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Note

Transformations of diglycolaldehyde dithioacetals in the presence of boron trifluoride–ether complex*

F. J. LOPEZ APARICIO, F. ZORRILLA BENITEZ, AND F. SANTOYO GONZALEZ
Department of Organic Chemistry, University of Granada (Spain)
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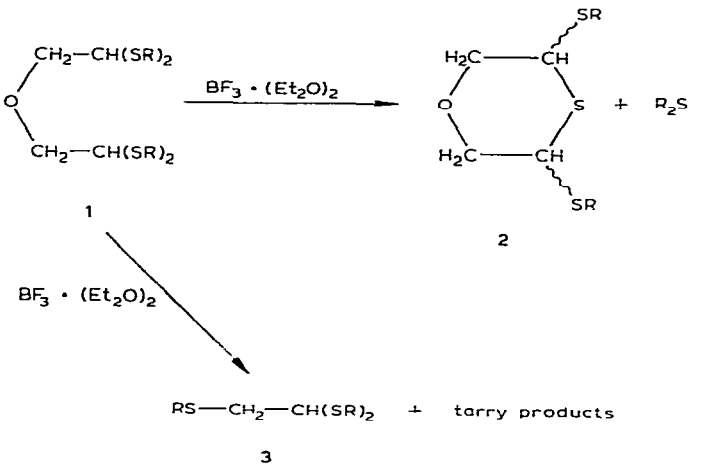
Diglycolaldehyde (2,2′-oxybisacetaldehyde) reacts with 2-methylpropane-2-thiol in acid media to yield mainly a mixture of *cis*- and *trans*-3,5-di(*tert*-butylthio) 1,4-oxathiane[1] (**2e**). We have now studied the ring-closure **1** → **2**.



The reaction **1** → **2** was effected by adding a small amount of the boron trifluoride–ether complex to anhydrous solutions of **1** in 1,4-dioxane at room temperature. The reactions were monitored by t.l.c., and the results are reported in Table I.

The rate of the reaction **1** → **3** increases with increase in the size of the alkylthio group in the series **1a**–**1c**, but **1d** reacted more slowly than **1c**. Compound **1e** was transformed rapidly into the mixture of stereoisomers **2e** in high yield: t.l.c. showed that **3e** was not formed. Compound **1f** did not react under the experimental conditions.

The reaction pathway followed by **1e** (Scheme 1) reflects the easy formation of the trimethylcarbenium ion and the steric effects when **1e** loses two *tert*-butylthio groups in the ring-closure process. However, for **1a**–**1d**, there is an alternative pathway

*Derivatives of Diglycolaldehyde, Part XIII. For Part XII, see ref. 1.

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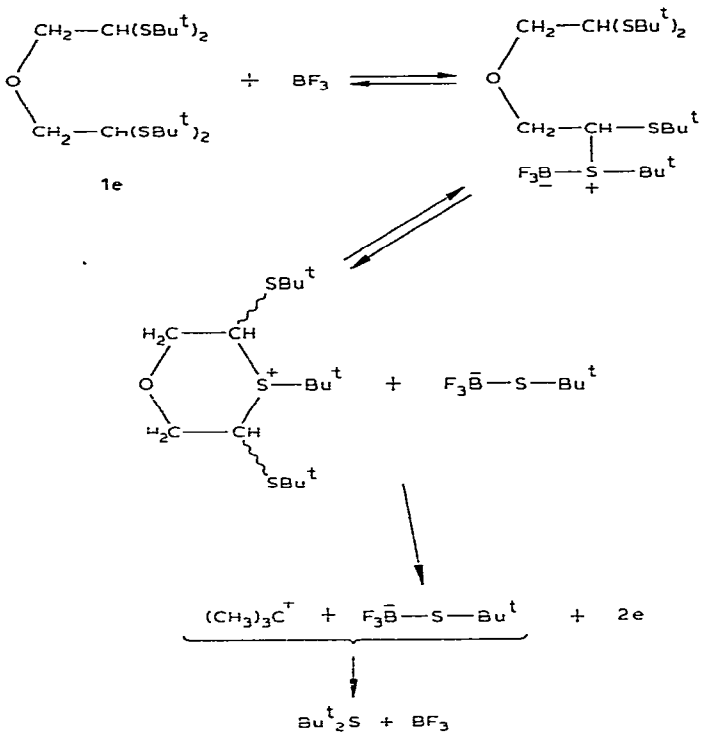
TABLE I

PRODUCTS AND YIELDS FOR THE REACTION OF **1** WITH $BF_3 \cdot (Et_2O)_2$

R	*Starting compounds*	*Products* **1** (%)[a]	**2** (%)	**3** (%)	*Time (days)*
Me	**1a**	**1a** (45.6)	—	**3a** (34.0)	30
Et	**1b**	**1b** (23.3)	—	**3b** (36.2)	30
Pr	**1c**	**1c** (25.0)	—	**3c** (44.1)	6
Pr^i	**1d**	**1d** (40.0)	—	**3d** (40.8)	12
Bu^t	**1e**	—	**2e** (76.0)	—	5
$-CH_2-$	**1f**	**1f** (85.0)	—	—	30

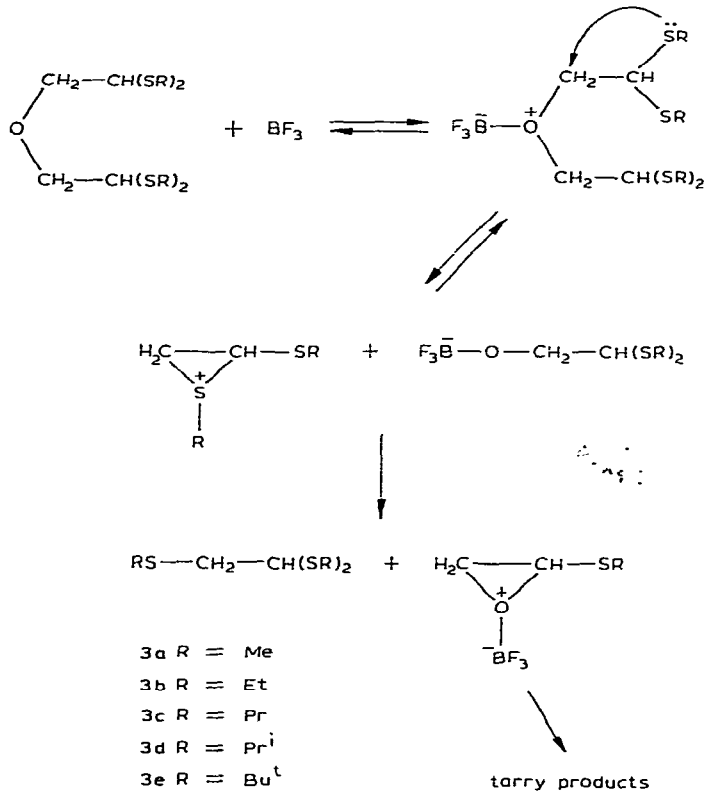
[a]Recovered starting-material.



Scheme 1

(Scheme 2). The driving-force in this pathway is the easy formation for the cyclic sulfonium salt. The lack of reactivity of **1f** reflects the stability of 1,3-dithiolane rings.

The 1,1,2-tri(alkylthio)ethanes (3) were identified by comparison with authentic samples obtained by the reaction of the 2-alkylthio-1,1-diethoxyethane and the corresponding thiol in acid media, Previously, these compounds were synthesised from bromoacetaldehyde diethyl acetal and the appropriate sodium thiolate.



Scheme 2

EXPERIMENTAL

General methods. — Organic solutions were dried over anhydrous Na_2SO_4. Solvents were evaporated under diminished pressure at <40°. Melting points are uncorrected and 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 CCl_4 (internal Me_4Si) with a Perkin–Elmer–Hitachi R-20 B spectrometer. Chemical shifts are given on the δ scale and couplings in Hz. Column chromatography was carried out on Silica gel 60 Merck (70–230 mesh, ASTM).

Reactions of diglycolaldehyde bis(dialkyl dithioacetals) (**1**) *in the presence of boron trifluoride–ether complex.* — Boron trifluoride–ether complex (1.5 ml) was added to a solution of the diglycolaldehyde bis(dialkyl dithioacetal)[1,2] (**1**) in anhydrous 1,4-dioxane. Each mixture was stored at room temperature for the reported time and then basified with 50% aqueous K_2CO_3, and the dioxane was evaporated. The aqueous mixture was extracted with ether (3 × 20 ml), and the combined extracts were dried, filtered, and concentrated to dryness. The amounts of reagents and reaction times are noted in Table II.

TABLE II

Reagents (g)	*1,4-Dioxane (ml)*	*Time (days)*
1a (3.62)	25	30
1b (2.15)	25	30
1c (3)	20	6
1d (6)	40	12
1e (2)	25	5
1f (4.6)	40	30

Distillation of the product from **1a** gave **3a** (0.8 g, 34.0%), b.p. 120–124°/14 mmHg, and **1a** (1.65 g, 45.6%), b.p. 140–145°/1 mmHg.

Likewise **1b** gave **3b** (0.52 g, 36.2%), b.p. 80–90°/0.6 mmHg, and **1b** (0.5 g, 23.3%), b.p. 150–152°/0.6 mmHg; **1c** gave **3c** (0.9 g, 44.1%), b.p. 90–98°/0.2 mmHg, and **1c** (0.76 g, 25.0%), b.p. 150°/0.2 mmHg; **1d** gave **3d** (1.94 g, 40.8%), b.p. 98–105°/0.5 mmHg, and **1d** (2.4 g, 40.0%), b.p. 140–144°/0.5 mmHg; **1e** gave a mixture of stereoisomers **2e** (1 g, 76.0%) isolated by column chromatography and identified by spectroscopic and chromatographic comparisons with an authentic sample[1].

Under the conditions noted above, **1f** did not react (indicated by t.l.c.) and 85% (3.9 g) was recovered; b.p. 155–160°/0.5 mmHg.

Synthesis of 2-alkylthio-1,1-diethoxyethanes (**4**). — Bromoacetaldehyde diethyl acetal and the selected thiol were added to methanolic sodium methoxide at room temperature. Each mixture was stirred and boiled under reflux, filtered, and concentrated at atmospheric pressure. Water (10 ml) was added, the mixture was extracted with dichloromethane (3 × 30 ml), and the combined extracts were dried, filtered, and concentrated. The amounts of reagents and reaction times are noted in Table III.

Compound **4a**[3,4] (2.5 g, 30%) had b.p. 75–78°/50 mmHg; **4b** (refs. 4 and 5) (8.6 g, 89%) had b.p. 90°/14 mmHg; **4c** (ref. 6) (4.83 g, 82.6%) had b.p. 98–99°/14 mmHg; **4d** (10.2 g, 83.7%) had b.p. 95–100°/14 mmHg, ν_{max} 1130, 1058, and 1010 cm^{-1}; ^{1}H-n.m.r. data: δ 4.40 (t, 1 H, J 5.6 Hz), 3.46 (m, 4 H), 2.90 (m, 1 H, J 6.3 Hz), 2.55 (d, 2 H, J 5.6 Hz), 1.25 (d, 6 H, J 6.3 Hz), and 1.18 (t, 6 H, J 7 Hz) (Found:

TABLE III

R in (4)	*Na (g)/MeOH (ml)*	*RSH (ml)*	*RX*[a] *(g)*	*Time (h)*
Me (**4a**)	5/80	MeSH (10)	10.0	6
Et (**4b**)	5/100	EtSH (18)	10.7	9
Pr (**4c**)	2.7/25	PrSH (8)	6.0	8
Pr^i (**4d**)	6/80	Pr^iSH (25)	12.5	8
Bu^t (**4e**)	5/80	Bu^tSH (25)	10.0	14

[a]Bromoacetaldehyde diethyl acetal.

TABLE IV

Starting material (g)	*RSH (ml)*	*H_2SO_4 (g)*	*Time (days)*	*Product*
4a[a] (2.3)	MeSH (3)	[a]	[b]	3a
4b (1.9)	EtSH (4)	0.5	2	3b
4c (4.6)	PrSH (10)	0.5	2	3c
4d (7.0)	Pr^iSH (20)	1.0	1	3d
4e (6.1)	Bu^tSH (15)	1.0	1	3e

[a] $BF_3 \cdot (Et_2O)_2$ (15 drops) was added. [b] 1 Day at 0° and then 2 days at 5°.

C, 56.1; H, 10.4; S, 16.6. $C_9H_{20}O_2S$ calc.: C, 55.9; H, 10.4; S, 16.6%); **4e** (8.9 g, 85%) had b.p. 102–104°/14 mmHg, ν_{max} 1114, 1058, and 1010 cm^{-1}; ^{1}H-n.m.r. data: δ 4.40 (t, 1 H, *J* 5.8 Hz), 3.47 (m, 4 H), 2.56 (d, 2 H, *J* 5.8 Hz), 1.30 (s, 9 H), and 1.18 (t, 6 H, *J* 7 Hz) (Found: C, 58.1; H, 10.6; S, 15.3. $C_{10}H_{22}O_2S$ calc.: C, 58.1; H, 10.7; S, 15.5%).

Synthesis of 1,1,2-tri(alkylthio)ethanes (3). — Conc. sulphuric acid was added to a stirred solution of **4a–e** in the selected thiol. Each mixture was left at room temperature for the reported time, basified with 20% aqueous NaOH, and extracted with ether (3 × 25 ml). The combined extracts were dried, filtered, and concentrated. The amounts of reagents and the reaction times are given in Table IV.

Compound **3a** (ref. 7) (1.9 g, 81%) had b.p. 120–122°/16 mmHg; **3b** (refs. 8–10) (1.76 g, 87%) had b.p. 78–80°/0.3 mmHg; **3c** (4.1 g, 68%) had b.p. 112–114°/0.4 mmHg, ν_{max} 1292, 1236, and 784 cm^{-1}; ^{1}H-n.m.r. data: δ 3.71 (t, 1 H, *J* 7.0 Hz), 2.78 (d, 2 H, *J* 7.0 Hz), 2.51 (m, 6 H), 1.52 (m, 6 H), and 1.0 (m, 9 H) (Found: C, 52.4; H, 9.5; S, 38.0. $C_{11}H_{24}S_3$ calc.: C, 52.3; H, 9.5; S, 38.1%); **3d** (ref. 11) (8.8 g, 95.8%) had b.p. 92–94°/0.2 mmHg; **3e** (7.4 g, 85%) had m.p. 80° (from ethanol–water), ν_{max} 1365, 1158, and 890 cm^{-1}; ^{1}H-n.m.r. data: δ 3.71 (t, 1 H, *J* 7.0 Hz), 2.77 (d, 2 H, *J* 7.0 Hz), 1.32 (s, 18 H), and 1.25 (s, 9 H) (Found: C, 57.4; H, 10.3; S, 32.7. $C_{14}H_{30}S_3$ calc.: C, 57.0; H, 10.2; S, 32.6%).

Bromoacetaldehyde diethyl acetal. — This compound was prepared from vinyl acetate[12] (76–78%) or from acetaldehyde diethyl acetal[13]. In the latter case, the yields were improved and the manipulation made easy by using the following modification. Bromine (80 g) was added to a cooled and vigorously stirred mixture of acetaldehyde diethyl acetal (59 g), anhydrous $CaCO_3$ (28 g), and CCl_4 or $CHCl_3$ (100 ml) during 1 h. The temperature of the mixture was kept at 10°. The mixture was left at room temperature for 14 h, and then basified with saturated, aqueous Na_2CO_3, filtered, and extracted with CCl_4 or $CHCl_3$ (2 × 100 ml). The combined extracts were dried, filtered, and concentrated, to give bromoacetaldehyde diethyl acetal (60 g, 60.9%; lit[13] 31.2–42.1%), b.p. 64–66°/14–15 mmHg.

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