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THE STEREOCHEMISTRY OF THIANE OXIDATION

PARTICIPATION OF NEIGHBORING GROUPS

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Abstract—Thianes not containing 4-OH or 4-CO groups are oxidized by wet bromine predominantly to equatorial thiane 1-oxides. The reaction is assumed to proceed by way of an equatorial electrophilic attack by hypobromous acid at the S atom. An electronic interpretation is given of the steric course of electrophilic reactions at the S atom in thianes. With thianes containing 4-OH or 4-CO groups, oxidation to thiane 1-oxides by wet bromine or by t-butyl hypochlorite resulted in a reversal of the usual stereospecificities of these reagents. A two step process involving participation by the 4-substituents is given to account for the different steric course of the reactions in these cases.

The steric course of the oxidation of substituted thianes was investigated by Johnson[1] who found large variations in the products ranging from predominantly axial sulfoxide formation to almost pure equatorial sulfoxide formation depending on the oxidizing agent. In this study only hydrocarbon substituents on the ring were used. However, functional groups are known to influence the steric course of reactions of sulfur compounds. Montanari[2] has summarized a number of reactions in which neighboring group participation by sulfoxide groups occurred. Reactions at a sulfoxide group such as reduction or racemization[3-5] may be influenced by neighboring groups. We have also found that the steric course of halogenation of thiane 1-oxides is affected by nearby OH groups.[6] It was therefore of interest to investigate the stereochemistry of oxidation of thianes containing functional groups and in particular compounds containing OH groups.

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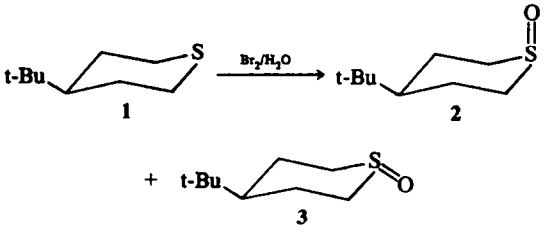
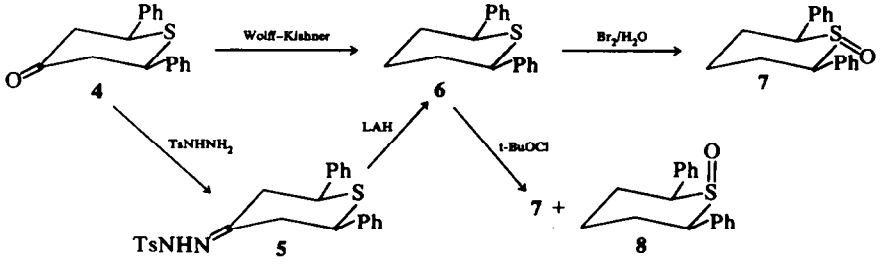
RESULTS

We first studied the oxidation of thianes with wet bromine, a method previously[7-9] used to oxidize sulfides to sulfoxides but whose steric course was unknown. Oxidation of 4-t-butylthiane (**1**) gave the isomeric thiane 1-oxides **2** and **3** in the ratio 1:4 (Table 1).



Similar oxidation of *cis*-2,6-diphenylthiane (**6**) (Scheme 1) yielded *trans,trans*-2,6-diphenylthiane 1-oxide (**7**). These results indicate that wet bromine oxidizes thianes preferentially to equatorial thiane 1-oxides. The sulfide **6** was prepared in low yield by Wolff-Kishner reduction of 4-keto-*cis*-2,6-diphenylthiane (**4**) or in better yield by reduction of the tosylhydrazone **5**. Oxidation of thianes with



SCHEME 1.

Table 1. Oxidation of thianes

Starting material	Oxidizing agent[a]	Product (yield, %)[b]
1	A	2 (12) + 3 (49)[c]
1	B	2 (18) + 3 (64)[c]
4	A	11 (83)
4	B	11 (74)
4	C	11 (30)
6	A	7 (24)
6	B	7 (43)
6	C	7 (10) + 8 (11)
9	A	10 (52)
9	C	10 (48)
9	Cl_2–pyridine–H_2O	10 (14)
14	B	15 (59)
14	C	15 (81)

[a] A = Br_2–H_2O; B = HOBr; C = t-BuOCl–MeOH.
[b] By isolation after purification by recrystallization unless otherwise indicated.
[c] From GLC analysis.

t-butyl hypochlorite has been shown[1] to be a highly stereospecific process leading almost entirely to the axial sulfoxides. However, in the case of **6**, t-butyl hypochlorite gave a 1:1 mixture of the equatorial and axial sulfoxides **7** and **8** in low yield.

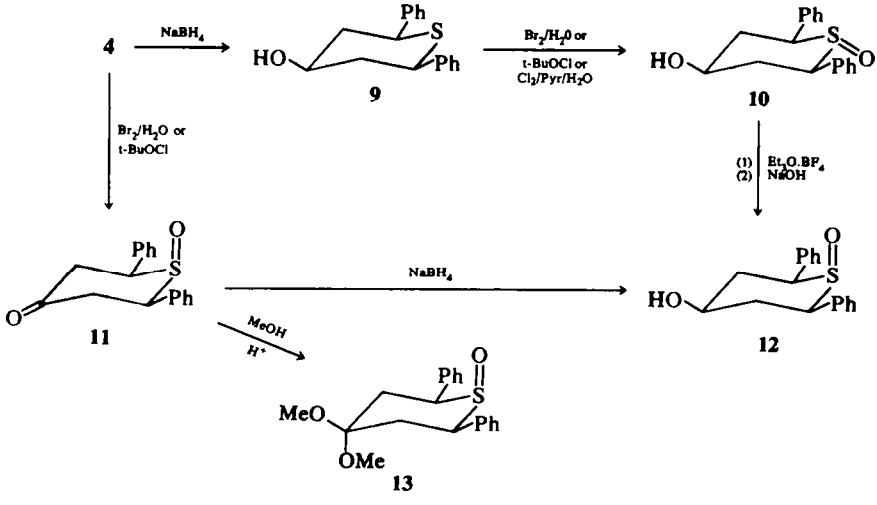
Wet bromine oxidation of 4-hydroxy-*cis,cis*-2,6-diphenylthiane (**9**) (Scheme 2), which was obtained by sodium borohydride reduction of **4**, gave the expected equatorial sulfoxide **10**, however, similar oxidation of **4** gave the unexpected axial sulfoxide **11**. With t-butyl hypochlorite, oxidation of **4** yielded the axial sulfoxide **11**, which is expected. However, oxidation of **9** resulted in the equatorial sulfoxide which is unexpected for this oxidizing agent. The oxidation of **9** to **10** was also effected by chlorine in the presence of pyridine followed by aqueous hydrolysis. While compounds **9**[10] and **11**[7] have previously been reported, the configuration of the sulfoxide group in the latter compound was not determined. The ketone **11** was converted to its dimethyl ketal **13** and also was reduced with sodium borohydride to the hydroxysulfoxide **12** which is isomeric with the hydroxysulfoxide **10**. By means of triethyloxonium fluoroborate, sulfoxide **12** was converted[11] to **10** thereby showing that **10** and **12** are isomeric in the sulfoxide function only. The sulfoxide groups in **11**, **12**, and **13** are assigned the axial configuration on the basis of their NMR spectra (Table 2) in which the β-axial protons appear at lower field than the β-equatorial ones.[12-14]

The unexpected equatorial oxidation of **9** using t-butyl hypochlorite was also exhibited with 4-hydroxythiane (**14**) and resulted in the *trans* sulfoxide **15** (Scheme 3).

It has been shown[15] that the diaxial conformation **15a** is the more stable one. Oxidation of **14** with wet bromine gave an unstable yellow product which is assumed to be a bromine complex,[16] however, oxidation with hyprobromous acid gave **15**. The isomeric *cis* sulfoxide **18** was prepared as shown in Scheme 3. Thus Scheme 3 provides convenient and stereospecific routes for the preparation of the isomeric sulfoxides **15** and **18**. It should be noted that *trans*-4-hydroxythiane l-oxide (**18**) has a higher melting point than its *cis* isomer **15** in contradiction to the generalization given by Martin and Uebel.[15]

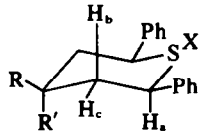
DISCUSSION

The steric course of the oxidation of thianes by reagents that involve direct oxygen transfer to sulfur such as peracids, hydroperoxides, ozone, etc was established from Johnson's[1] work to be preferentially equatorial. The reactions are known[17] to involve an electrophilic attack on sulfur. The



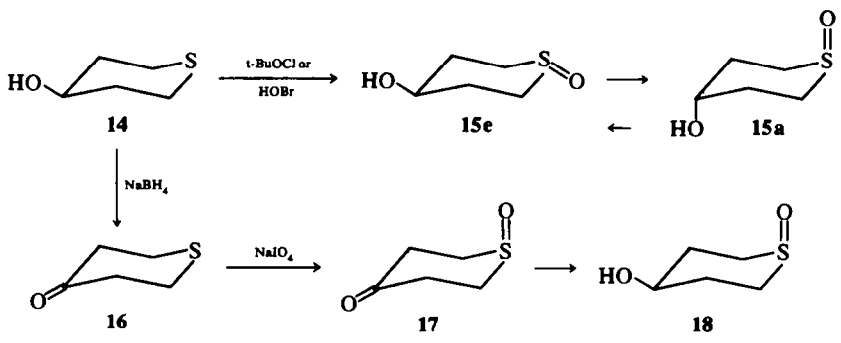
SCHEME 2.

Table 2. NMR spectroscopic data[a] for some derivatives of *cis*-2,6-diphenylthiane



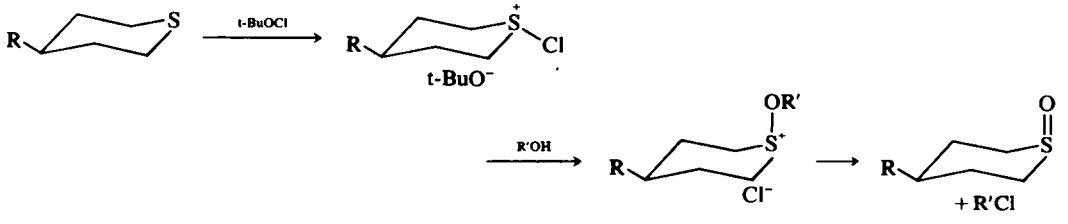
Comp.	δ (ppm)						J (Hz)			
	H_a	H_b	H_c	H_R	$H_{R'}$	Aromatic	$J_{ab} = J_{bc}$	J_{ac}	$J_{bR'}$	$J_{cR'}$
5	4·08 (q)[b]	3·07 (t)	2·73 (q)	2·37 (s); 7·55 (q)		7·27 (s)	12	3	—	—
6	4·07 (q)	2·07 (m)				7·30 (m)	10[c]	3	—	—
7	3·77 (q)	2·0 (m)				7·33 (m)	10[c]	4	—	—
8	3·70 (q)	2·75 (o)	1·9 (m)			7·33 (m)	12	2	12	3[d]
9	4·12 (q)	1·93 (q)	2·50 (sx)	1·9 (s)	3·70 (sx)	7·37 (m)	12	3	12	3
10	4·27 (q)	2·58 (m)		4·7 (s)	4·32 (m)	[e]	11[c]	3	—	—
11	4·20 (q)	3·76 (t)	2·70 (q)	—	—	7·38 (s)	13	2	—	—
12	4·18 (d)	3·07 (q)	2·35 (d)	—	5·29 (m)	[e]	12	—	12	—
13	4·0 (q)	2·82 (t)	2·20 (q)	3·32 (s); 3·25 (s)		7·38 (s)	14	3	—	—

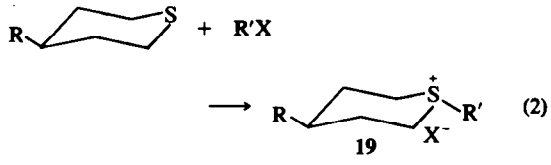
[a] In $CDCl_3$ with TMS internal standard.
[b] s = singlet; d = doublet; t = triplet; q = quartet; o = octet; m = multiplet; sx = sextet
[c] J_{ab}.
[d] J_{bR}.
[e] Solvent, pyridine.



SCHEME 3.

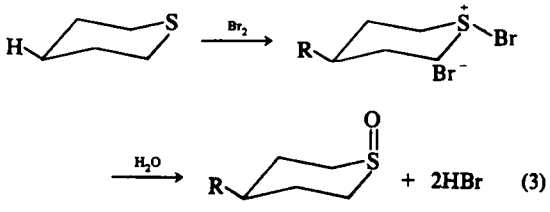
mechanism of the reaction of t-butyl hypochlorite with sulfides was shown[18–20] to involve an initial electrophilic attack by Cl^+ on sulfur to form a chlorosulfonium ion followed by a nucleophilic displacement of Cl^- from sulfur by an alcohol to form an alkoxysulfonium salt intermediate whose decomposition or hydrolysis results in the sulfoxide. The almost exclusive generation of axial thiane l-oxides by this reaction can again be rationalized by an electrophilic equatorial attack by Cl^+ on sulfur (Eq 1) followed by an axial attack of the alcohol. The high stereospecificity of the reaction indicates that there is neither isomerization in the first nor in the second step of the reaction. Katritzky has shown[21] that the reaction between thianes and alkyl halides (Eq 2) leads to a high preponderance of the equatorial sulfonium salts **19**. This reaction again may be considered as proceeding by an electrophilic attack by R'X on sulfur. We therefore can make the generalization that *electrophilic reactions on thianes proceed by equatorial attack.*





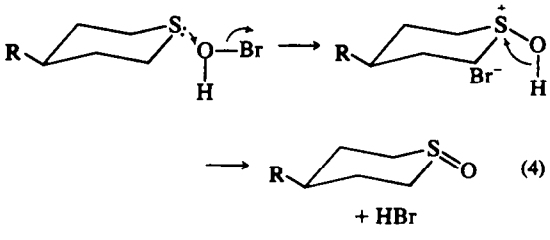
19 (2)

We have shown that oxidation of thianes by wet bromine preferentially yields the equatorial sulfoxides. Now it could be expected that this reaction proceeds by a two step process (Eq 3) which is



(3)

analogous with the reaction of t-butyl hypochlorite (Eq 1). Such a process, however, should yield the axial sulfoxide which contradicts our generalization. The formation of equatorial sulfoxides by wet bromine therefore suggests a direct oxygen transfer to sulfur (Eq 4) by hypobromous acid which is



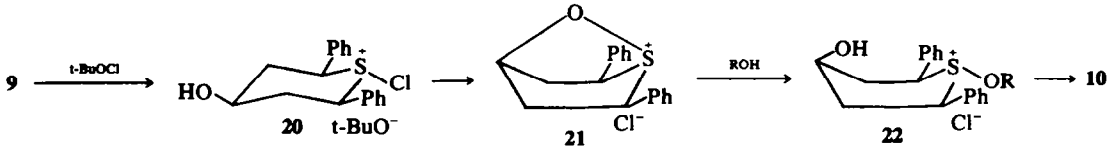
(4)

present in equilibrium with bromine in water. This assumption is confirmed by the identical product composition from the oxidation of thianes with either wet bromine or hypobromous acid solution. It seems that the affinity of sulfur for oxygen is greater than that for bromine and this makes reaction (4) the more favorable path relative to (3).

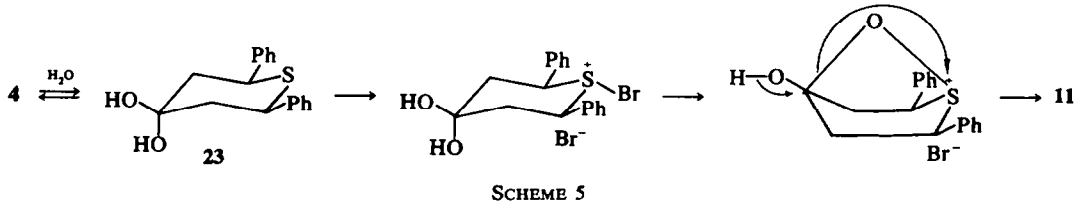
The unexpected formation of the equatorial sulfoxides **10** and **15e** in the t-butyl hypochlorite oxidation of the 4-hydroxythianes **9** and **14** respectively may be explained by participation of the 4-OH groups in the reaction as shown in Scheme 4. Equatorial attack at sulfur by Cl^+ gives the chlorosulfonium ion **20** which then undergoes an intermolecular nucleophilic displacement of chloride anion by the 4-OH group resulting in the cyclic alkoxysulfonium ion **21**. Nucleophilic attack at sulfur by the alcohol solvent with ring opening followed by hydrolysis or decomposition of the alkoxysulfonium ion **22** results in the equatorial sulfoxide **10**. Similar considerations with **14** account for the formation of the equatorial sulfoxide **15e**. Such participation by a 4-OH group was observed by us in the chlorination of thiane oxides.[6]

The reason for the unexpected formation of the axial sulfoxide **11** in the oxidation of **4** with wet bromine is less straightforward since several explanations can be advanced. One explanation is the attack at sulfur by bromine rather than hypobromous acid and subsequent displacement of bromide anion by water according to Eq (3). A modification of this mechanism (Scheme 5) involves formation of the ketone hydrate **23** followed by equatorial bromination at the sulfur and subsequent participation of the 4-OH group. However, it is difficult to assume that **4** is attacked by Br_2 whereas the very similar **6** reacts with HOBr under the same conditions according to Eq (4). An alternative mechanism involving hypobromous acid rather than bromine is shown in Scheme 6. The hypobromous acid preferentially adds to the ketone rather than attacks the sulfur because the approach to sulfur is hindered by the two Ph groups.

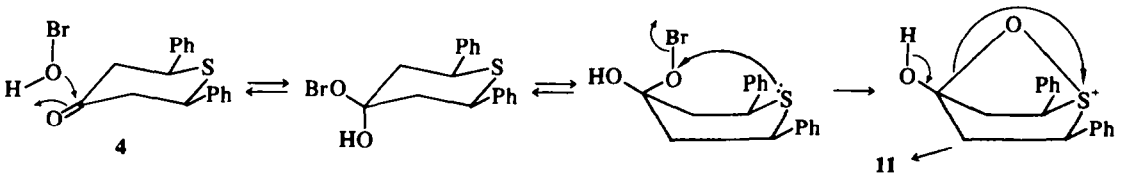
We have shown that electrophilic reactions of thianes occur by equatorial attack at sulfur. It is of interest to consider the reasons for this preferential equatorial attack. In analogy with the hydride re-



SCHEME 4



SCHEME 5



SCHEME 6

duction of cyclohexanones, Johnson proposed[1] that the stereochemical results of the oxidation of thianes are governed by "product development" and "steric approach" controls. While the validity of this analogy has been questioned,[22] the analogy of thiane oxidations with the reactions of cyclohexanones and methylenecyclohexanes seems to be correct when the recent proposal[23] for the factors governing reactions of the latter compounds is considered. It was proposed[23] that the stereochemistry of reactions of unhindered cyclohexanones and methylenecyclohexanes, is determined largely by electronic and not steric requirements and depends on the kind of the reaction. Nucleophilic attack at the carbon of an exocyclic double bond adjacent to the 6-membered ring proceeds preferentially from the axial direction and electrophilic attack from the equatorial direction. This is due to the interaction between the π orbitals of the exocyclic double bond and the symmetrical orbital of the β C–C σ bonds which results in different electron densities on the two faces of the double bond. The electron density of the HOMO is higher on the equatorial rather than on the axial side of the double bond and hence electrophilic attack proceeds preferentially from the equatorial side.

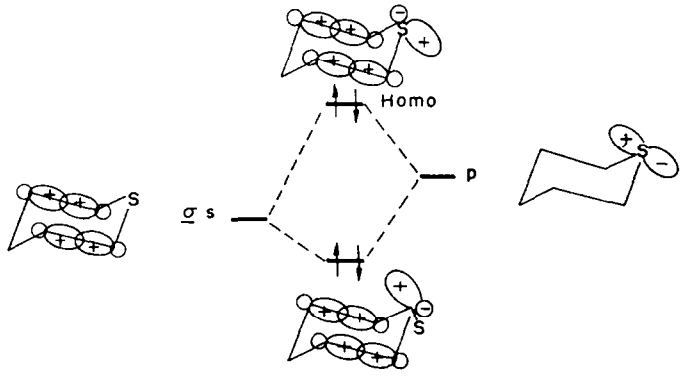
A similar situation prevails in thianes. The HOMO of H_2S consists[24] of a p orbital perpendicular to the plane of the molecule and, by analogy, we assume that in thianes the highest occupied orbital on the sulfur is perpendicular to the C–S–C plane. This orbital interacts with the β C–C symmetrical σ orbital (hyperconjugation) to give two new orbitals of different energies (Scheme 7). The more energetic of these is the HOMO of the system and this orbital will be attacked by electrophiles. Now the interaction between the p and the symmetrical σ orbital in the HOMO is of an antibonding nature and therefore the electron density on the equatorial side of the C–S–C plane will be larger than on the axial side. Hence electrophilic attack on thianes will be favored from the equatorial side as was observed.

EXPERIMENTAL

General details were the same as reported previously,[14] unless otherwise indicated. GLC was performed on an Aerograph A-700 instrument with a 2-m Carbowax column, 20% on Chromosorb W, at a column temp of 200°. TLC was performed using 0·75 mm thick layers of fluorescent silica gel (Merk GF_{254}) on 20 × 20 cm glass plates and the eluant is indicated in parentheses. Bands were observed under UV light or were developed by iodine vapor. The separated bands were extracted with methanol–$CHCl_3$ (1:1) and the pure products were isolated by evaporation of the solvent.

4-Keto-cis-2,6-diphenylthiane tosylhydrazone (5)

A soln of 4[7] (1·34 g; 5 mmole) and tosylhydrazine[25] (1·0 g; 5·5 mmole) in 25 ml alcohol was refluxed for 0·5 h during which time a heavy ppt formed. The mixture was cooled and filtered giving 2·0 g (92%) of product, m.p. 188–194°. Recrystallization from CH_2Cl_2-hexane gave the analytical sample: m.p. 190–191° (dec); IR 3225 (NH), 1645 cm^{-1} (C=N). (Found: C, 66·00; H, 5·66; N, 5·98; S, 14·45. $C_{24}H_{24}N_2S_2O_2$ requires: C, 66·03; H, 5·54; N, 6·42; S, 14·69%).



SCHEME 7.

cis-2,6-*Diphenylthiane* (6)

(a) *Wolff–Kishner reduction of* 4-*keto*-cis-2,6-*diphenylthiane* (4). A soln of 4[7] (5 g; 18·5 mmole), 90% hydrazine hydrate (5 ml) and KOH (3 g) in 45 ml of diethylene glycol was refluxed for 1 h, distilled until the internal temp was 175°, and refluxed for an additional h at 175°. After cooling the soln, 75 ml of water was added and the soln was extracted with ether. The combined organic solns were washed with water, dried ($MgSO_4$), and the solvent was removed under vacuum. The resulting yellow crystalline residue was recrystallized from AcOH using charcoal to give 635 mg (13·5%) of product, m.p. 96–97° (lit.[7] m.p. 98°).

(b) *Reduction of* 4-*keto*-cis-2,6-*diphenylthiane tosylhydrazone* (5). To a slurry of $LiAlH_4$ (22·3 g; 0·59 mole) in 250 ml dry THF was added dropwise with stirring a soln of 5 (20·4 g; 0·047 mole) in 250 ml dry THF. When addition was complete the soln was refluxed overnight, 50 ml water was carefully added, and the resulting grey slurry was diluted with 300 ml ether. The solid was filtered out and washed with ether several times and the combined organic solns were dried ($MgSO_4$) and the solvent was removed under vacuum. The resulting residue was recrystallized from alcohol to give 5·65 g (48%) of product, m.p. 96–98°. Concentration of the mother liquor gave an additional 840 mg (7%) of product.

4-*Hydroxy*-cis,cis-2,6-*diphenylthiane* (9)

A soln of 4 (2·68 g; 0·01 mole) in 100 ml MeOH was stirred while cooling in an ice bath and $NaBH_4$ (1·0 g; 0·026 mole) was added. When gas evolution had ceased, the ice bath was removed and stirring was continued overnight. The soln was acidified with dil HCl, concentrated under vacuum, diluted with water, and extracted with ether. The combined organic solns were washed with sat $NaHCO_3$ aq, dried ($MgSO_4$), and the solvent was removed under vacuum. Recrystallization from $CHCl_3$–hexane gave 1·76 g (65%) of product, m.p. 151–154°. Further recrystallization from MeOH gave m.p. 155–156° (lit.[10] m.p. 155–156°).

cis-4-*Hydroxy*-cis,cis,2,6-*diphenylthiane* 1-*oxide* (12)

Compound 11 (2·84 g; 0·01 mole) was reduced with $NaBH_4$ (1·90 g; 0·05 mole) in 250 ml MeOH as described. Dilution with water caused a heavy ppt to form. This was filtered and recrystallized from MeOH to give 2·17 g (76%) of product, m.p. 238–240° (dec). An additional 100 mg (4%) of product, m.p. 242–245° (dec) was obtained by concentrating the mother liquor. Further recrystallization from MeOH gave the analytical sample: m.p. 243–244° (dec); IR 3350 (OH), 1020 cm^{-1} (S=O). (Found: C, 71·07; H, 6·56; S, 11·58. $C_{17}H_{18}SO_2$ requires: C, 71·29; H, 6·33; S, 11·19%).

cis-4-*Hydroxythiane* 1-*oxide* (18)

Compound 17[26]* (3·5 g; 0·0265 mole) was reduced with $NaBH_4$ (2·5 g) in 150 ml MeOH as described. The MeOH soln was neutralized with conc H_2SO_4, the solvent was removed under vacuum, and the residue was extracted with boiling $CHCl_3$. The combined organic solns were evaporated under vacuum and the residue was recrystallized from CH_2Cl_2–ether to give 2·55 g (72%) of product: m.p. 119–121°; IR 3390 (OH), 1060 cm^{-1} (S=O); NMR: δ 3·7 (1H, CH–OH, half-width 15 Hz) (lit.[15] δ 3·8, half-width 16 Hz). (Found: C, 45·07; H, 7·30; S, 24·33. $C_5H_{10}SO_2$ requires: C, 44·75; H, 7·51; S, 23·90%). The product is hygroscopic.

Oxidation of 4-t-*butylthiane* (1)

(a) *Method A* (*wet bromine*). To a soln of 1[14] (158 mg; 1 mmole) in 10 ml ether was added 3 ml water and the mixture was cooled in an ice bath. Br_2 was added dropwise to the stirred mixture until the brown color of the Br_2 no longer faded. The ether layer was then separated and the aqueous layer was extracted with ether. The combined organic solns were washed with satd $NaHCO_3$ aq, dried ($MgSO_4$), and the solvent was removed in vacuum. GLC analysis of the oily residue (107 mg; 61%) indicated *cis*-2 and *trans*-3 in the ratio 1:4.

(b) *Method B* (*hypobromous acid*). An aqueous soln of HOBr was prepared, purified, and analysed immediately before use according to the procedure of Branch and Jones.[27] To a soln of 1 (158 mg; 1 mmole) in 10 ml ether was added 0·064 N aqueous HOBr (15·6 ml; 1 mmole). The mixture was stirred overnight and then treated as in (a). GLC analysis of the oily residue (178 mg) indicated 20% of unreacted starting material together with the *cis*-2 and *trans* sulfoxide (3) in the ratio 22:78.

Oxidation of 4-*keto*-cis-2,6-*diphenylthiane* (4)

(a) *With wet bromine.* Treatment of 4 (5·36 g; 0·02 mole) with wet Br_2 according to Method A resulted in a white ppt. This was filtered off, washed with water and ether, and dried to give 11 (4·75 g; 83%), m.p. 186–190° (dec). Recrystallization from $CHCl_3$ gave m.p. 192–193° (dec) (lit.[7] m.p. 196–198°); IR 1725 (C=O), 1055 cm^{-1} (S=O).

(b) *With hypobromous acid.* Treatment of 4 (536 mg; 2 mmole) with 0·064 N aqueous HOBr (31·2 ml; 2 mmole) according to Method B resulted in a ppt which, after treatment as in part (a), gave 342 mg of 11, m.p. 190–197° (dec). An additional 75 mg of 11, m.p. 190–195° (dec) was obtained by concentrating the mother liquor, total yield, 74%.

(c) *Method C* (*t-butyl hypochlorite*). Treatment of 4 (5·36 g; 0·02 mole) with t-butyl hypochlorite (2·47 g; 0·0235 mole) according to the procedure of Johnson and McCants resulted in 5·88 g of CH_2Cl_2 extract. This material was triturated with ether and filtered to give 1·2 g of 11, m.p. 183–189° (dec). An additional 520 mg of 11, m.p. 188–192° (dec) was obtained by concentrating the mother liquor, total yield, 30%.

Oxidation of cis-2,6-*diphenylthiane* (6)

(a) *With wet bromine.* Treatment of 6 (1·26 g; 5 mmole) with wet Br_2 according to Method A resulted in a white ppt. The material was filtered and after two recrystallizations from CH_2Cl_2–hexane gave 7 (328 mg; 24%), m.p. 214–216°. Further recrystallization gave the analytical sample: m.p. 221–222°; IR 1038 cm^{-1} (S=O). (Found: C, 75·22; H, 6·56; S, 11·82. $C_{17}H_{18}SO$ requires: C, 75·51; H, 6·71; S, 11·86%). The mother liquors were combined, the solvent was removed in vacuum and the resulting gum was extracted with boiling hexane. The combined hexane solns were filtered (charcoal) and concentrated to give unreacted 6 (100 mg; 8%).

(b) *With hypobromous acid.* Treatment of 6 (254 mg; 1 mmole) with 0·044 N aqueous HOBr (45 ml; 2 mmole) according to Method B resulted in a white ppt. The mixture was extracted with CH_2Cl_2 and the combined organic solns were washed with satd $NaHCO_3$ aq, dried

*As this material is extremely water soluble, we found it advantageous to isolate the material by evaporating the aqueous soln to dryness under vacuum.

($MgSO_4$), and the solvent removed in vacuum to give 305 mg of a crystalline residue. TLC on three plates [$CHCl_3$–MeOH (98:2)] gave two fractions. The band at R_f 0·31 yielded 115 mg (43%) of *trans,trans*-7, m.p. 221–220° while the band at R_f 0·85 gave 98 mg of a yellow oil which was not characterized.

(c) *With t-butyl hypochlorite.* Treatment of **6** (1 mmole) with t-butyl hypochlorite (114 mg; 1·05 mmole) according to Method C resulted in 283 mg obtained from the CH_2Cl_2 extract. TLC on three plates as in part (b) gave three fractions. The band at R_f 0·31 yielded 27 mg (10%) of **7**, m.p. 221–222°. The band at R_f 0·5 yielded 29 mg (11%) of **8**: m.p. 220–221°; IR 1038 cm^{-1} (S=O). (Found: C, 75·25; H, 6·51; S, 12·10. $C_{17}H_{18}SO$ requires: C, 75·51; H, 6·71; S, 11·86%). The band at R_f 0·85 yielded 192 mg of yellow oil.

Oxidation of 4-*hydroxy*-cis,cis-2,6-*diphenylthiane* (**9**)

(a) *With wet bromine.* Treatment of **9** (2·5 g; 9·25 mmole) with wet Br_2 according to Method A resulted in a white ppt. This was filtered off, washed with water and ether, and dried. The material was slurried in $CHCl_3$, filtered, and recrystallized from MeOH to give **10** (1·38 g; 52%): m.p. 240–244° (dec); IR 3330 (OH), 1015 cm^{-1} (S=O). (Found: C, 71·10; H, 6·08; S, 10·88. $C_{17}H_{18}SO_2$ requires: C, 71·29; H, 6·33; S, 11·19%).

(b) *With t-butyl hypochlorite.* Treatment of **9** (932 mg; 3·45 mmole) with t-butyl hypochlorite (384 mg; 3·52 mmole) according to Method C resulted in 904 mg of a product from the CH_2Cl_2 extract. Recrystallization from MeOH gave **10** (468 mg; 48%), m.p. 230–240° (dec). A second recrystallization gave m.p. 240–241° (dec).

(c) *With chlorine.* A soln of **9** (270 mg; 1 mmole) and pyridine (0·4 ml) in 10 ml CH_2Cl_2 was chlorinated with Cl_2 according to the procedure described.[14] Fractional crystallization of the crude product from $CHCl_3$ yielded three fractions each with m.p. 225–234°. These were combined and recrystallized from MeOH to give **10** (40 mg; 14%), m.p. 235–243° (dec).

Oxidation of 4-*hydroxythiane* (**14**)

(a) *With hypobromous acid.* 4-Hydroxythiane **14** (354 mg; 3 mmole) was treated with 0·064 N aqueous HOBr (46·8 ml; 3 mmole) according to Method B with the following modifications. After stirring overnight, the mixture was neutralized with powdered $NaHCO_3$ and evaporated to dryness under vacuum in a rotary evaporator with a bath temp of about 50°. The white residue was extracted several times with CH_2Cl_2 and the combined organic solns were evaporated under vacuum. The resulting residue was recrystallized from $CHCl_3$–CCl_4 to give 238 mg (59%) of the *trans*-**15**: m.p. 159–161°; IR 3290 (OH), 990 cm^{-1} (S=O); NMR: δ 4·0 (1H, CH–OH, half-width 11 Hz) (lit.[15] δ 4·0, half-width 12 Hz). (Found: C, 44·49; H, 7·22; S, 23·80. $C_5H_{10}SO_2$ requires: C, 44·75; H, 7·51; S, 23·90%). The product is hygroscopic.

(b) *With t-butyl hypochlorite.* Treatment of **14** (4·0 g; 0·0336 mole) with t-butyl hypochlorite (3·76 g; 0·0346 mole) according to Method C resulted in 4·40 g of CH_2Cl_2 extract. Recrystallization from $CHCl_3$–CCl_4 gave **15** (3·64 g; 81%), m.p. 157–160°.

4-*Keto*-cis-cis-2,6-*diphenylthiane* 1-*oxide dimethylketal* (**13**)

To a soln of **11** (284 mg; 1 mmole) in 50 ml MeOH was added a small crystal of *p*-toluenesulfonic acid and the soln was refluxed for 1 h. The MeOH was then distilled off, an additional 50 ml MeOH was added and the procedure was repeated. The resulting residue was dissolved in 50 ml ether, the ether soln was washed with satd $NaHCO_3$ aq followed by water, dried ($MgSO_4$), and the solvent was removed under vacuum to give 300 mg (91%) of a product, m.p. 145–147°. Recrystallization from $CHCl_3$–hexane gave the analytical sample: m.p. 144–146°; IR 1040 cm^{-1} (S=O). (Found: C, 68·84; H, 6·51; S, 9·42. $C_{19}H_{22}SO_3$ requires: C, 69·07; H, 6·71; S, 9·71%).

trans-4-*Hydroxy*-trans-trans-2,6-*diphenylthiane* 1-*oxide* (**10**) *from* cis-4-*hydroxy*-cis,cis-2,6-*diphenylthiane* 1-*oxide* (**12**)

A soln of **12** (286 mg; 1 mmole) in 25 ml CH_2Cl_2 was treated with triethyloxonium fluoroborate (190 mg; 1 mmole) according to the procedure of Johnson and McCants.[11,28] As no ppt formed, the solvent was removed in vacuum and the resulting oily residue was mixed with water and titrated to the phenolphthalein endpoint with 0·1N NaOH. The mixture was then extracted with CH_2Cl_2, the combined organic solns were dried ($MgSO_4$), and the solvent was removed in vacuum. The resulting residue was recrystallized from MeOH–CCl_4 to give **10** (28 mg; 10%), m.p. 235–240° (dec), m.p. of its mixture with the starting material, 200–225°. An IR of the product was identical with that of the product obtained from the oxidation of **9**.

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