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ACETALS AND THIOACETALS FROM THIODIGLYCOLALDEHYDE: SOME OXIDATION PRODUCTS*

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ABSTRACT

Thiodiglycolaldehyde (2,2′-thiobisacetaldehyde, **1a**) reacted severally with methanol, ethanol, and 2-propanol to give mixtures variously of thiodiglycolaldehyde bis(dialkyl acetals) (**3a,b**), *cis*-2,6-dialkoxy-1,4-oxathianes (**5b–d**), and *trans*-2,6-dialkoxy-1,4-oxathianes (**7a–c**). Thiodiglycolaldehyde bis(di-isopropyl acetal) (**3c**) was not formed in the reaction of **1a** and 2-propanol, but **3c** was obtained after bromoacetaldehyde di-isopropyl acetal was treated with sodium sulfide. The stereoisomers corresponding to 2,6-dimethoxy-1,4-oxathiane (**5b**, **7a**) were obtained from the acyclic dimethyl acetal **3a**. The reaction between **1a** and thiols in acid media have been studied. With ethanethiol, thiodiglycolaldehyde bis(diethyl dithioacetal) was the only product, but a mixture of thiodiglycolaldehyde bis(di-*tert*-butyl dithioacetal), *cis*-2,6-bis(*tert*-butylthio)-1,4-dithiane, and *trans*-2,6-bis(*tert*-butylthio)-1,4-dithiane was obtained from 2-methyl-2-propanethiol. On oxidation to sulfones of the stereoisomers of 2,6-dialkoxy-1,4-oxathiane and 2,6-bis(alkylthio)-1,4-dioxane with hydrogen peroxide, the configurations were retained, but the stereoisomers of 2,6-bis(*tert*-butylthio)-1,4-dithiane were transformed into the same oxidation product.

INTRODUCTION

The reactions between diglycolaldehyde (**1b**) and alcohols and thiols in acid media have been reported[2,3]. The formation of diglycolaldehyde bis(dialkyl acetals) (**2a–d**) and mixtures of 2,6-dialkoxy-1,4-dioxanes (**4a–c**, **6a–c**) was observed when alcohols were used. Primary and secondary thiols gave diglycolaldehyde bis(dialkyl dithioacetals) (**8a–d**) and mixtures of 2,6-bis(alkylthio)-1,4-dioxanes (**11a–c**, **12a–c**), but a mixture of the acyclic dithioacetal (**8e**) and *cis*- and *trans*-3,5-bis(*tert*-butylthio)-1,4-oxathianes (**13a** and **13b**) was obtained from 2-methyl-2-propanethiol. On the other hand, no oxidation product was obtained[4] when either thiodiglycolaldehyde bis(diethyl acetal) (**3b**) or *cis*-2,6-diethoxy-1,4-oxathiane (**5c**) was treated with hydrogen peroxide in aqueous acetone.

We now report on the reactions of thiodiglycolaldehyde (**1a**) with alcohols and thiols in acid media, and on the oxidations of acetals and thioacetals of **1a**.

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*Derivatives of 3-Hetero-1,5-dialdehydes, Part II. For Part I, see ref. 1.

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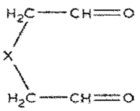
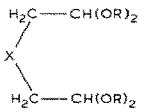
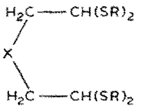


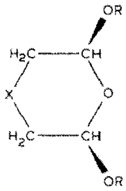
1a X = S
1b X = O



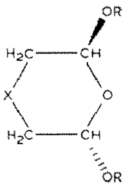
2a X = O, R = Me
2b X = O, R = Et
2c X = O, R = Pr
2d X = O, R = ^{i}Pr
3a X = S, R = Me
3b X = S, R = Et
3c X = S, R = ^{i}Pr
3d X = SO, R = Me
3e X = SO_2, R = Me
3f X = SO_2, R = Et



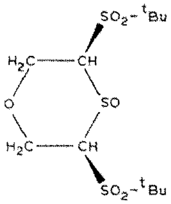
8a X = O, R = Me
8b X = O, R = Et
8c X = O, R = Pr
8d X = O, R = ^{i}Pr
8e X = O, R = ^{t}Bu
9a X = S, R = Et
9b X = S, R = ^{t}Bu



4a X = O, R = Et
4b X = O, R = Pr
4c X = O, R = ^{i}Pr
5a X = S, R = H
5b X = S, R = Me
5c X = S, R = Et
5d X = S, R = ^{i}Pr
13a X = SO_2, R = Me
13b X = SO_2, R = Et
13c X = SO_2, R = ^{i}Pr



6a X = O, R = Et
6b X = O, R = Pr
6c X = O, R = ^{i}Pr
7a X = S, R = Me
7b X = S, R = Et
7c X = S, R = ^{i}Pr
14a X = SO_2, R = Me
14b X = SO_2, R = Et
14c X = SO_2, R = ^{i}Pr



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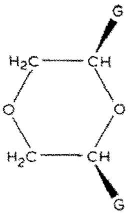
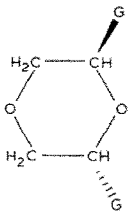
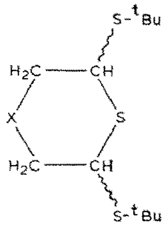


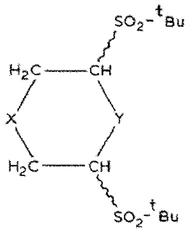
11a G = S-Et
11b G = S-Pr
11c G = S-^{i}Pr
19a G = SO_2Et
19b G = SO_2-Pr



12a G = S-Et
12b G = S-Pr
12c G = S-^{i}Pr
20a G = SO_2Et
20b G = SO_2-Pr



10 X = S (**10a** *cis*, **10b** *trans*)
15 X = O (**15a** *cis*, **15b** *trans*)



17 X = SO_2, Y = SO
18 X = SO, Y = SO_2

RESULTS AND DISCUSSION

When thiodiglycolaldehyde (**1a**) or its hemialdal form, *cis*-2,6-dihydroxy-1,4-oxathiane (**5a**), was treated with a large excess of an alcohol in the presence of a small proportion of conc. sulfuric acid at room temperature, mixtures of acyclic and cyclic acetals were obtained as noted in Table I.

Thiodiglycolaldehyde bis(dimethyl acetal) (**3a**) was the main product from the reaction between **1a** or **5a** and methanol, but traces of *cis*-2,6-dimethoxy-1,4-oxa-

TABLE I

PRODUCTS AND YIELDS FOR THE REACTIONS OF **1a** OR **5a** WITH ALCOHOLS IN ACID MEDIA

Alcohol	*Time (days)*	*Products (%)*	*Overall yields (%)*
MeOH	1	**3a** (83), **5b** + **7a** (traces)	83
EtOH	2.5	**3b** (50), **5c** + **7b** (24.7)	74.7
^{i}PrOH	7	**5d** + **7c** (61.3)	61.3

thiane (**5b**) and *trans*-2,5-dimethoxy-1,4-oxathiane (**7a**) were also formed. This behaviour contrasts with that reported[2] for diglycolaldehyde (**1b**) and methanol under similar conditions, as no cyclic products were detected.

With ethanol, thiodiglycolaldehyde bis(diethyl acetal) (**3b**) was obtained, but a relatively large amount of *cis*- and *trans*-2,6-diethoxy-1,4-oxathiane (**5c** and **7b**) was also formed. The ratio of cyclic and acyclic acetals was higher than that reported[2] for the reaction between diglycolaldehyde and ethanol.

With 2-propanol, *cis*- and *trans*-2,6-di-isopropoxy-1,4-oxathianes (**5c** and **7c**) were the only products. Thiodiglycolaldehyde bis(di-isopropyl acetal) (**3c**) was not formed, but could be prepared (88%) from bromoacetaldehyde di-isopropyl acetal and sodium sulfide.

The acyclic acetals **3** tended to cyclise to 2,6-dialkoxy-1,4-oxathianes. Thiodiglycolaldehyde bis(diethyl acetal) (**3b**) in anhydrous ether was transformed[4] into a crystalline 2,6-diethoxy-1,4-oxathiane on treatment with anhydrous hydrogen chloride, but the configuration was not established. We have found that, on storage in an open vessel, **3b** spontaneously and quantitatively cyclised to give a mixture of **5c** (major) and **7b** (minor). The ^{1}H-n.m.r. and melting point data showed that the material described by Clarke and Smiles[4] was *cis*-2,6-diethoxy-1,4-oxathiane (**5c**). The above transformation did not take place when **3b** was stored in a sealed container. Thiodiglycolaldehyde bis(dimethyl acetal) (**3a**) was transformed into a mixture of **5b** (major) and **7a** (minor) on treatment[4] with acid.

In the reactions between diglycolaldehyde (**1b**) and alcohols in acid media[2], the *trans*-2,6-dialkoxy-1,4-dioxanes (**6a–c**) were the main stereoisomers when cyclic products were formed; for thiodiglycolaldehyde (**1a**) or its hemialdal form **5a**, the *cis*-2,6-dialkoxy-1,4-oxathianes (**5b–d**) were the main products. Since the reaction times were so large, it may be assumed that equilibria were reached. The anomeric and steric effects make the *trans*-2,6-dialkoxy-1,4-dioxanes (**6a–c**) more stable than the *cis* stereoisomers, but the "hockey-stick" effect[5] makes the *cis*-2,6-dialkoxy-1,4-oxathianes (**5b–d**) more stable than the *trans* stereoisomers (**7a–c**). The "hockey-stick" effect may also explain why the value (~11 Hz) for $J_{ax} + J_{bx}$ in the *cis*-2,6-dialkoxy-1,4-oxathianes (**5b–d**) is independent of the bulk of R, whereas those for the *cis*-2,6-dialkoxy-1,4-dioxanes (**4a–c**) increase from 10.5 for the 2,6-diethoxy

TABLE II

SPECTROSCOPIC PROPERTIES OF 5 AND 7

Products	ν_{max} *(cm⁻¹)*	δH_x	$J_{ax} + J_{bx}$ *(Hz)*
5b	1174, 1120, 1034 1014, 982, and 728	4.7	10.8
5c	1170, 1120, 1032 1010, 980, and 730	4.66	11.0
5d	1168, 1030, 1012 972, and 722	4.80	11.0
7a	1114, 960, 862, and 798	5.0	7.5
7b	1117, 962, 856, and 789	5.16	7.5
7c	1120, 965, 863, and 790	5.23	8.0

derivative **4a** to 11.2 Hz for the 2,6-di-isopropoxy derivative[2] **4c**. The values for $J_{ax} + J_{bx}$ in the *cis*-2,6-dialkoxy-1,4-oxathianes (**5b–d**) showed that diequatorial conformers were favoured in the same proportion in all cases (see Table II).

The reaction between thiodiglycolaldehyde (**1a**) and thiols were carried out after dissolving the hemialdal form **5a** in conc. hydrochloric acid. With ethanethiol, thiodiglycolaldehyde bis(diethyl dithioacetal) (**9a**, ~100%) was the sole product. This result contrasts with that reported[3] for diglycolaldehyde (**1b**), which gave a mixture (**11a,12a**) of the stereoisomers of 2,6-bis(ethylthio)-1,4-dioxane. With 2-methyl-2-propanethiol, a mixture of thiodiglycolaldehyde bis(di-*tert*-butyl dithioacetal) (**9b**), *cis*-2,6-bis(*tert*-butylthio)-1,4-dithiane (**10a**), and *trans*-2,6-bis(*tert*-butylthio)-1,4-dithiane (**10b**) was obtained and this behaviour was similar to that reported[2] for the analogous reaction of diglycolaldehyde (**1b**).

When *cis*- and *trans*-2,6-dialkoxy-1,4-oxathiane (**5b–d, 7a–c**) in acetic anhydride–acetic acid were treated with hydrogen peroxide, the sulfonyl derivatives **13a–c** and **14a–c**, respectively, were formed with retention of configuration. The values (~10.5 Hz) of $J_{ax} + J_{bx}$ showed that diequatorial conformers are favoured for the **13a–c** stereoisomers and that the conformational populations appear to be independent of the nature of R.

Oxidation of thiodiglycolaldehyde bis(dimethyl acetal) (**3a**) gave, first, sulfinyldiacetaldehyde bis(dimethyl acetal) (**3d**, 92.5% after 2 h at room temperature) and then sulfonyldiacetaldehyde bis(dimethyl acetal) (**3e**, 100% after 13 days). Likewise, **3b** was transformed into sulfonyldiacetaldehyde bis(diethyl acetal) (**3f**, 92.8%), but thiodiglycolaldehyde bis(di-isopropyl acetal) (**3c**) gave a mixture (93.4%) of *cis*- and *trans*-2,6-di-isopropoxy-1,4-oxathiane 4,4-dioxide (**13c** and **14c**). Sulfonyldiacetaldehyde bis(diethyl acetal) (**3f**) gave the **13b,14b** mixture on prolonged storage at room temperature.

When both steroisomers of 3,5-bis(*tert*-butylthio)-1,4-oxathiane (**15a,b**) were

TABLE III

SPECTROSCOPIC PROPERTIES FOR COMPOUNDS **13** AND **14**

Products	δH_x	$J_{ax} + J_{bx}$ *(Hz)*	*Products*	δH_x	$J_{ax} + J_{bx}$ *(Hz)*
13a	4.86	10.6	**14a**	5.24	8.1
13b	4.91	10.5	**14b**	5.35	8.0
13c	5.04	10.5	**14c**	5.45	8.1

treated[3] with hydrogen peroxide in acetic anhydride–acetic acid, one only product (**16**) was formed. Similar treatment of each stereoisomer of 2,6-bis(*tert*-butylthio)-1,4-dithiane (**10a,b**) gave a crystalline product, m.p. 200°, the elemental analysis of which accorded with $C_{12}H_{24}O_7S_4$; the ^{1}H-n.m.r. spectrum showed a high symmetry and hence the structures **17** and **18** are possible. The structure 2,6-bis(*tert*-butylsulfonyl)-1,4-oxathiane 1,4,4-trioxide (**17**) was considered to be the more probable, because S-1 is more hindered than S-4 in **10a,b**. The formation of one only compound in the oxidation of **10a,b** may be attributed to the acidic nature of C-H in **17** or in an appropriate intermediate. The oxidation of *cis*- and *trans*-2,6-bis(alkylthio)-1,4-dioxanes (**11a–b** and **12a–b**) did not result in isomerisation; *cis*- and *trans*-2,6-bis(alkylsulfonyl)-1,4-dioxanes (**19a,b** and **20a,b**), respectively, were formed, so that the presence of a sulfur atom flanked by C-H groups appears to play a significant role in the above isomerisation processes.

EXPERIMENTAL

General methods. — Organic solutions were dried over anhydrous Na_2SO_4. Solvents were evaporated under diminished pressure at <40°. Column chromatography was carried out on Silica gel 60 (Merck, 70–230 mesh, ASTM). Melting points (uncorrected) were obtained with an Electrothermal Melting Point apparatus. I.r. spectra were recorded for films on NaCl or KBr discs with a Pye–Unicam SP 1000 spectrometer. ^{1}H-N.m.r. spectra were recorded for solutions in various solvents (internal Me_4Si) with a Perkin–Elmer–Hitachi R-20 B spectrometer. Chemical shifts are given on the δ scale and couplings in Hz. Mass spectra were recorded with a Hewlett-Packard model 5930 A spectrometer.

Thiodiglycolaldehyde bis(dimethyl acetal) (**3a**, 90%) and thiodiglycolaldehyde bis(diethyl acetal) (**3b**, 93.6%) were prepared as previously described[1]. *cis*-2,6-Dihydroxy-1,4-oxathiane (**5a**) was obtained from **3a** or **3b** (>90%) by acid hydrolysis[1], and anhydrous thiodiglycolaldehyde (**1a**, 88%) was obtained after the hemialdal **5a** was distilled[1].

Reactions between thiodiglycolaldehyde (**1a**) *and alcohols in acid media.* — *cis*-2,6-Dihydroxy-1,4-oxathiane (**5a**) or anhydrous thiodiglycolaldehyde (**1a**) was dissolved in the appropriate alcohol, and conc. H_2SO_4 was added. The mixture was stored at room temperature and then basified (MeONa–MeOH), the alcohol was evaporated, aqueous 50% K_2CO_3 (20 mL) was added, the mixture was extracted with chloroform (3 × 50 mL), and the combined extracts were dried, filtered, and concentrated, to give a crude oil.

The following alcohols, reaction times, and amounts of **5a** or **1a** were used.

	MeOH	*EtOH*	*^{i}PrOH*
Vol. (mL)	70	75	120
Time (days)	1	2.5	7
5a (g)	8.16	5.87	8.16
or			
1a (g)	7.08	5.09	7.08

(*a*) *With methanol.* Distillation of the crude material yielded, first, a mixture (1.75 g) of thiodiglycolaldehyde bis(dimethyl acetal)[1] (**3a**, major), *cis*-2,6-dimethoxy-1,4-oxathiane (**5b**), and *trans*-2,6-dimethoxy-1,4-oxathiane (**7a**), b.p. 113–116°/14 mmHg; and then **3a** (8.5 g, 83%), b.p. 134–135°/14 mmHg; ν_{max} 1195, 1125, 1065, and 965 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 4.39 (t, 1 H, *J* 5.5 Hz), 3.26 (s, 6 H), and 2.68 (d, 2 H, *J* 5.5 Hz).

Compounds **5b** and **7a** were prepared as follows. A mixture of thiodiglycolaldehyde bis(dimethyl acetal) (**3a**, 6.5 g) and anhydrous ether (30 mL) at ~ −5° was treated with a stream of anhydrous hydrogen chloride for 15 min. The mixture was left at room temperature for 15 min, basified (MeONa–MeOH) at low temperature, and concentrated. Water (10 mL) was added, the mixture was extracted with ether (2 × 25 mL), and the combined extracts were dried, filtered, and concentrated, to give a crude oil. Column chromatography (20:1 hexane–ether) yielded, first, **5b** (1.0 g, 19%), m.p. 158–160° (from ethanol); ν_{max} 1304, 1275, 1174, 1156, 1120, 1014, 982, 790, and 728 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 4.7 (dd, 1 H, *J* 7 and 3.8 Hz), 3.45 (s, 3 H), and 2.5 (m, 2 H). Eluted second was **7a** (0.47 g, 9.3%); ν_{max} 1215, 1164, 1114, 1040, 1008, 960, 862, 798, and 735 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 5.0 (dd, 1 H, *J* 4.5 and 3 Hz), 3.43 (s, 3 H), and 2.6 (m, 2 H).

(*b*) *With ethanol.* Distillation of the crude material yielded, first, the **5c**,**7b** mixture (2.05 g, 24.7%), b.p. 80–84°/1 mmHg (Found: C, 49.9; H, 8.3; S, 16.7. $C_8H_{16}O_3S$ calc.: C, 50.0; H, 8.3; S, 16.7%); and then thiodiglycolaldehyde bis(diethyl acetal) (**3b**; 5.76 g, 50.1%), b.p. 127–130°/3 mmHg; ν_{max} 1207, 1162, 1117, 1058, and 1015 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 4.55 (t, 1 H, *J* 5.5 Hz), 3.53 (q, 4 H, *J* 6.5 Hz), 2.72 (d, 2 H, *J* 5.5 Hz), and 1.20 (t, 6 H, *J* 6.5 Hz).

Chromatography of the mixture (15:1 hexane–ether) gave, first, *cis*-2,6-diethoxy-1,4-oxathiane (**5c**), m.p. 101–102° (from ethanol) (lit[4]. m.p. 101°); ν_{max} 1170, 1120, 1080, 1032, 1010, 980, 900, 872, 855, 760, and 730 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 4.66 (dd, 1 H, *J* 7.5 and 3.5 Hz), 4.1–3.2 (m, 2 H), 2.44 (m, 2 H), and 1.18 (t, 3 H, *J* 7 Hz). Eluted second was *trans*-2,6-diethoxy-1,4-oxathiane (**7b**);

ν_{max} 1212, 1117, 1050, 1020, 962, 856, and 798 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 5.16 (dd, 2 H, $J_{ax} + J_{bx}$ 7.5 Hz), 4.2–3.37 (m, 4 H), 2.6 (m, 4 H), 1.32 (t, 3 H, J 6.7 Hz), and 1.26 (t, 3 H, J 6.7 Hz).

(*c*) *With 2-propanol.* Distillation of the crude material yielded the **5d**,**7c** mixture (8.1 g, 61.3%), b.p. 65–67°/0.1 mmHg (Found: C, 54.6; H, 9.3. $C_{10}H_{20}O_3S$ calc.: C, 54.5; H, 9.1%).

Chromatography of the mixture (15:1 hexane–ether) gave *cis*-2,6-di-isopropoxy-1,4-oxathiane (**5d**, 3.92 g), m.p. 41–42°; ν_{max} 1168, 1145, 1039, 1012, 972, 938, 825, and 722 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 4.8 (dd. 1 H, J 8 and 3 Hz), 4.0 (septet, 1 H, J 6.3 Hz), 2.83–2.0 (m, 2 H), 1.18 (d, 3 H, J 6.3 Hz), and 1.13 (d, 3 H, J 6.3 Hz). Eluted second was *trans*-2,6-di-isopropoxy-1,4-oxathiane (**7c**, 2.56 g); ν_{max} 1200, 1120, 1050, 1020, 965, 863, 822, and 790 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 5.23 (dd, 1 H, $J_{ax} + J_{bx}$ 8.0 Hz), 4.0 (septet, 1 H, J 6.3 Hz), 2.62 (m, 2 H), and 1.23 (m, 6 H).

Thiodiglycolaldehyde bis(di-isopropyl acetal) (**3c**). — A mixture of bromoacetaldehyde di-isopropyl acetal (22.5 g), ethanol (66 mL), water (32 mL), and $Na_2S \cdot 9\ H_2O$ (36 g) was heated under reflux for 28 h. The ethanol was evaporated, the mixture was extracted with ether (4 × 25 mL), and the combined extracts were dried, filtered, and concentrated. Distillation of the residue yielded **3c** (14.24 g, 88.4%), b.p. 99–102°/0.2 mmHg; ν_{max} 1120, 1102, and 1024 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 4.73 (t, 1 H, J 5.5 Hz), 3.75 (septet, 2 H, J 6 Hz), 2.66 (d, 2 H, J 5.5 Hz), 1.15 (d, 6 H, J 6 Hz), and 1.13 (d, 6 H, J 6 Hz).

Reactions between thiodiglycolaldehyde (**1a**) *and thiols in acid media.* — *cis*-2,6-Dihydroxy-1,4-oxathiane (**5a**, 4.08 g) in conc. hydrochloric acid (15 mL) at ~0° was treated with the appropriate thiol (15 mL). The mixture was stirred at room temperature, basified with aqueous 40% KOH, and extracted with ether (2 × 50 mL), and the combined extracts were dried and concentrated.

(*a*) *With ethanethiol.* Reaction time, 30 min. Column chromatography (hexane) of the crude product yielded thiodiglycolaldehyde bis(diethyl dithioacetal) (**9a**; 9.9 g, ~100%); ν_{max} 1255, 1040, 960, and 900 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 4.0 (t, 1 H, J 7.1 Hz), 3.06 (d, 2 H, J 7.1 Hz), 2.65 (q, 4 H, J 7 Hz), and 1.26 (t, 6 H, J 7 Hz). Mass spectrum: m/z 330 ($M^{+\cdot}$), 268, 209, 207, 195, 182, 181, 148, 145, and 135 (100%).

(*b*) *With 2-methyl-2-propanethiol.* Reaction time, 120 min. Distillation of the crude product yielded a fraction (4.33 g), b.p. 120–135°/0.5 mmHg; undistilled material was recovered.

Crystallisation of the distilled material from ethanol (30 mL) gave *trans*-2,6-bis(*tert*-butylthio)-1,4-dithiane (**10b**, 1.77 g), m.p. 100–101°; ν_{max} 1365, 1355, 1155, 946, 932, 862, 778, and 680 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 4.35 (dd, 1 H, J 7.3 and 3.3 Hz), 3.3–2.7 (m, 2 H), and 1.38 (s, 9 H). Mass spectrum: m/z 296 ($M^{+\cdot}$), 206, 183, 151, 150, 149, 117, and 57 (100%) (Found: C, 48.9; H, 8.4. $C_{12}H_{24}S_4$ calc.: C, 48.6; H, 8.1%).

The material in the mother liquor was subjected to column chromatography (hexane), to give *cis*-2,6-bis(*tert*-butylthio)-1,4-dithiane (**10a**, 0.2 g), m.p. 88–90° (from methanol); ν_{max} 1362, 1278, 1153, 1140, 932, 709, and 694 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 4.08 (dd, 1 H, J 9.0 and 5.5 Hz), 2.9–2.77 (m, 2 H), and 1.41 (s, 9 H). Mass spectrum: m/z 296 ($M^{+\cdot}$), 239, 206, 183, 151, 150, 149, 117, and 57 (100%).

A mixture of **10a,b** (2.36 g) was also obtained.

Column chromatography (50:1 hexane–ether) of the undistilled material gave **10a,b** (1.74 g), and then thiodiglycolaldehyde bis(di-*tert*-butyl dithioacetal) (**9b**, 2.38 g); ν_{max} 1360, 1210, 1157, 900, 750, and 714 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 4.0 (t, 1 H, J 6.7 Hz), 3.15 (d, 2 H, J 6.7 Hz), and 1.33 (s, 18 H). Mass spectrum: m/z 442 ($M^{+\cdot}$), 385, 352, 296, 239, 238, 237, 208, 207, 206, 191, 183, 149, 117, and 57 (100%).

Oxidation of 2,6-dialkoxy-1,4-oxathianes. — A mixture of 2,6-dialkoxy-1,4-oxathiane (**5b–d**, **7a–c**), acetic acid, acetic anhydride, and aqueous 30% hydrogen peroxide was stored in the dark at room temperature and then concentrated, and ethanol was distilled several times from the residue in order to remove traces of acetic anhydride and acetic acid. The following conditions were used.

Starting material (g)	*AcOH–Ac$_2$O (1:1, mL)*	*Aqueous 30% H$_2$O$_2$ (mL)*	*Time (days)*	*Products (g, %)*
5b (0.15)	8	2	6	**13a** (0.12, 67.6)
7a (0.35)	8	2	7	**14a** (0.19, 45.7)
5c (0.262)	3.6	1	4	**13b** (0.174, 56.0)
7b (0.24)	6	1.5	8	**14b** (0.2, 71.4)
5d (0.55)	12	3	7	**13c** (0.474, 75.2)
7c (0.35)	8	2	7	**14c** (0.232, 57.9)

cis-2,6-Dimethoxy-1,4-oxathiane 4,4-dioxide (**13a**) had m.p. 165–166° (from methanol); ν_{max} 1302, 1256, 1170, 1155, 1118, 1030, 1010, 980, and 787 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 4.86 (dd, 1 H, $J_{ax} + J_{bx}$ 10.6 Hz), 3.55 (s, 3 H), and 3.2 (m, 2 H) (Found: C, 36.9; H, 6.2. $C_6H_{10}O_5S$ calc.: C, 36.7; H, 6.1%).

trans-2,6-Dimethoxy-1,4-oxathiane 4,4-dioxide (**14a**) had m.p. 133–134° (from ethanol); ν_{max} 1317, 1308, 1282, 1216, 1202, 1140, 1130, 1100, 1025, 976, 874, 818, 775, and 754 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 5.24 (dd, 1 H, $J_{ax} + J_{bx}$ 8.1 Hz), 3.48 (s, 3 H), and 3.28 (m, 2 H).

cis-2,6-Diethoxy-1,4-oxathiane 4,4-dioxide (**13b**) had m.p. 103–105° (from ethanol); ν_{max} 1313, 1260, 1165, 1122, 1031, 987, and 896 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 4.91 (dd, 1 H, $J_{ax} + J_{bx}$ 10.5 Hz), 4.16–3.3 (m, 2 H), 3.3–3.0 (m, 2 H), and 1.23 (t, 3 H, J 6.7 Hz) (Found: C, 42.9; H, 7.1. $C_8H_{16}O_5S$ calc.: C, 42.9; H, 7.2%).

trans-2,6-Diethoxy-1,4-oxathiane 4,4-dioxide (**14b**) had m.p. 125–127° (from ethanol); ν_{max} 1320, 1270, 1203, 1122, 1106, 1038, 1018, and 978 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 5.35 (dd, 1 H, $J_{ax} + J_{bx}$ 8 Hz), 4.15–3.5 (m, 2 H), 3.25 (m, 2 H), and 1.23 (t, 3 H, J 6.7 Hz) (Found: C, 43.0; H, 7.1. $C_8H_{16}O_5S$ calc.: C, 42.9; H, 7.2%).

cis-2,6-Di-isopropoxy-1,4-oxathiane 4,4-dioxide (**13c**) had m.p. 132–133° (from ethanol); ν_{max} 1300, 1259, 1228, 1172, 1130, 1030, 982, 936, and 770 cm^{-1}. ^{1}H-N.m.r. (CDCl$_3$) data: δ 5.04 (dd, 1 H, J_{ax} + J_{bx} 10.5 Hz), 4.06 (septet, 1 H, J 6 Hz), 3.07 (m, 2 H), 1.25 (d, 3 H, J 6 Hz), and 1.18 (d, 3 H, J 6 Hz) (Found: C, 47.8; H, 8.1. $C_{10}H_{20}O_5S$ calc.: C, 47.6; H, 8.0%).

trans-2,6-Di-isopropoxy-1,4-oxathiane 4,4-dioxide (**14c**) had m.p. 130–131° (from ethanol); ν_{max} 1322, 1270, 1204, 1123, 1091, 1045, 1020, and 982 cm^{-1}. ^{1}H-N.m.r. (CDCl$_3$) data: δ 5.45 (dd, 1 H, J_{ax} + J_{bx} 8.1 Hz), 4.05 (septet, 1 H, J 6 Hz), 3.21 (m, 2 H), 1.26 (d, 3 H, J 6 Hz), and 1.18 (d, 3 H, J 6 Hz) (Found: C, 47.8; H, 7.9. $C_{10}H_{20}O_5S$ calc.: C, 47.6; H, 8.0%).

Oxidation of thiodiglycolaldehyde bis(dialkyl acetals) (**3a–c**). —These compounds were oxidised as described for the 2,6-dialkoxy-1,4-oxathianes (**5**,**7**), using the following conditions.

Starting compound (g)	*AcOH–Ac$_2$O (1:1, mL)*	*Aqueous 30% H$_2$O$_2$ (mL)*	*Time*	*Products (g, %)*
3a (1)	4.8	1.4	2 h	**3d** (0.99, 92.5)
3a (2.04)	32	8	13 days	**3e** (2.34, 100)
3b (5.29)	64	16	15 days	**3f** (5.5, 92.8)
3c (0.94)	10	2.5	14 days	**13c** + **14c** (0.6, 93.4)

For sulfinyldiacetaldehyde bis(dimethyl acetal) (**3d**), the crude product was treated with CHCl$_3$ (25 mL) and then extracted with aqueous 45% K$_2$CO$_3$ (20 mL). The organic layer was dried, filtered, and concentrated, to give **3d**, m.p. 49–50°; ν_{max} 1360, 1124, 1087, 1057, 1019, 980, and 825 cm^{-1}. ^{1}H-N.m.r. (CDCl$_3$) data: δ 4.70 (t, 1 H, J 5.7 Hz), 3.3 (s, 3 H), 3.26 (s, 3 H), and 2.96 (d, 2 H, J 5.7 Hz) (Found: C, 42.5; H, 8.2. $C_8H_{18}O_5S$ calc.: C, 42.6; H, 8.0%).

For sulfonyldiacetaldehyde bis(dimethyl acetal) (**3e**), the crude product was stored in a desiccator over conc. H$_2$SO$_4$ and KOH until the weight remained constant. Compound **3e** was obtained as a liquid; ν_{max} 1306, 1112, 1070, 980, and 826 cm^{-1}. ^{1}H-N.m.r. (CCl$_4$) data: δ 4.77 (t, 1 H, J 5.3 Hz), 3.37 (s, 6 H), and 3.25 (d, 2 H, J 5.3 Hz).

For sulfonyldiacetaldehyde bis(diethyl acetal) (**3f**), the crude product was stored in a desiccator over conc. H$_2$SO$_4$ and KOH until the weight remained constant. Compound **3f** was obtained as a liquid; ν_{max} 1313, 1265, 1114, 1068, 1023, and 810 cm^{-1}. ^{1}H-N.m.r. (CDCl$_3$) data: δ 5.0 (t, 1 H, J 5.5 Hz), 3.6 (m, 4 H), 3.4 (d, 2 H, J 5.5 Hz), and 1.21 (t, 6 H, J 6.7 Hz).

When **3f** (0.722 g) was left at room temperature for 4 months, **13b**,**14b** (0.53 g, 97.6%) was obtained.

Oxidation of **3c** gave a mixture of *cis*- and *trans*-2,6-di-isopropoxy-1,4-oxathiane 4,4-dioxide (**13c** and **14c**) in almost quantitative yield.

Oxidation of 2,6-bis(tert-*butylthio*)*-1,4-dithiane* (**10a**,**b**). — A mixture of *trans*-

2,6-bis(*tert*-butylthio)-1,4-dithiane (**10b**, 0.5 g), acetic acid (12 mL), acetic anhydride (12 mL), and aqueous 30% hydrogen peroxide (6 mL) was stored in the dark at room temperature for 7 days and then partially concentrated. The resulting solid material was collected, washed with ethanol several times, and dried, to give 2,6-bis-(*tert*-butylsulfonyl)-1,4-dithiane 1,4,4-trioxide (**17**; 0.68 g, 98.7%), m.p. 200° (from ethanol); ν_{max} 1340, 1310, 1250, 1180, 1128, 1113, 935, 890, 731, and 660 cm^{-1}. ^{1}H-N.m.r. (Me_2SO-d_6) data: δ 6.1–5.7 (m, 1 H), 4.3–4.0 (m, 2 H), and 1.41 (s, 9 H) (Found: C, 35.3; H, 5.7. $C_{12}H_{24}O_7S_4$ calc.: C, 35.3; H, 5.9%).

When *cis*-2,6-bis(*tert*-butylthio)-1,4-dithiane (**10a**) was oxidised in a similar way, **17** (92.7%) was obtained.

Oxidation of 2,6-bis(alkylthio)-1,4-dioxanes (**11,12**). — A mixture of 2,6-bis(alkylthio)-1,4-dioxane (**11a–c**, **12a–c**), acetic acid, acetic anhydride, and aqueous 30% hydrogen peroxide was stored in the dark at room temperature for 14 days and then concentrated. Ethanol was distilled several times from the residue in order to remove traces of acetic acid and acetic anhydride.

The following conditions were used.

Starting material (mg)	*AcOH–Ac₂O (2:1, mL)*	*Aqueous 30% H₂O₂ (mL)*	*Products (mg, %)*
11a (80)	3	1	**19a** (90, 86)
12a (33)	1.5	0.5	**20a** (30, 69.7)
11b (70)	3	1	**19b** (50, 61.8)
12b (44)	1.5	0.5	**20b** (35, 62.6)

cis-2,6-Bis(ethylsulfonyl)-1,4-dioxane (**19a**) had ν_{max} 1322, 1310, 1140, 1100, 1034, 930, 892, 870, 795, and 710 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 4.78 (dd, 1 H, *J* 10.4 and 3.3 Hz), 4.26 (dd, 1 H, *J* 11.6 and 3.3 Hz), 3.74 (dd, 1 H, *J* 11.6 and 10.4 Hz), 3.07 (q, 2 H, *J* 7 Hz), and 1.4 (t, 3 H, *J* 7 Hz) (Found: C, 35.4; H, 5.7. $C_8H_{16}O_6S_2$ calc.: C, 35.3; H, 5.9%).

trans-2,6-Bis(ethylsulfonyl)-1,4-dioxane (**20a**) had m.p. 94–95° (from ethanol); ν_{max} 1310, 1295, 1155, 1118, 1100, 1048, 995, 955, 855, 784, and 706 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 5.2 (t, 1 H, *J* 9.8 Hz), 4.2 (m, 2 H), 3.17 (q, 2 H, *J* 7 Hz), and 1.38 (t, 3 H, *J* 7 Hz) (Found: C, 35.4; H, 5.8. $C_8H_{16}O_6S_2$ calc.: C, 35.3; H, 5.9%).

cis-2,6-Bis(propylsulfonyl)-1,4-dioxane (**19b**) had m.p. 131–133° (from ethanol); ν_{max} 1320, 1308, 1284, 1144, 1132, 1098, 1080, 892, 874, 776, and 719 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 4.78 (dd, 1 H, *J* 10.4 and 3.3 Hz), 4.27 (dd, 1 H, *J* 11.8 and 3.3 Hz), 3.76 (dd, 1 H, *J* 11.8 and 10.4 Hz), 3.12 (m, 2 H), 1.85 (m, 2 H), and 1.10 (t, 3 H, *J* 7 Hz) (Found: C, 39.9; H, 6.6. $C_{10}H_{20}O_6S_2$ calc.: C, 40.0; H, 6.7%).

trans-2,6-Bis(propylsulfonyl)-1,4-dioxane (**20b**) had m.p. 101–103° (from ethanol); ν_{max} 1320, 1290, 1152, 1138, 1114, 1047, 986, 950, 858, 770, and 744 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$) data: δ 5.14 (t, 1 H, *J* 9.7 Hz), 4.2 (m, 2 H), 3.08 (m, 2 H), 1.9 (m, 2 H), and 1.15 (t, 3 H, *J* 7 Hz) (Found: C, 39.9; H, 6.6. $C_{10}H_{20}O_6S_2$ calc.: C, 40.0; H, 6.7%).

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