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THE REARRANGEMENT OF MONO-*O*-ISOPROPYLIDENE DERIVATIVES OF ALDOSE DIETHYL DITHIOACETALS*

T. BRUCE GRINDLEY AND CHANDRA WICKRAMAGE
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3 (Canada)

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ABSTRACT

Acid-catalyzed rearrangements of terminal mono-*O*-isopropylidene derivatives of some aldose diethyl dithioacetals in *N,N*-dimethylformamide have been studied. The 4,5-*O*-isopropylidene derivatives of D-arabinose and D-xylose diethyl dithioacetal respectively rearrange to the 2,3- and a mixture of the 2,3- and 3,4-*O*-isopropylidene derivatives. The 5,6-*O*-isopropylidene derivatives of D-galactose, D-mannose, and D-glucose rearrange to the 4,5-, 3,4-, and a mixture of the 2,3- and 3,4-*O*-isopropylidene derivatives, respectively. These rearrangements were shown to be intramolecular by means of a cross-over experiment, and by consideration of the structures of the products obtained and of the rates of rearrangement. 3,4-*O*-Isopropylidene-D-mannose diethyl dithioacetal was also prepared directly from D-mannose diethyl dithioacetal. Consistent ratios of product to starting material indicated that the 4,5-*trans*-disubstituted 2,2-dimethyl-1,3-dioxolane products are $\sim$1.2 kcal.mol^{-1} more stable than the 4-substituted 2,2-dimethyl-1,3-dioxolane starting-materials. Reaction of D-glucose diethyl dithioacetal with an excess of 2-methoxypropene in the presence both of high and low concentrations of acid gave mainly the 2,3:5,6-di-*O*-isopropylidene derivative.

INTRODUCTION

We have recently shown[1] that terminal mono-*O*-isopropylidene derivatives of aldose diethyl dithioacetals can be obtained readily by kinetic isopropylidenation using 2-methoxypropene in *N,N*-dimethylformamide. These results reflected the two principal advantages of kinetic acetalation; primary hydroxyl groups react considerably faster than secondary hydroxyl groups, and the number of acetal groups added can be controlled by the number of equivalents of acetalating agent used[2]. However, it would be advantageous to have methods available for the preparation of nonterminal *O*-isopropylidene derivatives in a predictable manner. We report herein a study of rearrangements of some terminal *O*-isopropylidene derivatives of aldose diethyl dithioacetals in order to achieve this goal.

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TABLE I

^{13}C-N.M.R. CHEMICAL SHIFTS

Compound	*Chemical shifts*[a]									
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*SCH_2*	*SCH_2CH_3*	*Acetal C*	*$C(CH_3)_2$*
2a	55.1	71.9	70.9	71.6	64.1		24.4, 24.6	14.5		
2c	53.3	83.5	79.3	73.2	64.1		25.2, 25.5	14.4	110.2	27.1, 27.3
3a	54.6	74.2	70.6	73.2	63.4		24.6, 24.9	14.5		
3e	53.1	81.1	79.7	70.2	65.3		25.1, 25.4	14.4	110.2	27.2
5a	55.2	74.1	69.7	70.3	71.9	64.0	24.4, 25.3	14.7, 14.8		
5b	55.0	74.1	70.7	70.7	76.1	66.8	25.6, 25.5	14.6, 14.7	109.3	26.5, 26.8
5c	54.8	75.9	81.5	79.7	72.9	63.9	25.8, 26.0	14.5, 14.7	109.5	26.9
5d	54.7	75.1	80.0[b]	79.8[b]	71.1	65.6	25.8, 26.1	14.5, 14.8	109.8	26.9
6a	54.5	75.5	69.3	73.3	71.5	63.7	24.6, 25.2	14.5, 14.8		
6c	56.1	73.3	77.3[b]	78.3[b]	71.2	64.1	24.5, 25.4	14.5	109.8	26.9, 27.4
6d	53.1	79.9[b]	79.1[b]	70.6	73.1	64.1	25.2, 25.5	14.5	109.9	27.3
6e	53.3	79.7[b]	79.4[b]	71.2	76.7	66.9	25.4, 26.9	14.4	109.4, 109.9	26.9, 27.2
6f	56.0	70.9	77.8[b]	79.2[b]	77.4[b]	67.9	24.5, 25.1	14.5	109.8, 109.8	27.3, 26.8, 26.8, 25.4
6g	53.1	79.0	77.9	72.7	63.8	64.4	25.4, 25.6	14.4, 14.5	99.0, 110.1	26.8, 27.3, 19.4, 28.3

[a]In p.p.m. downfield from internal tetramethylsilane in chloroform-*d* at 20 MHz. data for the **a** compounds from ref. 1, except for that for **5a**, which is from ref. 20. [b]Assignments may have to be interchanged.

TABLE II

^{1}H-N.M.R. CHEMICAL SHIFTS

Compound	*Chemical shifts*[a]									
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-5' or H-6'*	*H-6'*	SCH_2	SCH_2CH_3	$C(CH_3)_2$
2ca	3.847	4.265	4.318	5.215	4.141	4.526		2.69–2.76	1.275, 1.277[b]	1.414, 1.474
3e[c]		3.50–4.40						2.72, 2.75	1.30[d]	1.45, 1.50
5b[c]		3.45–4.18						2.63	1.29[d]	1.38, 1.43
5c[c]		3.45–4.18						2.65	1.27[e]	1.41
5ca	4,125	5.320	4.427	4.151	5.162	4.186	4.413	2.648, 2.724	1.264, 1.289[f]	1.412, 1.434
5d		3.60–4.55						2.681, 2.731	1.294, 1.298[g]	1.378, 1.384
5da	4.049	5.253	4.345	4.093	5.119	4.237	4.435	2.579, 2.657	1.193, 1.218[h]	1.345, 1.368
6b[c]		3.55–4.17						2.60, 2.66	1.22[i]	1.28, 1.33
6c[c]		3.54–4.17						2.70[d]	1.24[d]	1.36
6ca	3.989	4.940	4.563	3.815	5.072	4.017	4.451	2.50–2.75	1.165, 1.208[j]	1.339, 1.353
6d[c]		3.56–4.43						2.73[d]	1.20[d]	1.40
6da	3.858	4.007	4.245	5.344	5.270	4.228	4.444	2.61–2.81	1.259, 1.263[k]	1.383, 1.426
6e[c]		3.67–4.30						2.69[d]	1.20[d]	1.28, 1.36
6ea	3.808	3.956	4.343	5.207	4.230	3.846	3.957	2.55–2.75	1.192, 1.195[l]	1.290, 1.336, 1.340, 1.384
6f[c]		3.60–4.65						2.75[d]	1.28[d]	1.34, 3 × 1.40
6g[c]		3.45–4.60						2.76[d]	1.36[d]	1.44, 1.48, 1.51, 1.51

[a]In p.p.m. downfield from internal tetramethylsilane in chloroform-*d* at 361.06 MHz, unless otherwise indicated. [b]*J* 8.02, 7.42 Hz. [c]At 60 MHz. [d]*J* 7.5 Hz, [e]*J* 7.2 Hz. [f]*J* 7.41, 7.43 Hz. [g]*J*7.41, 7.41 Hz, [h]*J* 7.42, 7.43 Hz, [i]*J* 8 Hz. [j]*J* 7.51, 7.46 Hz. [k]*J* 7.43 Hz. [l]*J* 7.41, 7.42 Hz.

TABLE III

^{1}H-N.M.R. COUPLING CONSTANTS[a]

Compound	*Coupling constant (Hz)*						
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{4,5'}$ *or* $J_{5,6'}$	$J_{5,5'}$ *or* $J_{6,6'}$
2ca	3.97	6.50	6.31	6.31		2.89	12.25
5ca	2.88	8.53	6.48	4.72	3.17	6.97	12.17
5da	3.03	8.41	6.32	5.12	6.92	2.78	12.21
6ca	9.23	2.46	7.12	7.11	5.86	3.02	12.20
6da	5.32	7.13	2.05	5.82	6.50	2.49	12.46
6ea	5.83	7.08	1.99	6.11	5.80	6.28	8.80

[a]By first-order analysis.

RESULTS AND DISCUSSION

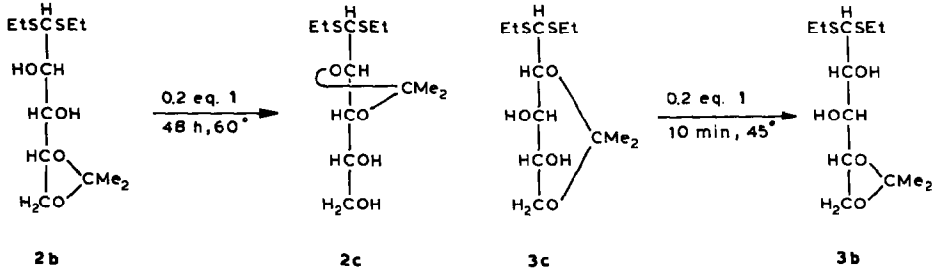
Structure determination. — The structures of all rearranged products were established by a combination of ^{1}H- and ^{13}C-n.m.r. spectroscopy. The sizes of the acetal rings in the products were established from the ^{13}C-n.m.r. chemical shifts of the acetal carbon atoms[3] (see Table I). The locations of the acetal rings were derived from first-order analysis of the high-field (361.06 MHz), ^{1}H-n.m.r. spectra of the peracetylated derivates of the products (see Tables II and III). The signals of hydrogen atoms on secondary carbon atoms bearing acetoxyl groups were observed to be in the range 4.9–5.3 p.p.m., that is, ~1 p.p.m. downfield of the signals of those on carbon atoms bearing acetalated oxygen atoms, in agreement with literature results[4]. In only one case, **6ea**, was it necessary to perform decoupling experiments in order to clarify assignments.

As previously observed[1], the signals of secondary carbon atoms bearing oxygen atoms involved in five-membered-ring isopropylidene acetals were shifted significantly downfield in comparison with the unsubstituted compounds (see Table I).

It is worth noting that the formation of an acetal linkage involving O-2 always resulted in an upfield shift of 1–2 p.p.m. for the signal of C-1 (see Table I). The observation of this shift alone was not considered sufficient to establish that the acetal formed involved O-2, as a change in orientation of the main carbon chain from *anti* to *gauche* about the C-2–C-3 bond could also cause a shift of this magnitude.

Reactions. — 4,5-*O*-Isopropylidene-D-arabinose diethyl dithioacetal (**2b**)*

*The numbering system is based on the following: the number indicates the aldose configuration, the first letter indicates the type of derivative (**a** indicates a parent aldose diethyl dithioacetal: **b**, a terminal *O*-isopropylidene derivative); and a second **a**, the peracetylated derivative of the compound having the same first two symbols.



2b **2c** **3c** **3b**

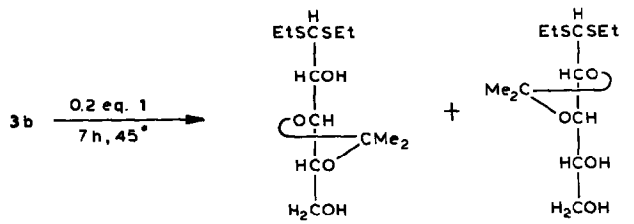
rearranged in *N,N*-dimethylformamide containing 0.2 equiv. of *p*-toluenesulfonic acid (**1**), in 48 h at 60°, to the known[5] compound, its 2,3-isomer (**2c**) in 32% yield.

2,5-*O*-Isopropylidene-D-xylose diethyl dithioacetal (**3c**) rearranged much more easily; compound **3c** had completely reacted within 10 min at 45° on using the same proportion of acid. At short reaction-times, the 4,5-*O*-isopropylidene isomer (**3b**) was the major product. Compound **3b** was shown to rearrange more slowly at the same temperature to the 3,4-isomer (**3d**), and then to the 2,3-isomer (**3e**), and these were eventually present in nearly equal amounts.

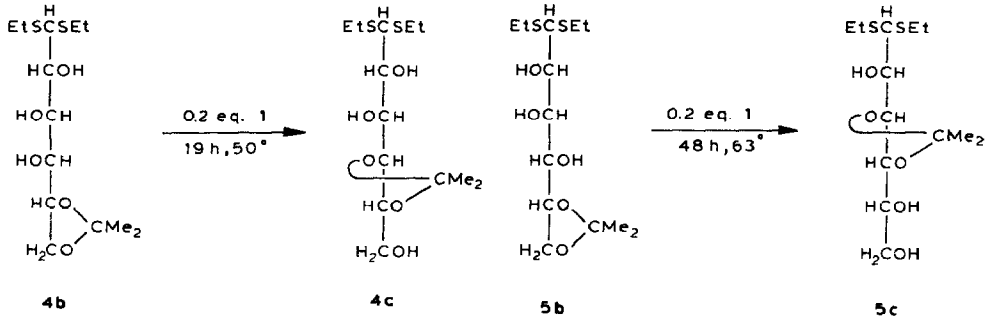
5,6-*O*-Isopropylidene-D-galactose diethyl dithioacetal (**4b**) rearranged, with the same proportion of acid, in 19 h at 50°, to the known[6] 4,5-*O*-isopropylidene derivative (**4c**) in 53% isolated yield.

5,6-*O*-Isopropylidene-D-mannose diethyl dithioacetal (**5b**) was prepared in the same way as other terminal *O*-isopropylidene derivatives[1]. At 63°, compound **5b** needed 48 h to equilibrate with its 3,4-isomer (**5c**) using 0.2 equiv. of **1**. Compound **5c** was prepared directly from D-mannose diethyl dithioacetal (**5a**) and 2-methoxypropene in better yield (42%) by using one equivalent of acid for 6 h at 50°. A minor product (3% yield) of the reaction at higher acid concentration was the 6-*O*-formyl derivative (**5d**) of **5c**.

The direct reaction of an aldose diethyl dithioacetal with 2-methoxypropene under rearrangement conditions was also explored with the D-glucose derivative. The two principal products, under exactly the same conditions as for **5a**, were the 3,4- (**6c**) (21% yield) and 2,3-*O*-isopropylidene derivative (**6d**) (24% yield). The known 5,6-*O*-isopropylidene derivative was the major product at short reaction-times. Some 2,3:5,6-di-*O*-isopropylidene-D-glucose diethyl dithioacetal (**6e**) (17%



3d **3e**

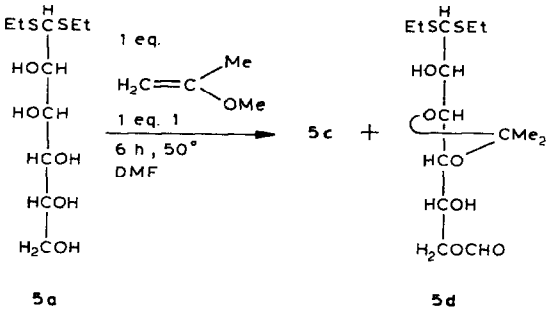


4b 4c 5b 5c

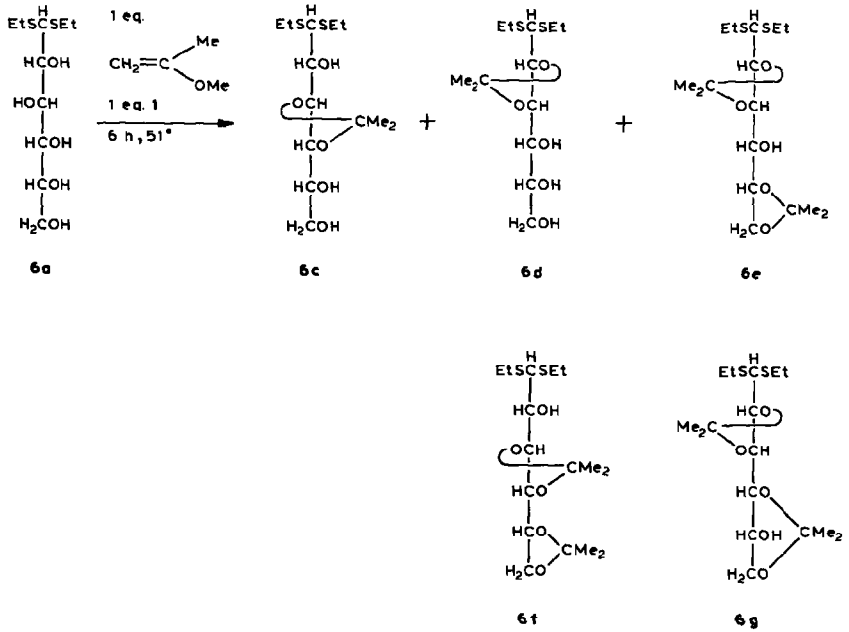
yield) was also isolated from this reaction. Its structure had previously been established tentatively[6]; the ^{1}H-n.m.r. spectrum of its acetate confirmed the previous assignment.

The observation that only one di-*O*-isopropylidene derivative of D-glucose diethyl dithioacetal (**6a**) was obtained in the foregoing reaction prompted attempts to prepare **6e** alone. The reaction of **6a** with 4 equiv. of 2-methoxypropene in the presence of 1 equiv. of **1** gave mainly **6e** (75% yield), but also some of the known[6] 3,4:5,6-di-*O*-isopropylidene derivative (**6f**) (17% yield).

The major product of the reaction of **6a** with 3 equiv. of 2-methoxypropene at low concentration of acid was also compound **6e** (53% yield), accompanied by some 2,3:4,6-di-*O*-isopropylidene-D-glucose diethyl dithioacetal (**6g**) (13% yield). The structure of the latter compound was established by ^{13}C-n.m.r. spectroscopy (see Table I). The chemical shifts of the acetal carbon atoms (99.0 and 110.1 p.p.m.) and the isopropylidene methyl groups[3], and the observation of a very upfield shift for a secondary carbon atom (63.8 p.p.m.)[1], established that **6g** contains both five- and six-membered *O*-isopropylidene rings. The stereochemistry of the starting material limits possible structures to two: the 2,3:4,6- and 2,4:5,6-isomers. It had previously been observed that formation of a five-membered isopropylidene acetal from a diol caused the chemical shifts of the diol carbon atoms to become ~4 p.p.m. larger; the effect of forming a six-membered ring on the chemical shifts of these two carbon atoms was negligible[1]. Comparison of the



5a 5d



chemical shifts of **6g** with those of **6a** showed that the signals of two secondary carbon atoms had shifted downfield, consistent only with the 2,3:4,6-di-*O*-isopropylidene structure. The signal of the primary carbon atoms appeared at 63.7 and 64.4 p.p.m. in the spectra of **6a** and **6g**, respectively. The small change is again consistent with the 4,6-*O*-isopropylidene structure. Larger changes, 3.2 and 4.2 p.p.m., were observed for the signals of C-6, when the spectra of **6e** and **6f** were respectively compared with that of **6a**.

Discussion. — The mechanism of these rearrangement reactions could be either intermolecular or intramolecular[7]. Cross-over experiments provide a definitive method for choosing between these two reaction-pathways. The rearrangement of 5,6-*O*-isopropylidene-D-galactose diethyl dithioacetal (**4b**) was

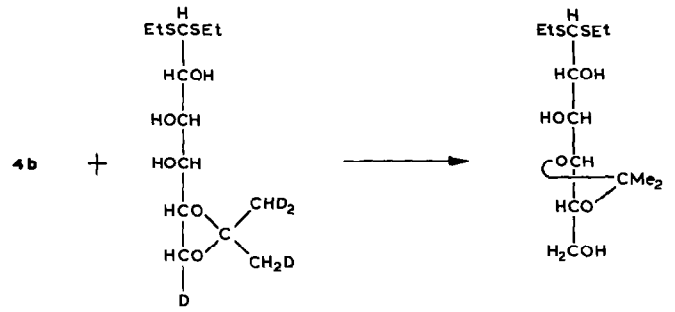


TABLE IV

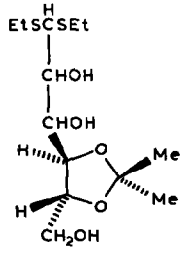
DEUTERIUM DISTRIBUTION IN REARRANGEMENT REACTION

m/z	*Fractional intensities*								
	Nondeuterated **4b**[a]	*Deuterated* **4b**[a]	*Mixed* **4b**[b]	*Recovered* **4b**[b]	*% change*[c]	**4c**[a]	*% change*[c]	*Calc. for intermolecular*[d]	*% change*[c]
326	0.779	0.0	0.387	0.321	−17	0.375	−7	0.202	−48
327	0.133	0.028	0.080	0.157	+96	0.104	+30	0.244	+205
328	0.088	0.119	0.104	0.122	+17	0.104	0	0.135	+30
329		0.245	0.123	0.141	+15	0.130	+6	0.157	+28
330		0.292	0.147	0.130	−12	0.136	−7	0.135	−8
331		0.205	0.103	0.083	−19	0.095	−8	0.084	−18
332		0.086	0.043	0.035	−19	0.043	0	0.035	−19
333		0.025	0.013	0.011	−15	0.013	0	0.010	−23

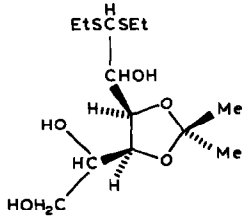
[a]Obtained from peak heights. [b]Column 1 × 0.497 + column 2 × 0.503. [c][(Value − value for mixed **4b**)/value for mixed **4b**] × 100%. [d]See text for method of calculation.

chosen for examination by this method. D-Galactose-*C-6-d*$_1$ was prepared by the method of Maradufu *et al.*[8]. Partially deuterated 2-methoxypropene was prepared from acetone-d_6 *via* the dimethyl acetal, as for the nondeuterated compound[9]. Compound **4b** deuterated at C-6 and partially deuterated on the isopropylidene methyl groups was prepared as for the nondeuterated analog[1]. Table IV shows the deuterium content in all relevant compounds. Deuterated compound **4b** was mixed with an equivalent weight of nondeuterated **4b**, and the rearrangement was performed using nondeuterated **1** as the catalyst. Some **4b** was recovered after the reaction. Its deuterium content indicated that there had been some hydrogen exchange in the acetal during the reaction. The deuterium content of the rearranged product (**4c**) was intermediate between that of the recovered **4b** and that of the starting material, as expected for an intramolecular reaction. The deuterium content for **4c** which would result from an intermolecular reaction was calculated (assuming no exchange in **4b** before rearrangement) from the observed isotopic ratios in D-galactose diethyl dithioacetal (both deuterated and nondeuterated) and in the deuterated and nondeuterated acetone. The deuterium content in the deuterated acetone potentially released from deuterated **4b** was calculated from the measured deuterium contents of **4b** and deuterated D-galactose diethyl dithioacetal. The pattern of masses observed for isolated **4c** was very different from that calculated (see Table IV). In particular, the product of an intermolecular rearrangement would give a much smaller peak at *m/z* 326 (M^+) and a much larger peak at *m/z* 327. Thus, the reaction is predominantly intramolecular; exchange of the acetal protons, and experimental uncertainties in the mass-spectral peak-heights, make it difficult to determine whether any of the reaction proceeded by an intermolecular pathway.

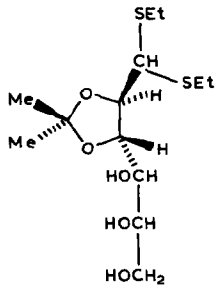
Additional support for this conclusion comes from the nature of the products. It is well known that *trans*-4,5-disubstituted 1,3-dioxolane rings are considerably more stable than their *cis* isomers[7,10]. Products having *trans*-4,5-disubstituted 1,3-dioxolane acetal rings were not obtained if the intramolecular route to them required a *cis* intermediate and if other stable rearrangement-products could be formed. For instance, no 2,3-*O*-isopropylidene-D-galactose diethyl dithioacetal (**4e**)



4c



4f



4e

was obtained in the rearrangement of compound **4b**. Compound **4e** would contain a *trans*-4,5-disubstituted 1,3-dioxolane ring, as does the product of the reaction, its 4,5-isomer (**4c**), and these two isomers should have similar stability. An intramolecular-rearrangement route to the 2,3-derivative would have to proceed through unstable acetals, such as the 3,4-isomer (**4f**) (a *cis*-4,5-disubstituted 1,3-dioxolane), or 1,3-dioxane or 1,3-dioxepane derivatives, known to be less stable[7].

In addition, reactions in which a 4-monosubstituted 2,2-dimethyl-1,3-dioxolane was converted into a 4,5-*trans*-disubstituted 2,2-dimethyl-1,3-dioxolane in which one of the ring-oxygen atoms was also part of the original ring were fast. Examples include the conversions of **3b** into **3d**, and **6c** into **6d**. Similarly, interconversions of isomers having different 4,5-*trans*-disubstituted 2,2-dimethyl-1,3-dioxolane rings with a single oxygen atom in common were reasonably facile, although slower. Examples include the conversions of **3d** into **3c**, and **6c** into **6d**. Rearrangements of compounds in which the two terminal secondary OH groups had the *erythro* configuration required more vigorous conditions. The rearrangements of **2b** and **5b** to their 2,3- and 3,4-*O*-isopropylidene isomers, respectively required either longer reaction-times or higher acid-concentrations than the other rearrangements. In contrast to these structurally dependent rates observed, the rates of all intermolecular rearrangements are expected to be similar.

Thus, the evidence that these reactions entail an intramolecular mechanism is overwhelming. This result is surprising, in view of conclusions drawn that rearrangements in acetone are intermolecular[11,12]. The properties of acetone are similar to those of *N,N*-dimethylformamide; both are polar, aprotic solvents, although acetone is somewhat less polar (ε 20.7 *vs.* 37.0, μ 2.9 *vs.* 3.9)[13]. Herve du Penhoat and Perlin[11] studied the rearrangement of 1,2:4,5-di-*O*-isopropylidene-β-D-psicopyranose to 1,2:3,4-di-*O*-isopropylidene-β-D-psicofuranose (**7**). In acetone-d_6, the signals of the 4,5-*O*-isopropylidene group decreased markedly in 0.5 h while the 1,2-signals disappeared more slowly. After 3.5 h, the observable spectrum corresponded to that of **7**. Dais and Perlin showed that all isopropylidene methyl signals exchange with acetone-d_6, although isopropylidene groups attached to one secondary and one primary oxygen atom exchange faster than those attached to two secondary oxygen atoms[14]. The evidence reported[11] did not establish that the rate of rearrangement was equal to the rate of exchange. In view of the results in this publication, it is likely that the rate of rearrangement was higher than the rate of exchange, and a fast intramolecular rearrangement occurred competitively with slower intermolecular exchange and rearrangement processes.

McCasland and Zanlungo[12] studied the rearrangement and hydrolysis of 1,2:5,6-di-*O*-isopropylidene-3,4-dithio-D-iditol to 3,4-*S*-isopropylidene-3,4-dithio-D-iditol in aqueous trifluoroacetic acid in the presence and absence of added acetone-d_6. Through product analysis, it was demonstrated conclusively that the reaction of the dithiol derivative with acetone-d_6 was faster than the intramolecular rearrangement reaction. However, an intermolecular rearrangement requires a decomposition step followed by a recombination step. The present results indicated

that decomposition steps, in *N,N*-dimethylformamide at least, are slower than rearrangement. Because it is now known[14] that *O*-isopropylidene acetals exchange with acetone-d_6, these results[12] are consistent with exchange reactions occurring simultaneously with intermolecular or intramolecular rearrangements, or both. The evidence presented[12] was not sufficient to determine which process is the faster for this compound.

The product mixtures obtained from the rearrangements of **2b** and **5b**, and from the reactions under rearrangement conditions but at different temperatures of **5a** and **6a**, all contained a small proportion of the starting material in addition to the major product. In each case, the major product was a *trans*-disubstituted 1,3-dioxolane derivative. Observation of the progress of the reactions suggested that all had come close to reaching equilibrium. The similarity of the product ratios obtained from the two different conditions is in agreement with this suggestion. Equilibrium constants obtained from the product ratios were used to calculate ΔG^0 values. These ranged from -1.1 to -1.3 Kcal.mol^{-1} for the equilibrium from the 4-substituted 2,2-dimethyl-1,3-dioxolanes to the 4,5-*trans*-disubstituted 2,2-dimethyl-1,3-dioxolanes. This is the first measurement of the difference in stability of these ring systems, although a number of authors have noted that the latter are more stable[7]. No starting material was obtained in the rearrangement of **4b** to its 4,5-isomer. Here, one of the groups attached to the 4,5-*trans*-disubstituted 1,3-dioxolane ring is smaller, a CH_2OH group, and the lessened steric interaction between the two substituents resulted in the product being of sufficiently greater stability that the starting material was not observed. The product mixture from the rearrangement of **3b** for 7 h contained a higher percentage of starting material, but the shorter reaction period was probably not sufficient for equilibrium to be reached.

Conclusion. — Terminal *O*-isopropylidene derivatives of aldose diethyl dithioacetals rearrange in *N,N*-dimethylformamide containing 0.2 to 1 equiv. of **1** at 40 to 70° to internal *O*-isopropylidene derivates in fair yield. Only products containing *trans*-4,5-disubstituted 2,2-dimethyl-1,3-dioxolane rings were obtained, *i.e.*, those derived from *threo*-diol units. The conditions required for the rearrangements became the more vigorous the farther the pair of *threo* oxygen atoms was from the terminus of the chain. Single products were obtained when only a single *threo* pair was accessible, *i.e.*, from arabinose, mannose, and galactose derivatives. The same products could be obtained by reaction of the parent aldose diethyl dithioacetals with 2-methoxypropene under rearrangement conditions.

EXPERIMENTAL

For most of the general methods, see ref. 1. Solvents used for chromatography were mixtures of ethyl acetate and petroleum ether (b.p. 30–60°): *A*, 1:1; *B*, 2:3; *C*, 3:2; *D*, 2:1; *E*, 1:10; and *F*, 1:4. Exact masses were determined with a VG 7070 mass spectrometer.

5,6-O-Isopropylidene-D-mannose diethyl dithioacetal (**5b**). — D-Mannose diethyl dithioacetal (**5a**; 7.250 g, 25.3 mmol), *p*-toluenesulfonic acid (**1**: 150 mg), and 2-methoxypropene (1.52 g, 25.3 mmol) were kept in *N,N*-dimethylformamide (60 mL) for 14 h at 0°. Standard workup (see ref. 1) yielded a solid (4.007 g, 55.2%) which was recrystallized twice from dichloromethane–pet. ether, to give colorless crystals of **5b** (2.962 g, 48.3%); m.p. 91.5–92° (lit.[5] 89–90°); $[\alpha]_D^{22}$ +16.1° (*c* 3.455, chloroform) (lit.[5] −11.3° in tetrachloroethane); ^{1}H-n.m.r.: δ 2.61, 2.98, 3.18 (3 br s, exchanged with D_2O, 3 OH), for remainder, and for ^{13}C-n.m.r. data, see Tables I and II.

Anal. Calc. for $C_{13}H_{26}O_5S_2$: C, 47.70; H, 7.97; S, 19.70. Found: C, 47.79; H, 8.03; S, 19.70.

General method for rearrangement of isopropylidene derivatives of aldose diethyl dithioacetals. — To a solution of an *O*-isopropylidene-D-aldose diethyl dithioacetal (5 mmol) in anhydrous *N,N*-dimethylformamide (25 mL) at the specified temperature was added compound **1** (171 mg, 0.2 equiv.). The homogeneous mixture was kept, with exclusion of moisture, until t.l.c. indicated that all starting material had reacted, or equilibrium had been reached, and then poured into a 2% (w/v) solution of sodium hydrogencarbonate (100 mL). This mixture was extracted with diethyl ether (4 × 100 mL). The extracts were combined, washed with water (2 × 100 mL), dried (magnesium sulfate), and filtered, and the filtrate was evaporated.

Rearrangement of 4,5-O-isopropylidene-D-arabinose diethyl dithioacetal (**2b**). — Compound **2b** (ref. 1; 1.48 g, 5.0 mmol) and **1** (171 mg, 1.0 mmol) in *N,N*-dimethylformamide (25 mL) were kept for 48 h at 60°. Standard workup gave a yellowish oil (0.766 g, 51.7%) which was separated by chromatography on a column of silica gel (35 g), using solvent *A* as the eluant, into fractions A (0.061 g) and B (0.423 g, 32%) (R_F 0.44, 0.62 in solvent *B*).

Fraction A was starting material (**2b**). Fraction B was syrup 2,3-*O*-isopropylidene-D-arabinose diethyl dithioacetal (**2c**); $[\alpha]_D^{26}$ +87.3° (*c* 1.54, chloroform) (lit.[15] +93.8°); for ^{13}C-n.m.r. data, see Table I; *m/z*: 296 (24, M^+), 235 (49, M − ·SEt), 177 (49), 173 (6, 235 − HSEt), 135 (100), 107 (23), 105 (7), and 75 (98).

4,5-Di-O-acetyl-2,3-O-isopropylidene-D-arabinose diethyl dithioacetal (**2ca**). — Compound **2c** (0.142 g), acetic anhydride (0.35 mL), and pyridine (0.4 mL) were kept for 1 h at 0° and 12 h at 23°, and then poured into ice–water. The mixture was extracted with dichloromethane, and the extracts were combined, successively washed with sodium hydrogencarbonate, ice-cold sulfuric acid, and water, dried ($MgSO_4$), and evaporated to a syrup (0.153 g, 86%) of **2ca**: $[\alpha]_D^{24}$ +65.8° (*c* 1.730, chloroform); ^{1}H-n.m.r.: δ 2.071, 2.105 (2 s, 6 H, 2 $COCH_3$), for remainder, see Tables II and III.

Rearrangement of 2,5-O-isopropylidene-D-xylose diethyl dithioacetal (**3c**). — Compounds **3c** (ref. 1; 1.647 g, 5.56 mmol) and **1** (0.191 g, 1.11 mmol) in *N,N*-dimethylformamide (25 mL) were kept for 2.5 h at 45°. Standard workup gave a

yellow syrup (0.936 g, 56.8%) which was separated by chromatography on a column of silica gel (100 g), using solvent *B* as the eluant into three fractions, A (0.347 g, 21.1%; solid), B, (0.342 g, 20.8%; syrup), and C (0.051 g, 3.1%; syrup) (R_F in solvent *C*: 0.72, 0.63 and 0.54, respectively).

Fraction A was 4,5-*O*-isopropylidene-D-xylose diethyl dithioacetal (**3b**); m.p. 77.5–78°, lit.[16] 78–79°; $[\alpha]_D^{24}$ +48° (*c* 1.54, chloroform), lit.[16] +48°.

Fraction B was 3,4-*O*-isopropylidene-D-xylose diethyl dithioacetal (**3d**); $[\alpha]_D^{24}$ +47° (*c* 1.54, chloroform), lit.[17] +45°.

Fraction C was 2,3-*O*-isopropylidene-D-xylose diethyl dithioacetal (**3e**); $[\alpha]_D^{24}$ −55° (*c* 1.2, chloroform) (lit.[16] −60°); for ^{13}C-n.m.r. data, see Table I; ^{1}H-n.m.r.: δ 3.26, 4.55 (2 br s, exchanged with D_2O, 2 OH), for remainder, see Table I; *m/z* 296 (13, M^+), 235 (1, M − ·SEt), 177 (15), 173 (1), 135 (63), 107 (11), 105 (4), 75 (55), and 59 (100).

When the reaction, performed in exactly the same way, was monitored by t.l.c., the spot caused by **3c** had completely disappeared within 10 min. The major product was **3b**. Spots due to compounds **3d** and **3e** were present after 10 min, and increased in intensity with time.

*Rearrangement of 4,5-*O*-isopropylidene-*D*-xylose diethyl dithioacetal* (**3b**). — Compound **3b** (1.480 g, 5 mmol) and **1** (0.171 g, 1 mmol) in *N,N*-dimethylformamide (25 mL) were kept for 7 h at 45°. Standard workup gave a yellow syrup (0.993 g, 66%) which was separated by chromatography on a column of silica gel (100 g), using solvent *B* as eluant, into three fractions, namely, A (0.109 g, 7.4%; solid), B (0.298 g, 20.4%; syrup), and C (0.242 g, 16.4%; syrup); R_F in solvent *C*: 0.72, 0.61, and 0.51, respectively. Fractions A, B, and C were shown to be compounds **3b, 3d**, and **3e**, respectively.

*Rearrangement of 5,6-*O*-isopropylidene-*D*-galactose diethyl dithioacetal* (**4b**). — Compounds **4b** (0.408 g, 1.25 mmol) and **1** (0.043 g, 0.25 mmol) in *N,N*-dimethylformamide (12.5 mL) were kept for 19 h at 50°. Standard workup gave a pale yellow solid (0.236 g, 58%), recrystallized from dichloromethane-pet. ether to give colorless crystals of **4c** (0.216 g, 53%); m.p. 83.5–84.5° (lit.[6] 82–83°), $[\alpha]_D^{24}$ +15.0° (*c* 1.06, methanol) (lit.[6] +19°).

D-Galactose-C-6-d_1 *diethyl dithioacetal.* — D-Galactose-*C-6-*d_1 was prepared from D-galactose as previously[8], and converted into its diethyl dithioacetal derivative by the standard method[18]. Mass-spectral intensity measurements indicated that the deuterium content was 95.7%.

2,2-Dimethoxypropane-d_6. — Acetone-d_6 (10 g, 155 mmol) trimethoxyorthoformate (18.55 g, 175 mmol), methanol (4.97 g, 155 mmol), and dry Amberlite IR-120 (H^+) ion-exchange resin (2.0 g) were stirred under reflux for 2 h, cooled, and the suspension filtered. The filtrate was fractionally distilled. The fraction having b.p. 80–82° was the title compound; yield 10 g, 59%; ^{1}H-n.m.r.: δ 3.20 (s, OCH_3) and 1.32 (br s, very low intensity, CD_2H).

2-Methoxypropene-d_5. — The title compound was prepared from 2,2-dimethoxypropene-d_6 as described for the nondeuterated compound[9]. The deuterium content was 47% by integration of the ^{1}H-n.m.r. spectrum.

5,6-O-Isopropylidene-d_5*-D-galactose-C-6-*d_1 *diethyl dithioacetal* (**4d**). — D-Galactose-*C-6-*d_1 diethyl dithioacetal (1.46 g, 5 mmol), was treated with 2-methoxypropene-d_5 at 0° as described for the nondeuterated analogs[1], to give the title compound (0.420 g). The deuterium content, determined by mass spectrometry, is given in Table IV.

Rearrangement of a mixture of deuterated and nondeuterated 5,6-O-isopropylidene-D-galactose diethyl dithioacetal. — Compounds **4b** (0.195 g, 597 μmol), **4d** (0.200 g, 604 μmol), and **1** (0.042 g, 0.24 mmol) were stirred in *N,N*-dimethylformamide (12 mL) for 19 h at 50°. Standard workup gave a yellow solid (0.210 g, 53%) which was separated by chromatography on a column of silica gel (8 g), using solvent *D* as the eluant, into three fractions A, B, and C. Fraction A was starting material (0.05 g, 13%), B was **4c** (0.10 g, 25%), and C was 4,6-*O*-isopropylidene-D-galactose diethyl dithioacetal (0.01 g, 3%), identified by comparison with authentic material[1]. The deuterium contents were determined by mass spectrometry, and are listed in Table IV.

Calculation of deuterium content of deuterated acetone potentially liberated by the decomposition of deuterated **4b**. — The peak-height ratios measured for deuterated D-galactose diethyl dithioacetal (M^+, 0.034; M + 1, 0.772; M + 2, 0.107; M + 3, 0.087) and deuterated **4b** (see Table IV) were used to set up a series of eight linear equations to predict the relative intensities of the M^+ to M + 7 peaks for deuterated acetone liberated. A computer program, incorporating the NAG Fortran subroutine EO2GCF[19] for the solution of a system of linear equations, was written to obtain these values. The relative fractional intensities obtained were: M^+ 0.0, M + 1, 0.085, M + 2, 0.242; M + 3, 0.324; M + 4, 0.234; M + 5, 0.096; M + 6, 0.028; and M + 7, 0.004.

3,4-O-Isopropylidene-D-mannose diethyl dithioacetal (**5c**). — (*a*) *By rearrangement of 5,6-O-isopropylidene-D-mannose diethyl dithioacetal* (**5b**). Compounds **5b** (3.26 g, 10 mmol) and **1** (0.344 g, 2 mmol) in *N,N*-dimethylformamide (25 mL) were kept for 43 h at 63°. Standard workup gave a yellow syrup (1.754 g, 53.8%) which was fractionated by chromatography on a column of silica gel (90 g), using solvent *B* as the eluant, into two pure components: starting material (**5b**) (0.107 g, 3.2%), R_F 0.45, (solvent *C*), and a syrup (0.698 g, 21.4%), R_F 0.33, of **5c**, $[\alpha]_D^{20}$ +1.2° (*c* 1.00, chloroform); for ^{13}C-n.m.r. data, see Table I; ^1H-n.m.r.: δ 2.00, 2.61 (2 br s, exchanged with D_2O, 2 OH), for remainder, see Table II; *m/z*: 326 (M^+), 265 (1, M − ·SEt), 247 (10, 265 − H_2O), 203 (1, 265 − HSEt), 135 (100), 107 (16), 105 (7), and 75 (22).

Calc. for $C_{13}H_{26}O_5S_2$: 326.1223. Found: 326.1214.

Treatment of compound **5c** (0.162 g, 0.49 mmol) with acetic anhydride–pyridine, as previously, gave 2,5,6-tri-*O*-acetyl-3,4-*O*-isopropylidene-D-mannose diethyl dithioacetal (**5ca**), a syrup; $[\alpha]_D^{24}$ +32.4° (*c* 1.280, chloroform); ^1H-n.m.r.: δ 2.077, 2.115, 2.171 (3 s, 9 H, 3 $COCH_3$), for remainder, see Tables II and III.

(b) From D-mannose diethyl dithioacetal (**5a**). — Compounds **5a** (4.29 g, 15 mmol), **1** (2.58 g, 15 mmol), and 2-methoxypropene (1.08 g, 15 mmol) in *N,N*-di-

methylformamide (40 mL) were kept for 6 h at 50°. Standard workup gave a pale-yellow syrup (3.445 g, 71%) which was fractionated by chromatography on a column of silica gel (130 g), using solvent *D* as the eluant, into three components, A (0.155 g, 3%), B (0.362 g, 7%), and C (2.080 g, 42%). B and C were found to be compounds **5b** and **5c**.

A was a syrup, 6-*O*-formyl-3,4-*O*-isopropylidene-D-mannose diethyl dithioacetal (**5d**); $[\alpha]_D^{24}$ +39.1° (*c* 0.940, chloroform); ^{13}C-n.m.r.: δ 161.2 (formyl C), for remainder, see Table I; ^{1}H-n.m.r.: δ 8.142 (formyl H), for remainder, see Table II; *m/z* 354 (8, M^+), 339 (s, M − $\cdot CH_3$), 326 (2, M − CO), 293 (2, M − ·SEt), 275 (6), 235 (5), 217 (4), 189 (6), 135 [100, $^+CH(SEt)_2$], 85 (13), and 59 (36).

Treatment of compound **5d** with acetic anhydride–pyridine yielded 2,5-di-*O*-acetyl-6-*O*-formyl-3,4-*O*-isopropylidene-D-mannose diethyl dithioacetal (**5da**), a syrup; $[\alpha]_D^{24}$, +50.4° (*c* 1.020, chloroform); ^{1}H-n.m.r. (361.06 MHz): δ 2.048, 2.097 (2 s, 6 H, 2 $COCH_3$), 7.996 (s, 1 H, formyl H), for remainder, see Tables II and III.

Reaction of D-*glucose diethyl dithioacetal* (**6a**) *under rearrangement conditions.* — Compounds **6a** (4.29 g, 15 mmol), **1** (2.58 g, 15 mmol), and 2-methoxypropene (1.08 g, 15 mmol) were stirred for 6 h at 51°. Standard workup gave a yellow syrup (3.115 g, 64%). Backwashing the combined aqueous extracts with ether (3 × 100 mL) gave more product (0.372 g, 8%). The combined material was separated by chromatography on a column of silica gel (100 g), using solvent *B* as the eluant, into four fractions: A (0.812 g, 17%, R_F 0.84 with solvent *C*), B (0.154 g, 3%, R_F 0.37), C (1.010 g, 21%, R_F 0.30), and D (1.147 g, 24%, R_F 0.14). T.l. chromatograms made during the reaction indicated that *B* and *C* were present within 20 min of the start of the reaction. The amount of *D* present increased gradually from a very slight amount at this time to about as much as *C* when the reaction was stopped.

Fraction A was a syrup, 2,3:5,6-di-*O*-isopropylidene-D-glucose diethyl dithioacetal (**6e**); $[\alpha]_D^{24}$ −51.2° (*c* 2.54, methanol) (lit.[6] −44°); ^{1}H-n.m.r.: δ 2.21 (br d, 1 H, *J* 8.5 Hz, exchanged with D_2O, OH), for remainder, and for ^{13}C-n.m.r. data, see Tables I and II.

Treatment of compound **6e** with acetic anhydride–pyridine, as previously, gave 4-*O*-acetyl-2,3:5,6-di-*O*-isopropylidene-D-glucose diethyl dithioacetal (**6ea**), a syrup; $[\alpha]_D^{24}$ −34.8° (*c* 1.050, chloroform); ^{1}H-n.m.r.: δ 2.067 (s, 3 H, $COCH_3$), for remainder, see Tables II and III.

Fraction B was recrystallized from dichloromethane–pet. ether, to give fine colorless needles of 5,6-*O*-isopropylidene-D-glucose diethyl dithioacetal (**6b**); m.p. 72–73° (lit.[6] 68–69°); $[\alpha]_D^{22}$ −11.0° (*c* 1.010, methanol) (lit.[6] −11°); ^{1}H-n.m.r.: δ 3.14 (br d, exchanged with D_2O, *J* 8 Hz, OH), 3.45, 3.67 (br s, exchanged with D_2O, 2 OH), for remainder, see Table II.

Fraction C was a syrup, 3,4-*O*-isopropylidene-D-glucose diethyl dithioacetal (**6c**); $[\alpha]_D^{23}$ +29.7° (*c* 2.050, chloroform); ^{1}H-n.m.r.: δ 3.20 (br d on a very br s, 2 H, exchanged with D_2O, *J* 6.5 Hz, 2 OH), 4.54 (dd, 1 H, *J* 7.5, 1.5 Hz), for remainder and for ^{13}C-n.m.r. data, see Tables I and II; *m/z*: 326 (11, M^+), 311 (4, M −

·Me), 2.65 (1, M − ·SEt), 247 (6, 265 − H_2O), 207 (5), 191 (2), 189 (4), 173 (6), 161 (3), 147 (2), 135 [100, $^+CH(SEt)_2$], 133 (7), 117 (4), 115 (5), 107 (12), 105 (6), 104 (8), 103 (15), 101 (5), 85 (7), 75 (14), and 59 (56).

Calc. for $C_{13}H_{26}O_5S_2$: 326.1223. Found: 326.1249.

On treatment with acetic anhydride–pyridine, as previously, compound **6c** gave 2,5,6-tri-*O*-acetyl-3,4-*O*-isopropylidene-D-glucose diethyl dithioacetal (**6ca**), a syrup; $[\alpha]_D^{24}$ +28.2° (*c* 1.800, chloroform); ^{1}H-n.m.r.: δ 1.996, 2.045, 2.098 (3 s, 9 H, 3 $COCH_3$), for remainder, see Tables II and III.

Fraction D, a solid, was recrystallized twice from dichloromethane–pet. ether, to give fine colorless needles of 2,3-*O*-isopropylidene-D-glucose diethyl dithioacetal (**6d**); m.p. 38–40°, $[\alpha]_D^{24}$ −40.0° (*c* 2.110, chloroform); ^{1}H-n.m.r.: δ 2.37–3.04 (3 H, 3 OH), for remainder, and for ^{13}C-n.m.r. data, see Tables I and II: *m/z* 326 (12, M^+), 308 (7, M − H_2O) (metastable 291.0), 247 (3), 207 (13), 149 (18), 145 (17), 135 [98, $^+CH(SEt)_2$], 133 (100), 117 (20), 87 (46), and 59 (95).

Calc. for $C_{13}H_{26}O_5S_2$: 326.1223. Found: 326.1201.

Anal. Calc. for $C_{13}H_{26}O_5S_2$: C, 47.70; H, 7.97; S, 19.70. Found: C, 47.33; H, 7.76; S, 19.45.

Treatment of compound **6d** with acetic anhydride–pyridine, as previously, gave 4,5,6-tri-*O*-acetyl-2,3-*O*-isopropylidene-D-glucose diethyl dithioacetal (**6da**), a syrup; $[\alpha]_D^{24}$ −24.2° (*c* 1.410, chloroform); ^{1}H-n.m.r.: δ 2.042, 2.079, 2.127 (3 s, 9 H, 3 $COCH_3$), for remainder, see Tables II and III.

Di-O-isopropylidenation of D-*glucose diethyl dithioacetal* (**6a**). — (*a*) *Under rearrangement conditions*. Compounds **6a** (1.144 g, 4 mmol), **1** (0.688 g, 4 mmol), and 2-methoxypropene (1.153 g, 16 mmol) were stirred for 6 h at 50°. Standard workup gave a red syrup (1.54 g) which was separated by chromatography on a column of silica gel (25 g), using solvent *E* as the eluant, into two fractions, A (0.251 g, 17%; R_F 0.83 in solvent *F*), and B (1.099 g, 75%, R_F 0.62).

Fraction A, a syrup was 3,4:5,6-di-*O*-isopropylidene-D-glucose diethyl dithioacetal (**6f**), $[\alpha]_D^{23}$ −10.0° (*c* 1.025, methanol) (lit.[6] −9°); ^{1}H-n.m.r.: δ 2.89 (d, 1 H, *J* 7 Hz, exchangeable, OH), for ^{13}C-n.m.r. data and remainder of ^{1}H-n.m.r. data, see Tables I and II; *m/z*: 366 (17, M^+), 351 (9), 247 (4), 231 (19), 173 (17), 143 (59), 135 [100, $^+CH(SEt)_2$], and 101 (23). Fraction B was compound **6e**.

(*b*) *With low concentration of acid*. Compounds **6a** (0.572 g, 2 mmol), **1** (6.88 mg, 0.04 mmol) and 2-methoxypropene (0.433 g, 6 mmol) were stirred for 24 h. Standard workup gave a yellow syrup (0.689 g, 94%) which was separated by chromatography on a column of silica gel (10 g), using solvent *E* as the eluant, into two fractions, A (0.384 g, 43%; R_F 0.62 in solvent *F*), and B (0.093 g, 13%; R_F 0.46).

Fraction A was shown to be compound **6e**. Fraction B, a syrup, was 2,3:4,6-di-*O*-isopropylidene-D-glucose diethyl dithioacetal (**6g**); $[\alpha]_D^{25}$ −53.2° (*c* 1.165, chloroform); ^{1}H-n.m.r.: δ 1.91 (br s, 1 H, exchanged with D_2O, OH), for remainder and ^{13}C-n.m.r. data, see Tables I and II; *m/z*: 366 (13, M^+), 351 (2, M − ·Me), 305 (0.4), 293 (2), 247 (4), 231 (19), 189 (7), 177 (5), 173 (48), 171 (5), 155 (4), 149

(12), 145 (12), 135 [59, $^{+}CH(SEt)_2$], 131 (14), 129 (8), 117 (7), 115 (31), 113 (6), 107 (5), 103 (9), 101 (19), 87 (25), 75 (24), 73 (16), 71 (14), 69 (11), and 59 (100).

Calc. for $C_{16}H_{30}O_5S_2$: 366.1536. Found: 366.1515.

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REFERENCES

1 T. B. GRINDLEY, J. C. P. COTE, AND C. WICKRAMAGE, *Carbohydr. Res.*, 140 (1985) 215–238.
2 J. GELAS AND D. HORTON, *Heterocycles*, 16 (1981) 1587–1601.
3 J. G. BUCHANAN, A. R. EDGAR, D. I. RAWSON, P. SHAHIDI, AND R. H. WIGHTMAN, *Carbohydr. Res.*, 100 (1982) 75–86.
4 L. D. HALL, *Adv. Carbohydr. Chem.*, 19 (1964) 51–88.
5 E. PACSU AND C. V. KARY, *Ber.*, 62 (1929) 2811–2814.
6 P. A. J. GORIN, *Can. J. Chem.*, 43 (1965) 2078–2084.
7 D. M. CLODE, *Chem. Rev.*, 79 (1979) 491–513.
8 A. MARADUFU, G. M. CREE, AND A. S. PERLIN, *Can. J. Chem.*, 49 (1971) 3429–3437.
9 M. S. NEWMAN AND M. C. VANDER ZWAN, *J. Org. Chem.*, 38 (1973) 2910.
10 J. A. MILLS, *Adv. Carbohydr. Chem.*, 10 (1955) 1–53.
11 P. C. M. HERVE DU PENHOAT AND A. S. PERLIN, *Carbohydr. Res.*, 71 (1979) 149–167.
12 G. E. MCCASLAND AND A. B. ZANLUNGO, *Carbohydr. Res.*, 17 (1971) 475–477.
13 C. REICHARDT, *Solvent Effects in Organic Chemistry*, Verlag Chemie, New York, 1979, p. 270.
14 P. DAIS AND A. S. PERLIN, *Carbohydr. Res.*, 146 (1986) 177–191.
15 H. ZINNER, G. REMBARZ, AND H. KLOCKING, *Chem. Ber.*, 90 (1957) 2688–2699.
16 D. G. LANCE AND J. K. N. JONES, *Can. J. Chem.*, 45 (1967) 1533–1538.
17 T. VAN ES, *Carbohydr. Res.*, 32 (1974) 370–374.
18 P. A. LEVENE AND G. M. MEYER, *J. Biol. Chem.*, 74 (1927) 695–699.
19 *NAG Fortran Library, Mark 11*, Numerical Algorithm Group, Oxford, 1984.
20 T. B. GRINDLEY, S. KUSUMA, AND T. S. CAMERON, *Can. J. Chem.*, 64 (1986) 2388–2396.