ_{CCl_4}	4.94 ax	4.52 eq	4.32 ax	3.76 ax	4.83 eq	4.17 ax
$\delta_{C_6H_6}$	4.40	3.61	3.28	—	4.15	3.64
Δ	0.54	—	1.04	—	0.68	—

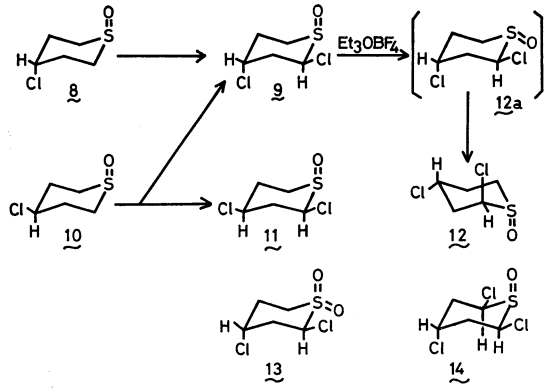

Fig. 2.

132°C) in a 71% yield.

The chlorination of conformationally rigid *trans*-4-phenylthiane 1-oxide(**15**) and *cis*-4-phenylthiane 1-oxide (**16**) in the presence of potassium acetate gave a single identical product, 2a-chloro-4e-phenylthiane 1e-oxide (**17**) (mp 160—160.5°C), in 83% and 66% yields respectively (Fig. 3). In the presence of pyridine, *cis*-oxide(**16**) gave **17** in a 45% yield. The product (**17**) was converted with Et_3OBF_4 into 2a-chloro-4e-phenylthiane 1a-oxide (**18**) (mp 94.5—95°C) in an 82% yield. The stereoformulas (**17** and **18**)[22] were based on the NMR (Table 2) and tlc; compound **18** possessing an axial oxygen is higher than **17**, which possesses an equatorial one. After treatment with concentrated hydrochloric acid in dioxane, compound

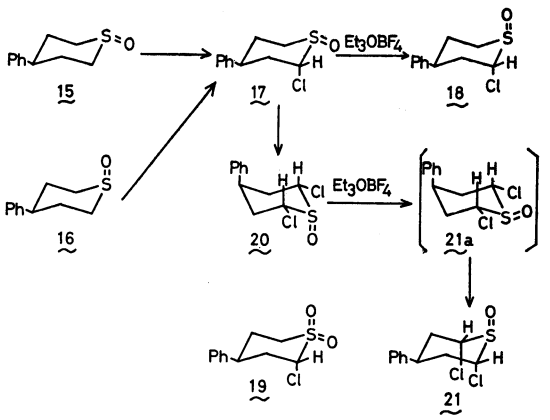

Fig. 3.

22) The stereoformulas of **17** and **18** together with **15** and **16** were unambiguously determined by the use of the shift-reagent, Eu(DPM)$_3$, and the decoupling study in the NMR spectra. M. Fukuyama, K. Sato, M. Fukuyama, S. Iriuchijima, and G. Tsuchihashi, Abstracts of the 26th Meeting of the Chemical Society of Japan: III, Kanagawa, Japan (1972). p. 1438.

17 was recovered quantitatively.

The oxidation of **17** gave *trans*-2-chloro-4-phenylthiane 1,1-dioxide(**19**) (mp 157.5—158.5°C) in a 93% yield.

The chlorination of **17** with 2.4 equivalents of *t*-butyl hypochlorite gave 2e,6e-dichloro-4a-phenylthiane 1a-oxide(**20**) (mp 119—120°C) in an 87% yield; this was then converted with Et_3OBF_4 into 2a,6a-dichloro-4e-phenylthiane 1a-oxide (**21**) (mp 101.5—102°C) in a 34% yield. The structures of **20** and **21** were established by the complete assignments of all their protons in the NMR spectra.

Mechanism of the Chlorination with t-*Butyl Hypochlorite.* The chlorination of the thiane 1-oxides(**1**, **2**, **3**, **8**, **10**, **15**, **16**, and **17**) with *t*-butyl hypochlorite described above gives products in which chlorine was always introduced at a *cis*-position to the sulfinyl oxygen, and it seems to occur when the oxygen is equatorial; compounds **15** and **17**, which possess an equatorial oxygen, are chlorinated at a *cis*-position to the oxygen, as is shown in Fig. 4. Compounds **1** and **8** which can easily take the conformations **1a** and **8a** by the inversion of the ring, are chlorinated at a *cis*-position to the equatorial oxygen in **1a** and **8a**. Compounds **2** and **3** seem to be chlorinated mainly in a manner similar to **1** and **8**. Compound **10**, the ring of which is appreciably fixed by an equatorial chlorine at C_4, is chlorinated partly by passing through the conformation **10a** (Route *a* in Fig. 4) and partly by passing through **8a**, with an inversion of the sulfoxide configuration (Route *b* in Fig. 4) to produce a mixture of **11** and **9**. The possibility of the intermediacy of **8a** is supported by the fact that the isomerization of

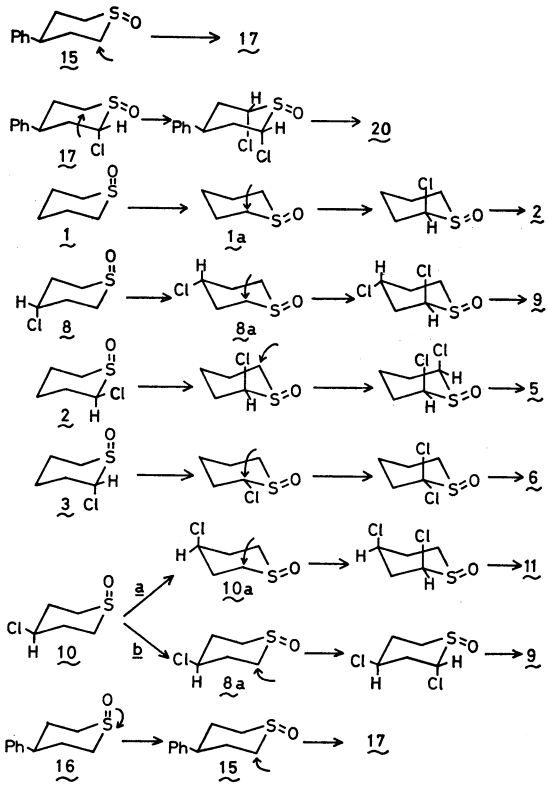

Fig. 4.

10 to **8** was observed in the chlorination of **10** with 0.3 equivalent of *t*-butyl hypochlorite. Compound **16**, the ring of which is rigidly fixed by a phenyl group, gives product **17**, accompanied by a complete sulfoxide inversion. Compound **16** might be chlorinated mainly *via* **15**, because the isomerization of **16** to **15** was observed in the chlorination of **16** with 0.5 equivalent of *t*-butyl hypochlorite.

It has been proposed that α-chlorosulfoxides can be obtained from the chloro-oxosulfonium ions *via* the ylids, either by a concerted rearrangement[23] or by an elimination-addition sequence analogous to a Pummerer-type rearrangement.[24] Our result is not compatible with the concerted rearrangement because the formation of the *trans*-product (**26**) should be expected by the process, as is shown in Fig. 5. Here, we would like to propose the mechanism shown in Fig. 6. The first step is the formation of the chloro-

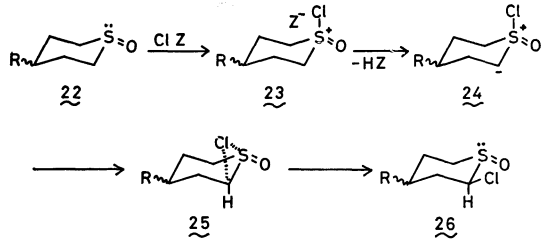

Fig. 5. Z=*t*-BuO, Cl; R=H, Cl, Ph.

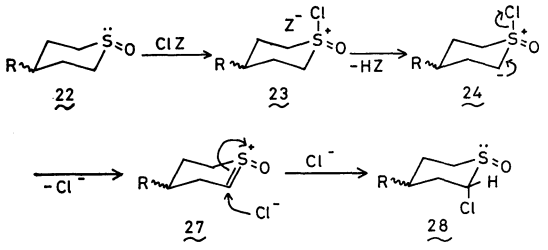

Fig. 6. Z=*t*-BuO, Cl; R=H, Cl, Ph.

oxosulfonium ion(**23**) by the attack of a positive chlorine of *t*-butyl hypochlorite on the sulfinyl lone pair. The second step is the formation of the hypothetical intermediate (**27**); the chloro-oxosulfonium ion (**23**) gives the ylid (**24**) by the action of the counter anion Z^-, which, in the present case, is the *t*-butoxide anion, and then **24** gives rise to **27** by the elimination of the chloride ion. The final step is the addition of the chloride ion to **27**, thus producing the α-chlorosulfoxide(**28**), in which the chlorine atom and sulfinyl lone pair are in the *trans* relationship. Although we do not have any direct evidence of the intervention of the chloride ion, an analogous mechanism has been proposed in the Pummerer rearrangement.[25] We have stated that chlorine is always introduced at a *cis*-position to the sulfinyl oxygen, but according to this mechanism we should say that chlorine is always introduced at a *trans*-position to the sulfinyl lone pair.

The Conformational Stability of the Substituted Thiane 1-Oxides. It is known that thiane 1-oxide(**1**)[19] and *trans*-4-chlorothiane 1-oxide(**8**)[8] exhibit a conformational preference for the forms with the sulfoxide oxygen axial, and that, in 4-substituted thiane 1-oxides such as **15** and **16**, the isomer bearing the axial oxygen is more stable.[26] In addition to this knowledge, we have found that a preferable conformer of **3** is **3a** in the polar solvents and **3b** in the non-polar solvents. Moreover, **7** is a preferable conformer to **7a**, probably because **7a** possesses two axial chlorine atoms which are highly unfavorable because of a 1,3-diaxial relationship, although it possesses a favorable axial oxygen. In **17** an equatorial phenyl group can hold the ring against the unfavorable equatorial sulfinyl oxygen and axial chlorine. In **20**, however, the phenyl group cannot hold the ring against the 1,3-diaxial chlorine atoms and equatorial oxygen; instead, the diequatorial chlorine atoms and axial oxygen keep the ring against the unfavorable axial phenyl group. In compound **21** which was obtained by the inversion of the sulfoxide configuration of **20** with Et_3OBF_4, the equatorial phenyl group and the axial oxygen together keep the ring against the 1,3-diaxial chlorine atoms. Thus, in the thiane 1-oxide ring, (1) an equatorial phenyl group keeps both a sulfinyl oxygen equatorial and a chlorine atom axial (Ph> >S=O+Cl); (2) the combination of 1,3-diequatorial chlorine atoms and an axial sulfinyl oxygen keeps a phenyl group axial(1,3-diCl+ >S=O> Ph), and (3) the combination of an euqatorial phenyl group and an axial sulfinyl oxygen keeps two chlorine atoms diaxial (Ph+ >S=O>1,3-diCl).

The Chlorination with Other Chlorinating Agents. The chlorination of **15** with 0.8 equivalent of sulfuryl chloride in the presence of pyridine produced, stereospecifically, **17**, the same product as was obtained with *t*-butyl hypochlorite, in a 79% yield. The chlorination of **16** with 0.8 equivalent of sulfuryl chloride furnished the same product(**17**) in a 62% yield, while with 1.2 equivalent it gave a mixture of **17** (79% yield) and **20** (16% yield).

The chlorination of **1** with chlorine in the presence of pyridine gave a mixture of **2**(54.5% yield) and **5** (18% yield), though 19% of **1** was also recovered. The chlorination of **8** afforded **9** in a 68% yield, together with **11**(7% yield), while **10** gave, in an 87% yield, a mixture of **9** and **11** in a 3 : 7 ratio, a converse ratio to that obtained in the chlorination with *t*-butyl hypochlorite. In the reaction with *t*-butyl hypochlorite in the presence of potassium acetate, **10** was chlorinated, mainly *via* Route *b*, to produce **9** as the major product, whereas with chlorine in the presence of pyridine **10** was chlorinated, mainly *via* Route *a*, to give **11** as the major component. Compound **15** furnished **17** in a 63% yield, plus small amounts of **20**. **16** also gave **17** in 80% and 62% yields, plus small amounts of **20**.

The chlorination of the cyclic sulfoxides with sul-

23) M. Cinquini, S. Colonna, and F. Montanari, *Chem. Commun.*, **1970**, 1442.
24) T. Durst and K.-C. Tin, *Can. J. Chem.*, **49**, 2374 (1971).
25) C. R. Johnson and W. G. Phillips, *J. Amer. Chem. Soc.*, **91**, 682 (1969).
26) C. R. Johnson and D. McCants, Jr., *ibid.*, **86**, 2936 (1964)

furyl chloride or chlorine in the presence of pyridine seems to be nearly the same as the reaction with *t*-butyl hypochlorite, except that dichlorides can be easily obtained and that the ratio of the isomers (if any are obtained) may be different. Accordingly, the mechanism shown in Fig. 6 can also be applied to the reaction with sulfuryl chloride or chlorine (Z=Cl) in the presence of pyridine.

Experimental

Unless otherwise noted, the NMR spectra were measured with a Varian HA-100 spectrometer and/or a Hitachi R-20B spectrometer in a concentration of 40—50 mg in 0.4 ml of $CDCl_3$, while the IR spectra were recorded with a KBr pellet using a Hitachi EPI-G3 spectrometer. HHW in the NMR spectral data means half-height width. In the crystallization solvents, B, C, and H stand for benzene, cyclohexane, and hexane respectively, and B/C/H means that the crystal was dissolved in benzene, followed by the successive addition of cyclohexane and hexane.

*Chlorination of Thiane 1-Oxide(**1**) to* cis*-2-Chlorothiane 1-Oxide(**2**) with* t*-BuOCl.* *(a) In the Presence of Potassium Acetate*: To a stirred mixture of **1**(405 mg, 3.16 mmol) and potassium acetate(0.82 g, 8.4 mmol) in 20 ml of CH_2Cl_2 was added 0.34 ml(3.1 mmol) of *t*-BuOCl at 0°C. After the mixture had then been stirred for 2 hr, 20 ml of water was added. The mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4 and evaporated to give white crystals. Recrystallization from C/H afforded 423 mg(2.78 mmol; 88%) of **2**, which was then recrystallized to give mp 65.5—66.5°C. IR: 755, 1050(S=O) cm^{-1}. IR(5% in CS_2): 763(C-Cl_{eq}), 1047, 1080(S=O) cm^{-1}. NMR($CDCl_3$): 1.2—3.4(8H), 4.91(1H, octet, J=1, 3, 8). NMR(CCl_4): 1.2—3.3(8H), 4.88(1H, q, J=3.2, 9.3). NMR(C_6H_6): 0.4—2.75(8H), 4.23(1H, q, J=3.1, 9.6). NMR(D_2O): 1.85—3.8(8H), 5.71(1H, octet, J=1, 4, 8.3). NMR(CD_3CN): 1.3—3.1(8H), 4.95(1H, octet, J=1,3.3, 10). NMR(CF_3COOH): 1.5—3.65(8H), 5.33(1H, octet, J=1.5, 2.7, 6.6). Mass: *m/e* 152(M^+), 41 (base peak). Found: C, 39.59; H, 6.13; Cl, 23.34%. Calcd for C_5H_9ClOS: C, 39.35; H, 5.94; Cl, 23.23%.

(b) In the Presence of Pyridine: To a stirred solution of **1**(0.50 g, 3.91 mmol) and pyridine(0.63 ml, 7.82 mmol) in 20 ml of CH_2Cl_2 at 0°C was added *t*-BuOCl(0.43 ml, 3.91 mmol). The solution was stirred for 1.5 hr, and then 25 ml of 0.5 N aqueous sulfuric acid was added and it was extracted with CH_2Cl_2. The subsequent evaporation of the solvent and the crystallization of the residue from B/C gave 407 mg(2.67 mmol; 68.2%) of **2**, identified by means of mp, IR, NMR, and tlc.

*Transformation of **2** to* trans*-2-Chlorothiane 1-Oxide(**3**) with Et_3OBF_4.* 1.2 g(6.3 mmol) of Et_3OBF_4 was added to a solution of 625 mg(4.1 mmol) of **2** in 5 ml of CH_2Cl_2. After the mixture had been stirred at room temperature for 1 hr, 40 ml of anhydrous ether was added at 0°C to give oily ethoxysulfonium salt as a precipitation. After the mixture had been stirred for 2 hr, the solvents were removed by decantation, and to the residue was added 20 ml of a 0.5 N NaOH solution. The mixture was then extracted with CH_2Cl_2. The solvent was dried over Na_2SO_4 and evaporated to give a residue which was subsequently chromatographed on silica gel with benzene. Elution with benzene containing 2% ethyl acetate then furnished 465 mg(3.05 mmol; 74.3%) of **3**. The continuation of the elution gave a small amount of **2**. **3** is eluted faster and is detected higher than **2** on a thin-layer plate. Recrystallization from B/C/H at 0°C gave mp 43—44°C. **3** is hygroscopic. IR(Nujol): 697, 954, 1029, 1059(S=O) cm^{-1}. IR(5% in CS_2): 696 (C-Cl_{ax}), 950, 1030, 1063(S=O) cm^{-1}. NMR($CDCl_3$): 1.45 —3.28 (8H), 4.69(1H, m, HHW=11). NMR(CCl_4): 1.43—3.2 (8H), 4.72(1H, m, HHW=10). NMR(C_6H_6): 0.8—2.7 (8H), 4.29(1H, m, HHW=11). NMR(CF_3COOH): 1.5—3.65(8H), 5.02(1H, q, J=3, 7.5). NMR(CD_3OD): 1.42—3.4(8H), 4.84(1H, octet, J=1, 3, 7.5). NMR(D_2O): 1.8—4.03(8H), 5.36(1H, q, J=3.4, 8.7). Mass: *m/e* 152 (M^+). Found: C, 39.60; H, 6.07; Cl, 23.23%. Calcd for C_5H_9ClOS: C, 39.35; H, 5.94; Cl, 23.23%.

*Oxidation of **2** to 2-Chlorothiane 1,1-Dioxide (**4**).* The oxidation of **2** by the usual method with 30% H_2O_2 in acetic acid gave **4**. Recrystallization from B/C/H afforded mp 68—69.5°C. IR(Nujol): 1127, 1161, 1280, 1312 cm^{-1}. NMR: 1.3—3.7(8H), 4.75(1H, octet, J=2, 3.5, 6.5). Mass: *m/e* 168(M^+), 42(base peak). Found: C, 35.95; H, 5.36%. Calcd for $C_5H_9ClO_2S$: C, 35.61; H, 5.38%.

*Chlorination of **2** with* t*-BuOCl.* 153 mg(1 mmol) of **2** was chlorinated with 0.13 ml(1.15 mmol) of *t*-BuOCl in the presence of potassium acetate(0.32 g, 3.26 mmol) in 5 ml of CH_2Cl_2 at room temperature for 2 hr. The NMR spectrum of the crude extract after the usual work-up indicated that 2e,6e-dichlorothiane 1a-oxide (**5**) was obtained as the major product. Crystallization from B/C at 0°C gave 0.70 g(0.374 mmol; 37.4%) of **5**. Recrystallizations from CCl_4 gave mp 134—135°C. IR(Nujol): 752, 1060(S=O) cm^{-1}. NMR: 1.3—2.7(6H), 4.69(2H, q, J= 3.8, 12.2). NMR(7 mg in 1 ml of CCl_4): 4.45(q, J=3, 12). NMR(25 mg in 0.3 ml of C_6H_6): 0.45—1.60(4H), 1.80—2.60(2H), 3.82(2H, q, J=3.5, 12). Mass: *m/e* 186(M^+), 75(base peak). Found: C, 32.18; H, 4.27; Cl, 37.89%. Calcd for $C_5H_8Cl_2OS$: C, 32.10; H, 4.31; Cl, 37.90%.

*Chlorination of **3** with* t*-BuOCl.* *(a) With 1.1 equiv of* t*-BuOCl*: 177 mg(1.16 mmol) of **3** was chlorinated with 0.145 ml(12.8 mmol) of *t*-BuOCl in the presence of potassium acetate(0.34 g, 3.48 mmol) in 10 ml of CH_2Cl_2 at room temperature for 1 hr. The NMR of the extract showed the major product to be 2,2-dichlorothiane 1-oxide (**6**). Chromatography with benzene/hexane (7 : 3), followed by elution with a (8 : 2) mixture, afforded 145 mg(0.775 mmol; 66.7%) of **6**, which was then crystallized at −20°C. Recrystallization from hexane at 0°C gave mp 34.5—36°C. IR (Nujol): 776, 945, 958, 1034, 1080, 1411 cm^{-1}. NMR: 1.55—3.37(8H) [1.55—2.6(5H), 2.75—3.37 (3H)]. Mass: *m/e* 186(M^+), 151(base peak). Found: C, 32.24; H, 4.31; Cl, 37.64%. Calcd for $C_5H_8Cl_2OS$: C, 32.10; H, 4.31; Cl, 37.90%.

(b) With 0.5 equiv of t*-BuOCl*: A mixture of **3**(101 mg, 0.665 mmol), potassium acetate(40 mg, 0.41 mmol), and *t*-BuOCl(0.036 ml, 0.33 mmol) in 10 ml of CH_2Cl_2 was stirred at room temperature for 3 hr. The usual work-up gave 98 mg of the white crystals, in which **2** was not detected by studying the NMR spectrum.

*Transformation of **5** to 2e,6e-Dichlorothiane 1e-Oxide (**7**).* A solution of **5**(425 mg, 2.27 mmol) and Et_3OBF_4(0.65 g, 3.4 mmol) in 3 ml of CH_2Cl_2 was stirred at room temperature for 2 hr. The usual work-up gave a residue, which was then crystallized on standing. Recrystallization from B/C/H gave 255 mg(1.36 mmol; 60.0%) of **7**, showing mp 129—130°C(sintered at *ca.* 100°C) on further recrystallization. IR(Nujol): 758, 1071(S=O) cm^{-1}. NMR: 1.5—2.25(4H) 2.35—2.65(2H), 4.72(2H, q, J=3.5, 11). NMR(12 mg in 0.7 ml of CCl_4): 1.7—2.2(4H), 2.3—2.65(2H), 4.97(2H, J=3, 10.5). NMR(12 mg in 0.3 ml of C_6H_6): 0.5—2.0 (6H), 4.49(2H, q, J=4, 10.5). NMR(CF_3COOH): 1.7—

3.0(6H), 5.05(2H, q, J=3.5, 11.5). Found: C, 32.23; H, 4.10%. Calcd for $C_5H_8Cl_2OS$: C, 32.10; H, 4.31%.

Chlorination of **8** *to 2e,4a-Dichlorothiane 1a-Oxide (***9***) with* t-*BuOCl.* To a stirred, suspended solution of **5**(454 mg, 2.98 mmol) and potassium acetate (322 mg, 3.28 mmol) in 15 ml of CH_2Cl_2 at 0°C was added 0.36 ml(3.28 mmol) of *t*-BuOCl. The mixture was stirred at 0°C for 4 hr. The usual work-up gave a residue, which was then chromatographed with benzene. Elution with 1% ethyl acetate in benzene gave 0.39 g(2.09 mmol; 70.0%) of **9**. 80 mg(0.53 mmol) of **8**(containing 10% of **10**) was recovered with benzene–ethyl acetate(85 : 15). The recrystallizations of **9** with B/H gave mp 72.5—74°C. IR: 570, 688, 780, 1000—1090 cm^{-1}. IR(5% in CS_2): 572, 692, 787, 1076 cm^{-1}. NMR($CDCl_3$): 1.80—3.17(6H), 4.51(1H, m, HHW=9), 5.00(1H, q, J=3, 11). NMR(CCl_4): 4.52(1H, m, HHW=8.5), 4.94(1H). NMR(C_6H_6): 3.61(1H, m, HHW=9), 4.40(1H). NMR(CF_3COOH): 4.52(1H, m, HHW=11), 5.27(1H). Mass: *m/e* 186(M^+), 101(base peak). Found: C, 32.06; H, 4.24; Cl, 38.07%. Calcd for C_5H_8ClOS: C, 32.10; H, 4.31; Cl, 37.90%.

Chlorination of **10** *with* t-*BuOCl.* *(a) With 1.1 equiv of* t-*BuOCl*: To a stirred mixture of **10** (465 mg, 3.04 mmol) and potassium acetate (0.33 g, 3.36 mmol) in 15 ml of CH_2Cl_2 was added 0.37 ml (3.36 mmol) of *t*-BuOCl at 0°C. The mixture was stirred at 0°C for 2 hr. The NMR spectrum of the crude extract obtained by the usual work-up showed it to be a 67 : 33 mixture of **9** and 2e, 4e-dichlorothiane 1a-oxide(**11**). Chromatography with benzene, followed by elution with 1% ethyl acetate–benzene, gave 375 mg(2.0 mmol; 65.7%) of a mixture of **9** and **11**, while 108 mg(0.71 mmol) of a 35 : 65 mixture of **8** and **10** was recovered with a 1 : 1 mixture of benzene and ethyl acetate. Since **9** is eluted faster than **11** in silica gel chromatography, **9** was isolated from the first fractions, while **11** was isolated from the last. **9** was identified by mp, IR and NMR(CCl_4). **11** has mp 110—111.5°C from B/H. IR: 730, 792, 1000—1090 cm^{-1}. NMR: 1.80—3.43(6H), 3.96(1H, septet, J=4, 4, 8, 8), 4.62(1H, q, J=4.5, 11). NMR(4 mg in 0.4 ml of CCl_4): 3.76(1H), 4.32(1H). NMR(8 mg in 0.4 ml of of C_6H_6): 0.96—2.99(7H), 3.28(1H). NMR(8 mg in 0.5 ml of CF_3COOH): 3.95(1H), 4.78(1H). Mass: *m/e* 186(M^+), 101(base peak). Found: C, 32.10; H, 4.30; Cl, 38.09%. Calcd for $C_5H_8Cl_2OS$: C, 32.10; H, 4.31; Cl, 37.90%.

(b) With 0.3 equiv of t-*BuOCl*: A solution of **10** (100 mg, 0.655 mmol), potassium acetate (30 mg, 0.33 mmol), and *t*-BuOCl (0.023 ml, 0.204 mmol) in 8 ml of CH_2Cl_2 was stirred for 1.5 hr. The NMR spectrum of the extract showed that **8**, **9**, and **10** were obtained in a ratio of 35 : 89 : 100. A 26.5 : 73.5 mixture (33 mg) of **8** and **10** was recovered by chromatography.

Transformation of **9** *to 2a,4e-Dichlorothiane 1a-Oxide (***12***).* A solution of **9**(185 mg, 0.99 mmol) and Et_3OBF_4 (0.38 g, 1.99 mmol) in 3 ml of CH_2Cl_2 was stirred for 1 hr. The usual work-up gave white crystals at −20°C. Recrystallization from B/H afforded 153 mg(0.82 mmol; 82.7%) of **12**, with mp 92—93.5°C.

IR: 580, 650, 700, 800, 1000—1100 cm^{-1}. NMR(CDCl): 2.00—3.50(6H), 4.25(1H, nonet, J=3.5, 3.5, 11, 11), 4.86 (1H, m, HHW=10). NMR(CCl_4): 4.17(1H), 4.83(1H, m, HHW=7.5). NMR(C_6H_6): 3.64(1H), 4.15(1H, m, HHW=10). NMR(CF_3COOH): 4.38(1H, septet, J=3.5, 3.5, 7, 7), 5.31(1H, q, J=3.5, 8). Mass: *m/e* 186(M^+). Found: C, 32.17; H, 4.41; Cl, 38.02%. Calcd for $C_5H_8Cl_2OS$: C, 32.10; H, 4.31; Cl, 37.90%.

trans-*2,4-Dichlorothiane 1,1-Dioxide (***13***).* A solution of **9** (63 mg), **12**(65 mg), and 30% H_2O_2 (0.11 ml; 1.1 mmol) in 2 ml of acetic acid was kept at 45°C for 15 hr. The subsequent addition of Na_2CO_3, followed by extraction with CH_2Cl_2 and the evaporation of the solvent, gave 0.11 g (0.545 mmol; 71.0%) of **13** as white crystals. Recrystallizations from $CHCl_3$/H gave mp 131.5—132°C. IR: 1150, 1323 cm^{-1}. NMR: 2.66(4H, m), 3.40(2H, t, J=6, 6), 4.51(1H, quintet, J=5—6, 5—6, 5—6, 5—6), 5.00(1H, q, J=5.5, 8). Mass: *m/e* 202(M^+), 75(base peak). Found: C, 29.39; H, 3.98; S, 15.60%. Calcd for $C_5H_8Cl_2O_2S$: C, 29.57; H, 3.97; S, 15.79%.

*2e,4a,6e-Trichlorothiane 1a-Oxide (***14***).* To a stirred mixture of **8**(0.12 g, 0.785 mmol), **10**(0.12 g, 0.785 mmol), and potassium acetate(0.62 g, 6.3 mmol) in 15 ml of CH_2Cl_2 was added 0.69 ml (6.28 mmol) of *t*-BuOCl at 0°C, and the mixture was stirred for 1.5 hr. The usual work-up gave 0.33 g(1.49 mmol; 94.9%) of the white crystals (**14**). Recrystallizations from B/H gave mp 139.5—140.5°C. IR: 1056 cm^{-1}. NMR: 2.35(2H, sextet, J=3.5, 3.5, 15), 2.82(2H, septet, J=3.5, 12, 15), 4.52(1H, quintet, J=*ca.* 3.5, 3.5, 3.5, 3.5), 5.07(2H, q, J=3.5, 12). Mass: *m/e* 220(M^+), 135(base peak). Found: C, 27.33; H, 3.27; S, 14.52%. Calcd for $C_5H_7Cl_3OS$: C, 27.11; H, 3.19; S, 14.47%.

Chlorination of **15** *to 2a-Chloro-4e-phenylthiane 1e-Oxide (***17***) with* t-*BuOCl.* To a stirred mixture of **15**(159 mg, 0.815 mmol) and potassium acetate(0.16 g, 1.63 mmol) in 10 ml of CH_2Cl_2 was added 0.09 ml(0.82 mmol) of *t*-BuOCl at 0°C, and the mixture was stirred at 0°C for 2 hr. The usual work-up gave yellowish white crystals, which were later recrystallized from B/H to give 154 mg(0.675 mmol; 82.8%) of **17**. Further recrystallization from B/H gave mp 160—160.5°C. IR(Nujol): 689, 710, 773, 1072(S=O) cm^{-1}. NMR($CDCl_3$): 1.92—2.20 (2H), 2.30—2.25 (2H), 2.97—3.43 (3H), 5.30(1H, m, HHW=8), 7.23(5H, m). NMR-(CCl_4): 5.14 (1H, m, HHW=8). NMR(C_6H_6): 4.65(1H, m, HHW=8.5). NMR(CF_3COOH): 5.64(1H, m, HHW=8). Mass: *m/e* 228(M^+), 117(base peak). Found: C, 57.53; H, 5.84; Cl, 15.77%. Calcd for $C_{11}H_{13}ClOS$: C, 57.76; H, 5.73; Cl, 15.50%.

Chlorination of **16** *to* **17** *with* t-*BuOCl.* *(a) With 1.0 equiv of* t-*BuOCl*: A mixture of **16** (0.15 g, 0.77 mmol), potassium acetate(0.15 g, 1.54 mmol), and *t*-BuOCl(0.085 ml, 0.77 mmol) in 10 ml of CH_2Cl_2 was stirred at 0°C for 3.5 hr. The NMR spectra($CDCl_3$ and C_6H_6) of the crude crystals obtained by the usual work-up revealed that **17** was the sole product. Recrystallization from B/H gave 117 mg(0.51 mmol; 66.4%) of **17**, identified by mp, IR, NMR, and tlc.

(b) With 0.5 *equiv of* t-*BuOCl in the Presence of Potassium Acetate*: A solution of **16** (200 mg, 1.03 mmol), potassium acetate(51 mg, 0.52 mmol), and *t*-BuOCl (0.06 ml, 0.53 mmol in 10 ml of CH_2Cl_2 was stirred for 3 hr. The usual work-up followed by chromatography gave 120 mg (0.53 mmol) of **17** and 73 mg of a 23 : 77 mixture of **15** and **16**.

(c) In the Presence of Pyridine: A mixture of **16** (154 mg, 0.79 mmol), pyridine (0.14 ml, 1.74 mmol), and *t*-BuOCl (0.90 ml, 0.80 mmol) in 10 ml of CH_2Cl_2 was stirred at 0°C for 3 hr. The usual work-up followed by chromatography gave 81 mg (0.356 mmol; 45.0%) of **17**, eluted with 1% ethyl acetate in benzene.

Transformation of **17** *to 2a-Chloro-4e-phenylthiane 1a-Oxide (***18***).* A solution of **17**(148 mg, 0.647 mmol) and Et_3OBF_4 (0.25 g, 1.31 mmol) in 3 ml of CH_2Cl_2 was stirred at room temperature for 1 hr. The usual work-up gave a white solid, which was subsequently crystallized from C/H to afford 121 mg(81.6%) of **18**. Chromatographic purifi-

cation with benzene–ethyl acetate(99 : 1), followed by recrystallization from B/H gave, a pure sample with mp 94.5—95.0°C. IR: 691, 1053, 1497, 1602 cm^{-1}. NMR-($CDCl_3$): 1.65—3.43(7H), 4.89(1H, m, HHW=7), 7.25(5H, s). NMR(CCl_4): 4.75(1H, m, HHW=7). NMR(C_6H_6): 4.20(1H, m, HHW=6.5). Mass: *m/e* 228(M^+). Found: C, 57.51; H, 5.79; Cl, 15.75%. Calcd for $C_{11}H_{13}ClOS$: C, 57.76; H, 5.73; Cl, 15.50%.

*Treatment of Chlorothiane 1-Oxides(**2**, **3**, **8**, **10**, and **17**) with Concentrated Hydrochloric Acid(1 vol) in Dioxane (2 vol).*

*(a) **2***: To a stirred solution of **2** (50 mg) in 6 ml of dioxane was added 3 ml of concentrated HCl at room temperature, after which the mixture was stirred for 1 hr. The addition of water and subsequent extraction with CH_2Cl_2 gave 48 mg of white crystals, the NMR spectrum of which showed that **2** was recovered unchanged.

*(b) **3***: A solution of **3**(92 mg) in a mixture of concentrated HCl(3 ml) and dioxane (6 ml) was stirred at room temperature for 1 hr. The usual work-up gave 89 mg of white crystals, the NMR spectrum of which showed that **3** was recovered quantitatively.

*(c) **8***: A solution of **8** (50 mg) in the same reagent(9 ml) was stirred for 1 hr. The usual work-up gave a 52 : 48 mixture (49 mg) of **8** and **10**.

*(d) **10***: A solution of **10** (52 mg) in 9 ml of the reagent was stirred for 1 hr. A work-up gave a 53 : 47 mixture (47 mg) of **8** and **10**.

*(e) **17***: A solution of **17**(56 mg) in 9 ml of the reagent was stirred for 1 hr. A work-up afforded 52 mg of **17**.

*Oxidation of **17** to* trans*-2-Chloro-4-phenylthiane 1,1-Dioxide (**19**).* A solution of **17**(0.19 g, 0.83 mmol) and 30% H_2O_2(0.18 ml, 1.76 mmol) in 2 ml of acetic acid was kept at 45°C for 15 hr. The subsequent addition of water furnished white crystals, which were then filtered off, washed with water, and dried under a vacuum to give 188 mg(0.77 mmol; 93%) of **19**. Recrystallizations from B/H gave mp 157.5—158.5°C. IR: 1136, 1330 cm^{-1}. NMR: 2.10—3.97(7H), 4.82(1H, q, J=3.5, 6), 7.28(5H, s). Mass: *m/e* 244(M^+), 117(base peak). Found: C, 53.90; H, 5.42; S, 13.01%. Calcd for $C_{11}H_{13}ClO_2S$: C, 53.98; H, 5.35; S, 13.10%.

*Chlorination of **17** to 2e,6e-Dichloro-4a-phenylthiane 1a-Oxide (**20**) with* t*-BuOCl.* A mixture of **17**(250 mg, 1.09 mmol), potassium acetate(215 mg, 2.18 mmol), and *t*-BuOCl 0.12 ml, 1.06 mmol) in 15 ml of CH_2Cl_2 was stirred for 1 hr. An additional 0.06 ml(0.53 mmol) of *t*-BuOCl was then added, and after 1 hr's stirring, 0.10 ml(0.885 mmol) of *t*-BuOCl was added. After stirring for 1 more hr, the usual work-up furnished white crystals, which were recrystallized from $CHCl_3$/H to give 252 mg(0.95 mmol; 87.2%) of **21**. Further purification by chromatography and recrystallizations from $CHCl_3$/H gave an analytical sample with mp 119—120°C. IR: 1078, 1495, 1598 cm^{-1}. NMR: 2.25—3.70(5H), 4.73(2H, q, J=4, 10). NMR(15 mg in 0.6 ml of CCl_4): 2.47(H_{eq}–C_3 and –C_5, sextet, J=3—4, 3—4, 14), 2.89(H_{ax}–C_3 and –C_5, octet, J=3—4, 12, 14), 3.41(H_{eq}–C_4, quintet, J=3—4, 3—4, 3—4, 3—4), 4.52(H_{ax}–C_2 and –C_6, q, J=3—4, 12). NMR(25 mg in 0.4 ml of C_6H_6): 1.98(2H), 2.60(2H), 2.64(1H), 3.81(2H). Mass: *m/e* 262(M^+), 115 (base peak). Found: C, 49.97; H, 4.56; S, 12.24%. Calcd for $C_{11}H_{12}Cl_2OS$: C, 50.20; H, 4.60; S, 12.18%.

*Conversion of **20** to 2a,6a-Dichloro-4e-phenylthiane 1a-Oxide (**21**).* A solution of **20**(132 mg, 0.50 mmol) and Et_3O-BF_4(0.20 g, 1.05 mmol) in 4 ml of CH_2Cl_2 was stirred for 1 hr. The subsequent recrystallization from $CHCl_3$/H of the crude crystals obtained by the usual work-up gave 45 mg (0.172 mmol; 34.2%) of **21**, with mp 101.5—102°C. IR: 1052, 1493, 1600 cm^{-1}. NMR(CCl_4): 2.16(H_{eq}–C_3 and –C_5, sextet, J=3, 3, 15.5), 2.93(H_{ax}–C_3 and –C_5, octet, J=3, 11, 15.5), 3.47(H_{ax}–C_4, nonet, J=3, 3, 11, 11), 4.80 (H_{eq}–C_2 and –C_6, m). NMR(C_6H_6): 1.68(2H), 2.60(2H), 3.32 (1H), 4.28(2H). Mass: *m/e* 262(M^+). Found: C, 50.21; H, 4.64; S, 12.15%. Calcd for $C_{11}H_{12}Cl_2OS$: C, 50.20; H, 4.60; S, 12.18%.

*Chlorination of **15** to **17** with SO_2Cl_2.* To a stirred solution of **15** (120 mg, 0.617 mmol) and pyridine (0.15 ml, 1.86 mmol) in 15 ml of CH_2Cl_2 was added 0.04 ml(0.494 mmol) of SO_2Cl_2 at 0°C, after which the mixture was stirred for 1 hr. The usual work-up gave crude white crystals which were subsequently dissolved in 1.0 ml of $CDCl_3$ with 36.0 mg(0.153 mmol) of bromomethyl phenyl sulfone as the standard. The NMR spectrum of the solution showed that **17** was produced, and through the NMR integral of the H–C_2 of **17** and the –CH_2– of bromomethyl phenyl sulfone, the yield of **17** was estimated to be 79%.

*Chlorination of **16** with SO_2Cl_2. (a) With 0.8 equiv of SO_2Cl_2*: A solution of **16** (120 mg, 0.617 mmol), pyridine (0.15 ml, 1.86 mmol), and SO_2Cl_2(0.04 ml, 0.494 mmol) in 15 ml of CH_2Cl_2 was stirred at 0°C for 2 hr. The NMR spectrum of the reddish crystals obtained by the usual work-up showed that **17** was produced in a 61.7% yield, by the same method as has been described above.

(b) With 1.2 equiv of SO_2Cl_2: A solution of **16** (256 mg, 1.32 mmol), pyridine(0.32 ml, 4.0 mmol), and SO_2Cl_2(0.13 ml, 1.61 mmol) in 15 ml of CH_2Cl_2 was stirred at 0°C for 4 hr. The NMR spectrum of the crude crystals obtained by the usual work-up showed that **17** and **20** were produced in a ratio of 8 : 2. The mixture was chromatographed with benzene/hexane(8 : 2). 43 mg(0.162 mmol; 15.7%) of **20** was eluted with benzene, and 187 mg (0.814 mmol; 79.1%) of **17** was eluted benzene–ethyl acetate (98 : 2). **17** and **20** were identified by means of the mp, IR, and NMR spectra.

*Chlorination of **1** with Cl_2.* To a stirred solution of **1** (4.86 g, 41.2 mmol) and pyridine (9.9 ml, 123.6 mmol) in 50 ml of CH_2Cl_2 was added at 0°C a solution of Cl_2(more than 2.48 g; 35 mmol) in 35 ml of CCl_4 over a 0.5-hr period. The mixture was stirred for 1 hr. The usual work-up, followed by chromatography with benzene, gave 1.38 g (7.37 mmol; 17.9%) of **5** with benzene, and 3.43 g (22.5 mmol; 54.3%) of **2** with benzene containing 1—5% ethyl acetate. 0.91 g (7.7 mmol; 18.7%) of **1** was recovered by elution with benzene/ethanol (95 : 5). **2** and **5** were identified by means of mp, IR, and NMR spectra.

*Chlorination of **8** with Cl_2.* To a stirred solution of **8** (50 mg, 0.328 mmol) and pyridine(0.08 ml, 1.0 mmol) in 10 ml of CH_2Cl_2 was added a solution of Cl_2(more than 20.6 mg; 0.29 mmol) in 0.29 ml of CCl_4 at 0°C, after which the mixture was stirred for 2 hr. Further addition of 0.088 mmol of Cl_2 in CCl_4, followed by 2.5 hr's stirring; the usual work-up gave a crude residue which was dissolved in 0.5 ml of $CDCl_3$, with 69.6 mg(0.312 mmol) of dichloromethyl 4-methylphenyl sulfoxide as the standard. The NMR spectrum of the solution showed that a 91 : 9 mixture of **9** and **11** was produced in a 75% yield.

*Chlorination of **10** with Cl_2.* To a stirred solution of **10**(48 mg, 0.314 mmol) and pyridine(0.08 ml, 1.0 mmol) in 10 ml of CH_2Cl_2 was added a solution of Cl_2(ca. 0.29 mmol) in 0.29 ml of CCl_4 at 0°C, after which the mixture was stirred for 3 hr. The usual work-up, followed by NMR spectral measurement with 70.5 mg(0.316 mmol) of dichloromethyl 4-methylphenyl sulfoxide, showed that a 3 : 7 mixture of **9** and **11** was obtained in an 86.6% yield.

*Chlorination of **15** with Cl_2.* To a stirred solution of **15** (122 mg, 0.627 mmol) and pyridine(0.15 ml, 1.87 mmol)

in 15 ml of CH_2Cl_2 was added a solution of 0.55 mmol of Cl_2 in 0.55 ml of CCl_4 at 0°C, after which the mixture was stirred for 1.5 hr. The addition of 0.088 mmol of Cl_2(1.5 hr's stirring) and the further addition of 0.055 mmol of Cl_2 1.5 hr's stirring), followed by the usual work-up, gave 140 mg of white crystals. Their NMR spectrum with 36.2 mg (0.154 mmol) of bromomethyl phenyl sulfone showed that **17** and **20** were produced in 62.7% and 6.3% yields respectively.

Chlorination of ***16*** *with* Cl_2. *(a)*: To a stirred solution of **16** (247 mg, 1.27 mmol) and pyridine(0.3 ml, 3.75 mmol) in 15 ml of CH_2Cl_2 was added a solution of Cl_2(1.27 mmol) in 1.27 ml of CCl_4, after which the mixture was stirred for 2.5 hr. The usual work-up followed by crystallization from $CHCl_3$/H gave 234 mg(1.02 mmol; 80.3%) of **17**.

(b): To a stirred solution of **16** (121 mg, 0.622 mmol) and pyridine(0.15 ml, 1.87 mmol) in 15 ml of CH_2Cl_2 was added a solution of 0.50 mmol of Cl_2 in 0.50 ml of CCl_4 at 0°C, after which the mixture was stirred for 2.5 hr. An additional 0.13 mmol of Cl_2 in CCl_4 was added, and stirring was continued for 1.5 hr. The NMR measurement after the usual work-up showed that **17** was obtained in a 61.8% yield.

Synthesis of trans-*4-Chlorothiane 1-Oxide (****8****) and* cis-*4-Chlorothiane 1-Oxide (****10****).* To a stirred solution of 4-chlorothiane[27] (0.58 g, 4.25 mmol) in 100 ml of methanol was added a solution of $NaIO_4$(955 mg, 4.46 mmol) in 100 ml of water at 0°C. The mixture was stirred at 0°C for 5 hr and then at room temperature for 5 hr. 100 ml of water was added, and the mixture was extracted with CH_2Cl_2. The evaporation of the solvent gave 595 mg(3.9 mmol; 91.7%) of the white crystals which were a 60 : 40 mixture of **8** and **10** on the basis of the NMR spectrum.

4.20 g(30.8 mmol) of 4-chlorothiane was oxidized similarly, followed by chromatography with benzene. Elution with benzene–ethyl acetate(90 : 10) afforded 1.62 g(10.6 mmol; 34.4%) of **8**, 863 mg(5.65 mmol; 18.4%) of a mixture of **8** and **10**, and 1.295 g(8.48 mmol; 27.5%) of **10** containing a very small amount of **8** successively. The solubilities of **8** and **10** in cyclohexane at room temperature were 6 mg/ml and 1 mg/ml respectively. Accordingly, **10** can be easily isolated from a mixture of **8** and **10**. Recrystallization of **8** from B/C/H gave mp 108—109.5°C (sintered at *ca.* 85°C) (lit,[8] mp 104—105°C). IR(3.5% in CS_2): 573, 719, 980, 1055 cm^{-1}. NMR: 1.65—3.2(8H), 4.51(1H, m, HHW=9). Found: C, 39.45; H, 6.08%. Calcd for C_5H_9ClOS: C, 39.35; H, 5.94%. Recrystallization of **10** from C/H gave mp 120—121°C (lit,[8] mp 120—121°C). IR(0.5% in CS_2): 726, 753, 938, 1019, 1066 cm^{-1}. NMR($CDCl_3$): 1.85—3.40(8H), 4.12(1H, m, HHW=16—21.5).

Synthesis of 4-Phenylthiane. 4-Phenylthiane was prepared by a modification of a method previously reported.[28] A solution of 4-hydroxy-4-phenylthiane(2.32 g, 12 mmol) and *p*-toluenesulfonic acid monohydrate(0.30 g) in 15 ml of isopropyl acetate was refluxed for 10 hr, while being monitored by tlc. The subsequent evaporation of the solvent gave 2.11 g (12 mmol; 100%) of a crystalline residue, which was then treated with charcoal in cyclohexane.

A solution of dehydrated product(1.58 g, 8.96 mmol) in 30 ml of 99.5% ethanol was stirred with 2.37 g of 5% Pd-charcoal under H_2 for 40 hr at 100—120 atm/40—50°C. The mixture was filtered, and the filtrate was concentrated to a residue which was treated with charcoal in cyclohexane. The crystallization of the product from hexane at 0°C gave 0.95 g of 4-phenylthiane. The mother liquor was cooled to −20°C to furnish 0.32 g of the product. The total yield was 1.27 g(7.13 mmol; 79.5%). Recrystallization from methanol at −20°C gave mp 52—53°C (lit,[28] mp 55°C).

Synthesis of trans-*4-Phenylthiane 1-Oxide (****15****) and* cis-*4-Phenylthiane 1-Oxide (****16****).* To a stirred solution of $NaIO_4$(2.79 g, 13.0 mmol) in 300 ml of water was added a solution of 4-phenylthiane(2.07 g, 11.6 mmol) in 900 ml of methanol at 0°C; the mixture was stirred at 0°C for 5 hr and then at room temperature for 14 hr. It was then filtered, and the filtrate was concentrated to 400 ml which was subsequently extracted with CH_2Cl_2. The usual work-up gave 2.122 g(10.93 mmol; 94.2%) of white crystals, which were a 26 : 74 mixture of **15** and **16**, as determined by means of the 100 MHz NMR spectrum.[9] Fractional crystallization from cyclohexane gave 0.89 g (39.6%) of **16** with mp 148.5—149°C(lit,[9] mp 150—151°C).

A 2.82-g portion of a 1 : 1 mixture of **15** and **16** was chromatographed with benzene. After successive elutions with 1, 2, 4, 6, 8, 10, and 15% of ethyl acetate in benzene, elution with 15—20% of ethyl acetate, followed by fractional crystallizations from cyclohexane, afforded 867 mg(30.8%) of **16**, 834 mg(29.6%) of **15** with mp 121—123°C(lit,[9] mp 137—138.5°C), and 1.11 g(39.3%) of a 1.1 : 1 mixture of **15** and **16**.

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