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Note

Reactions between diglycolaldehyde dithioacetals and some nucleophiles*

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As part of a study[1] of derivatives of diglycolaldehyde (2,2′-oxybisacetaldehyde), the reaction between diglycolaldehyde bis(diethyl dithioacetal)[1,2] (**1**) and alcohols has been studied. The acyclic (**2a–d**) and cyclic (**3a–b**) products are noted in Table I. Primary alcohols gave only the acyclic acetals **2a–c**, 2-propanol gave both acyclic (**2d**) and cyclic (**3a**) acetals, and *tert*-butyl alcohol gave the cyclic acetal **3b** in low yield. All of the products were identified by comparisons with authentic specimens[1,2].

The acyclic acetal **2d** does not appear to be an intermediate in the formation of **3a**, because it does not react with 2-propanol.

The cyclic dithioacetal[2] **4** can be transformed into the acyclic bis(dimethyl acetal)[1,2] **2a** by reaction with methanol–$HgCl_2$–HgO. It did not react with mercuric

TABLE I

DATA FOR REACTION OF **1** WITH ALCOHOLS (R-OH)

R	*Amount of* **1** *(g)*	*ROH (ml)*	*HgO — $HgCl_2$ (g)*	*Reaction time (h)*	*Products*[a] *B.p. (mmHg) (degrees)*	*Yields (g)*
Me	4.50	70	34	7	**2a** 106–110 (16)	0.66 (30%)[b]
Et	6.28	75	52	6	**2b** 135–137 (16)	2.67 (53.4%)
Pr	2.50	50	24	6	**2c** 92–94 (0.5)	1.62 (66.5%)
Pr^i	12.00	150	108	7	**3a** 97–102 (16)	1.9 (24.4%)
					2d 144–145 (16)	5.0 (42.7%)
Bu^t	9.50	100	80	7	**3b** 105–110 (16)	1.25 (18%)[c]

[a]Identified by comparison of chromatographic and spectroscopic data with those for authentic specimens[1,2]. [b]For a similar reaction at room temperature, the yield was 24%. [c]Chromatography of the crude product revealed no other products.

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*Derivatives of Diglycolaldehyde, Part XII.

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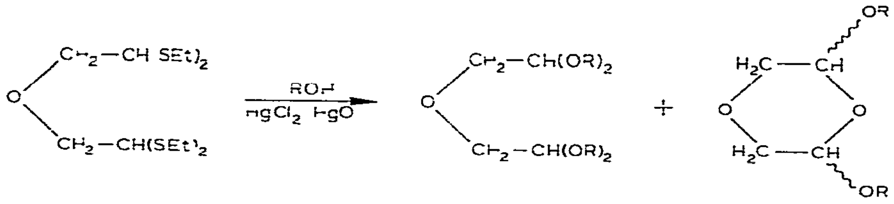
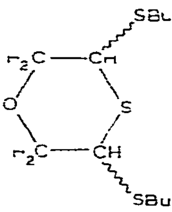


1 2a–d 3a–b



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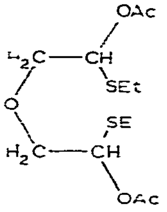

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acetate in 1,4-dioxane, but the acyclic dithioacetal **1** yielded the acetylated bis(hemithioacetal) **5** (*cf* refs 3 and 4)

EXPERIMENTAL

General methods — Solvents were evaporated under diminished pressure at <40° I r spectra were recorded for films on NaCl discs, using a Pye–Unicam SP 1000 spectrometer ^{1}H-N m r spectra were recorded for solution in $CDCl_3$ (internal Me_4Si) with a Perkin–Elmer–Hitachi R-20B spectrometer Chemical shifts (first order) are given on the δ scale with first-order coupling in Hz The mass spectrum was recorded with a Hewlett-Packard model 5930A spectrometer

Reaction of diglycolaldehyde bis(diethyl dithioacetal)$^{1\,2}$ (**1**) *with alcohols in the presence of mercuric salts* — A mixture of $HgCl_2$ and HgO (1 1) was added to a mixture of **1** and the selected alcohol After stirring under reflux for the reported time, the cold mixture was filtered and concentrated to dryness The residue was dissolved in ether (100 ml), and washed with several portions of 50% aqueous NaI to complete decoloration Salts are removed by washing with water (10 ml), and the organic layer was dried (Na_2SO_4), filtered, and concentrated If some precipitate appeared (mercuric salts), methanol (25 ml) and saturated methanolic Na_2S 9 H_2O (25 ml) were added, the mixture was filtered and concentrated, and a solution of the residue in ether was washed with water (20 ml), dried (Na_2SO_4), filtered, and concentrated The product, which was free of mercuric salts, was distilled under diminished pressure The results are recorded in Table I

When the acetal **2d** (2 66 g) was treated with 2-propanol (30 ml) and mercuric compounds (16 g), 96% of **2d** (2 55 g) was recovered No other products were detected by t l c

Reaction of **4** *with methanol* — The reaction was carried out essentially by the method described above with **4** (5 7 g) methanol (50 ml) HgO (20 g), and $HgCl_2$ (20 g) A solution of the product in chloroform (50 ml) was washed with 50% aqueous NaI to complete decoloration and then with 50% aqueous K_2CO_3 (20 ml) dried (Na_2SO_4), filtered, and concentrated Distillation of the residue yielded[1 2] **2a** (2 23 g, 56 5%), b p 106–109°/16 mmHg

Reaction of **1** *and* **4** *with mercuric acetate* — A mixture of **1** (6 4 g) and $Hg(OAc)_2$ (30 g) in 1,4-dioxane (50 ml) was stirred under reflux for 15 h, and then cooled, filtered and concentrated A solution of the residue in ether (27 ml) was washed with 50% aqueous NaI (4 × 25 ml) and water (2 × 25 ml), dried (Na_2SO_4), filtered, and concentrated Distillation of the residue yielded **5** (3 0 g 48%), b p 140–146°/0 1 mmHg, ν_{max} 1740, 1368, 1220, 1130, 1020, and 930 cm^{-1} ^{1}H-N m r data δ 5 99 (t, 2 H, J 5 7 Hz), 3 70 (d, 4 H, J 5 7 Hz), 2 62 (m, 4 H, J 7 1 Hz) 2 10 (s, 6 H) and 1 25 (t, 6 H, J 7 1 Hz) Mass spectrum m/z 310 (M^+), 250 (M^+ – AcOH), 219 (M^+ – Et_2SH), 190 (M^+ – 2 AcOH), 177 [M^+ – CH(OAc)SEt], 161, 146 [M^+ – $HOCH_2CH(OAc)SEt$], 133, 60, 45, and 43 (Ac^+, 100%)

When **4** (1 g) was treated with $Hg(OAc)_2$ (2 27 g) in 1 4-dioxane (25 ml) under similar conditions for 8 h, 80% of **4** (0 8 g) was recovered

Diglycolaldehyde bis(diethyl dithioacetal)[1 2] (**1**) — Compound **1**, prepared from diglycolaldehyde and ethanethiol in acid media[2], had b p 158–160°/0 5 mmHg ν_{max} (selected bands) 1456, 1166, 1117, and 977 cm^{-1} ^{1}H-N m r ($CDCl_3$) data δ 3 95 (m, 1 H, J 6 6 Hz), 3 72 (m, 2 H, J 6 6 Hz), 2 67 (m, 4 H, J 7 5 Hz), and 1 25 (t, 6 H, J 7 5 Hz) (Found C, 46 1, H, 8 5 S, 40 5 $C_{12}H_{26}OS_4$ calc C 45 8 H 8 3 S, 40 8)

Diglycolaldehyde bis(dialkyl acetals) **2a–d** *and 2,6-dialkoxy-1,4-dioxanes*[1 2] **3a,b** — These compounds were prepared by an acid-catalysed reaction between diglycolaldehyde and the corresponding alcohols

Dimethyl derivative[1] **2a** ν_{max} (selected bands) 1123 and 1072 cm^{-1} ^{1}H-N m r ($CDCl_3$) data δ 4 45 (t, 1 H, J 5 2 Hz), 3 49 (d, 2 H, J 5 2 Hz) and 3 42 (s 6 H) (Found C, 49 5, H, 9 3 $C_8H_{18}O_5$ calc C, 49 4 H, 9 3)

Diethyl derivative[1] **2b**, ν_{max} (selected bands) 1117 and 1063 cm^{-1} ^{1}H-N m r ($CDCl_3$) data δ 4 48 (t, 1 H, J 5 2 Hz), 3 75–3 25 (m, 6 H), and 1 12 (t 6 H) (Found C 57 6, H 10 2 $C_{12}H_{26}O_5$ calc C 57 6, H, 10 5)

Dipropyl derivative[1] **2c** ν_{max} (selected bands) 1123 and 1075 cm^{-1} ^{1}H-N m r ($CDCl_3$) data δ 4 58 (t 1 H, J 5 2 Hz), 3 8–3 2 (m 6 H) 1 57 (m 4 H), and 0 91 (t, 6 H) (Found C, 63 0, H, 10 8 $C_{16}H_{34}O_5$ calc C 62 7 H, 11 2)

Di-isopropyl derivative[2] **2d**, ν_{max} (selected bands) 1128 and 1040 cm^{-1} ^{1}H-N m r ($CDCl_3$) data δ 4 60 (t, 1 H J 5 1 Hz), 3 82 (m 2 H J 6 Hz), 3 40 (d 2 H, J 5 1 Hz), 1 12 (d, 6 H, J 6 Hz), and 1 10 (d, 6 H, J 6 Hz) (Found C, 62 9 H, 11 2 $C_{16}H_{34}O_5$ calc C, 62 7 H, 11 2)

The *cis,trans* mixture **3a**[1] (Found C, 59 0 H, 9 9 $C_{10}H_{20}O_4$ calc C 58 8 H, 9 9) was fractionated by column chromatography *cis*-**3a** had ν_{max} (selected bands) 967, 928, 898, and 828 cm^{-1}. ^{1}H-n m r ($CDCl_3$) data δ 4 75 (dd 1 H, J 8 2 and

3.0 Hz) 4 03 (m, 1 H, J 6 Hz), 3 45 (m, 2 H), 1 27 (d, 3 H, J 6 Hz), and 1 20 (d, 3 H, J 6 Hz), *trans*-**3a** had ν_{max} (selected bands) 891, 861, 829, and 758 cm^{-1}, ^{1}H-n m r (CDCl$_3$) data δ 4 99 (dd, 1 H, J 4 5 and 3 0 Hz), 3 98 (m, 1 H, J 6 Hz), 3 58 (m, 2 H), 1 30 (d, 3 H, J 6 Hz) and 1 20 (d, 3 H, J 6 Hz)

The *cis,trans* mixture **3b**[2] (Found C, 62 0, H, 10 5 C$_{12}$H$_{24}$O$_4$ calc C, 62 0 H, 10 4) was fractionated by column chromatography *cis*-**3b** had m p 50–51° (from hexane), ν_{max} (selected bands) 1125, 1042, 928, and 870 cm^{-1}, ^{1}H-n m r (CDCl$_3$) data δ 4 80 (dd, 1 H, J 8 5 and 3 0 Hz), 3 45 (dd, 1 H, J 11 1 and 3 0 Hz) 3 05 (dd, 1 H, J 11 1 and 8 5 Hz), and 1 22 (s, 9 H), *trans*-**3b** had m p 68–69° (from hexane), ν_{max} (selected bands) 1120, 1040, 924, and 880 cm^{-1}, ^{1}H-n m r (CDCl$_3$) data δ 5 12 (dd, 1 H, J 4.4 and 2 8 Hz), 3 65 (dd, 1 H, J 11 2 and 2 8 Hz), 3 34 (dd, 1 H, J 11 2 and 4 4 Hz), and 1.28 (s, 9 H)

cis,trans-*3,5-Di-*(tert-*butylthio*)*-1,4-oxathiane*[2] (**4**) — This product, which was prepared by an acid-catalysed reaction between diglycolaldehyde and 2-methylpropane-2-thiol, had ν_{max} (selected bands) 1365, 1265, 1160, and 1094 cm^{-1}, ^{1}H-n m r (CDCl$_3$) data δ 4 22–3 00 (m, 3 H) and 1 38 (s, 9 H) (Found, C 51 5, H, 8 4, S, 34 1 C$_{12}$H$_{24}$OS$_3$ calc C, 51 4, H, 8 6 S, 34 3)

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