Carbohydrate Research, 218 (1991) 83–93
Elsevier Science Publishers B.V., Amsterdam

The reduction of benzylidene derivatives of pentose diethyl dithioacetals with lithium aluminium hydride–aluminium trichloride

S. Prahlada Rao and. T. Bruce Grindley*
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3 (Canada)

(Received August 3rd, 1990; accepted for publication, October 17th, 1990)

ABSTRACT

Di-*O*-benzylidene derivatives of pentose diethyl dithioacetals were reduced to di-*O*-benzyl pentose diethyl dithioacetals in high yield. In three of the five cases studied, single products were obtained: 2,3:4,5-di-*O*-benzylidene-D-arabinose diethyl dithioacetal gave the 2,5-di-*O*-benzyl derivative; 2,4:3,5-di-*O*-benzylidene-D-xylose diethyl dithioacetal, the 2,3-di-*O*-benzyl derivative; and 2,4:3,5-di-*O*-benzylidene-D-lyxose diethyl dithioacetal, the 4,5-di-*O*-benzyl derivative. The others gave mixtures. It is suggested that the nature of the products obtained was determined by steric effects and by a preference for initial cleavage of secondary oxygen–acetal carbon bonds. The *O*-benzyl groups caused the conformations of the di-*O*-acetyl derivatives of these products to be significantly different than either the parent pentose diethyl dithioacetals or their peracetylated derivatives for four of the six compounds studied.

INTRODUCTION

Partially blocked free sugars were desired for studies of aldose equilibria. One potentially useful approach to a compound of this type is the reduction of a benzylidene acetal to a hydroxybenzyloxy derivative by lithium aluminium hydride–aluminium trichloride. This reaction is particularly attractive because the starting materials are readily prepared and because the reaction often proceeds in a highly regioselective manner[1–5]. The reduction is known to occur under kinetic control[6] and, for carbohydrate derivatives, steric effects have been found to be the most important factor in determining the regioselectivity of cleavage of a particular acetal group[1,5,6]. Aluminium trichloride complexes to the least hindered oxygen atom and the product has the benzyl group attached to the most hindered oxygen atom.

The series of 2,4:3,5-di-*O*-benzylidene acetals derived from pentose diethyl dithioacetals contain the same functional groups in different steric arrangements and thus provide an opportunity to test the ease of product prediction based on steric effects. It was also of interest to determine whether this reaction could be performed in the presence of a diethyl dithioacetal group.

* To whom correspondence should be addressed.

0008-6215/91/$03.50

RESULTS AND DISCUSSION

Reactions. — The 2,4:3,5.di-*O*-benzylidene acetals of D-ribose (**19**), D-xylose (**20**), and D-lyxose diethyl dithioacetal (**21**), were prepared by stirring the pentose diethyl dithioacetal with benzaldehyde and an acidic ion-exchange resin. These compounds were identical to the known di-*O*-benzylidene derivatives[7–9]. 2,3:4,5-Di-*O*-benzylidene-D-arabinose diethyl dithioacetal (**22**) was prepared as previously described[10]. 2,4:3,5-Di-*O*-benzylidene-D-arabinose diethyl dithioacetal (**23**) was a sample prepared earlier[11]. Because the conformation of the starting material determines the outcome of the reaction if it is sterically controlled, the ^{13}C-n.m.r. spectra of these compounds were recorded. Chemical shifts are listed in Table I.

Reductions of the *O*-benzylidene derivatives **19–23** by the lithium aluminium hydride–aluminium trichloride reagent occurred within 2 h at room temperature and products were obtained in very good yields. Reduction of the diethyl dithioacetal group did not occur to any extent under the conditions employed here. Thiophenyl glycosides are also not reduced by this reagent[12].

In most cases, the structures of the products were established from the ^{1}H-n.m.r. spectra of their di-*O*-acetyl derivatives. Chemical shifts of the acetates are listed in Table II. Proton connectivities were established through analyses of the first-order coupling patterns (Table III), supported in one doubtful case (**18**) by decoupling experiments. Comparison of the ^{13}C-n.m.r. chemical shifts of the di-*O*-benzyl derivatives (Table IV) with those of their parent diethyl dithioacetals[13] confirmed the structures and was

TABLE I

^{13}C-N.m.r. chemical shifts (δ)[a] for pentose diethyl dithioacetals **1**, **6**, **13**, and **16**, and their dibenzylidene derivatives **19–23**

Compd.	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*SEt*				*Ph quart*	*Acetal C*
						CH_2	CH_2	CH_3	CH_3		
1[b]	55.1	71.9	70.9	71.6	64.1	24.4	24.6	14.5	14.5		
22	53.6	83.8	80.4	77.1	68.5	24.5	25.2	14.2	14.3		104.6
											104.6
23[b]	50.6	76.8	75.9	67.6	69.1	24.1	24.8	14.1	14.2	137.4	97.0
										137.5	102.2
6	54.7	76.9	71.7	73.8	63.3	25.3	25.3	14.6	14.8		
19	51.0	83.7	75.3	72.5	68.7	25.3	25.3	14.5	14.6	137.0	101.6
										137.0	101.8
13	54.6	74.2	70.6	73.2	63.4	24.6	24.9	14.5	14.5		
20	49.9	81.6	70.7	70.0	69.8	24.9	26.0	14.5	14.7	137.8	100.9
										138.1	101.0
16[d]	55.1	74.0	70.6	69.8	63.2	24.9	25.1	14.9	14.9		
21	51.1	77.1	71.1	69.8	67.3	23.6	23.7	14.2	14.4	138.1	95.8
										138.1	101.0

[a] From the signal of internal tetrametylsilane in (^{2}H)chloroform unless otherwise specified. [b] From ref. 11. [c] Not observed. [d] For a solution in dimethyl ($^2H_3$)sulfoxide.

TABLE II

^{1}H-N.m.r. chemical shifts of acetates **5**, **8**, **10**, **12**, **15**, and **18**[a]

Compd.	*H-1*	*H-2*	*H-3*	*H-4*	*H-5a*	*H-5b*	*Ac*		*CH_2Ph*			
5	4.00	3.97	5.67	5.28	3.74	3.63	1.99	1.95	4.45	4.50	4.62	4.87
8	3.95	4.02	5.48	5.55	3.71	3.60	2.06	2.01	4.40	4.48	4.63	4.89
10	4.17	3.91	4.06	5.59	4.36	4.20	2.07	2.00	4.58	4.87	4.85	4.97
12	4.08	5.38	5.71	3.92	3.72	3.58	2.03	1.97	4.51	4.54	4.66	4.74
15	4.00	3.91	4.16	5.32	4.23	4.16	2.08	1.98	4.64	4.80	4.81	4.92
18	3.98	5.61	5.40	3.84	3.64	3.62	2.04	2.04	4.50	4.50	4.58	4.73

[a] From the signal of internal tetramethylsilane in (^{2}H)chloroform at 361.06 MHz.

TABLE III

^{1}H-N-m.r. coupling constants (in Hz) of acetates **5**, **8**, **10**, **10**, **12**, **15**, and **18**[a]

Compd.	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5a}$	$J_{4,5b}$	$J_{5a,5b}$
5	4.4	4.4	5.2	5.5	4.7	10.5
8	3.5	7.1	2.8	3.8	7.5	10.9
10	3.2	7.7	2.3	3.0	7.9	12.3
12	7.0	4.7	5.1	3.1	6.3	10.6
15	3.6	7.0	3.7	4.3	6.8	11.7
18	4.0	7.6	2.4	5.9	5.0	10.1

[a] Obtained by first-order analysis of 361.06-MHz spectra.

particularly useful when one benzyl group was attached to O-5. It had been established that conversion of a hydroxyl to an *O*-benzyl group causes the signal of the attached carbon atom to be shifted to larger frequency by significant amounts[14]. The ^{13}C-n.m.r. spectra of only two of the pentose diethyl dithioacetals had been assigned[13]; those of the D-ribose and D-lyxose derivatives were done by correlation with the ^{1}H-n.m.r. spectra that were in turn assigned by decoupling experiments.

For two di-*O*-benzyl derivatives (**2** and **3**), obtained from **23**, the acetyl derivatives were not prepared. The 4,5-di-*O*-benzyl structure was unambigously assigned to compound **2** from the increased shift of the signal for C-5 in comparison to its shift in the parent diethyl dithioacetal **6**. Only two di-*O*-benzyl derivatives with a benzyl group attached to O-5 can be obtained from a 2,4:3,5-di-*O*-benzylidene derivative, the 2,5- and 4,5-derivatives. The 2,5-structure had been assigned to **4** and was different from that of **2**.

The structure of **3** was also established from its ^{13}C-n.m.r. chemical shifts. From the ^{13}C-n.m.r. shift of the C-5 signal, it was determined that **3** does not contain a benzyl group attached to O-5. Two possible structures remained, the 2,3- and 3,4-di-*O*-benzyl derivatives. When the chemical shifts of the C-1 signals for the benzyl derivatives, **4**, **7**, **9**, and **14**, were compared with those of the parent pentose diethyl dithioacetals, it was noted that the signal of C-1 moved to lower frequency by 1.0 to 1.4 p.p.m. when O-2 was

TABLE IV

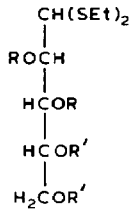
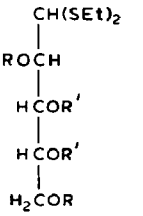
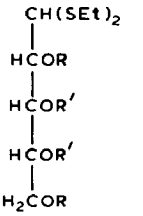
^{13}C-N.m.r. chemical shifts for benzyl derivatives **2–4**, **7**, **9**, **11**, **14**, and **17**

Compd.	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*SEt*				*CH_2Ph*	*Ph quart.*
						CH_2	*CH_2*	*CH_3*	*CH_3*		
2	55.4	73.4	72.9	78.5	70.5	23.9	25.3	14.4	14.4	70.5	137.8
										70.5	138.1
3	52.1	82.3	78.6	71.1	63.5	25.5	25.7	14.3	14.4	74.1	137.6
										74.4	137.6
4	53.6	79.9	73.5	75.2	70.8	25.2	25.8	14.5	14.5	72.0	138.0
										72.0	138.1
7	53.3	83.5	72.0	73.3	70.8	25.6	26.6	14.5	14.5	73.8	[a]
										74.0	
9	53.7	83.5	80.3	72.6	63.5	25.3	26.2	14.4	14.5	73.8	137.6
										75.0	138.1
11	54.8	74.7	73.7	78.5	69.5	25.6	25.6	14.5	14.5	72.1	[a]
										72.1	
14	55.4	73.4	72.9	78.5	70.5	23.9	25.3	14.4	14.4	70.5	137.8
										70.5	138.1
17	54.9	73.3	72.4	76.2	71.1	25.7	26.1	14.6	14.7	73.5	138.1
										73.5	138.1

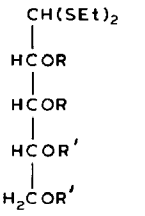
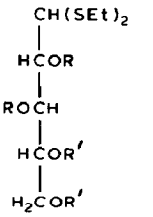
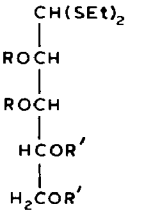
[a] Not observed.

substituted. When O-2 was unsubstituted, *i.e.*, in **2**, **11**, and **17**, the chemical shift for C-1 was within 0.3 p.p.m. of that for the parent compound. The signal for C-1 of **3** appeared at a 3.0-p.p.m. lower frequency than that of compound **1**, indicating that **3** is the 2,3-di-*O*-benzyl derivative.

The conformations of starting 2,4:3,5-di-*O*-benzylidene derivatives influence the outcome of the reactions. The *trans-ring* junction present in **19** and **23** makes prediction of their conformations straightforward and, furthermore, that of **19** has been established by X-ray analysis[11]. Compounds **20** and **21** could be formed in "O"-inside or "H"-inside conformations. The "O"-inside conformation is known to be much more stable[15,16] and di-*O*-benzylidene derivatives normally are formed in it[16,17]. In the "O"-inside conformation of **20**, the $CH(SEt)_2$ group is in an equatorial orientation. The conformation adopted can be established from the ^{13}C-n.m.r. chemical shifts of the acetal carbon atoms. Signals of acetal carbon atoms in 2-phenyl-1,3-dioxane rings in chair conformations without axial substituents range from δ 100.6 to 102.2. With one axial substituent at C-4 or C-6 of the 1,3-dioxane ring, values range from δ 93.7 to 97.0[11,18]. The ^{13}C-n.m.r. chemical shifts for the acetal carbon atoms of **20** at δ 100.9 and 101.0 confirmed that **20** is present in the "O"-inside conformation. Compound **21** has the $CH(SEt)_2$ group axial at C-4 of a 1,3-dioxane ring in its "O"-inside conformation. In the "H"-inside conformation, the $CH(SEt)_2$ group is in an equatorial orientation but C-5 is axial at position-6 of one 1,3-dioxane ring, the 2,4-*O*-benzylidene ring, and C-2 is axial at position-4 of the other 1,3-dioxane ring, the 3,5-*O*-benzylidene ring. The observation of ^{13}C-n.m.r. chemical shifts for acetal carbon atoms at δ 97.0 and 102.2 and ^{1}H-n.m.r. chemical shifts at δ 5.58 and 5.87 for the acetal protons indicated that only one

1 R = R′ = H 4 R = Bn,R′ = H 6 R = R′ = H
2 R = H,R′ = Bn 5 R = Bn,R′ = Ac 7 R = Bn,R′ = H
3 R = Bn,R′ = H 8 R = Bn,R′ = Ac

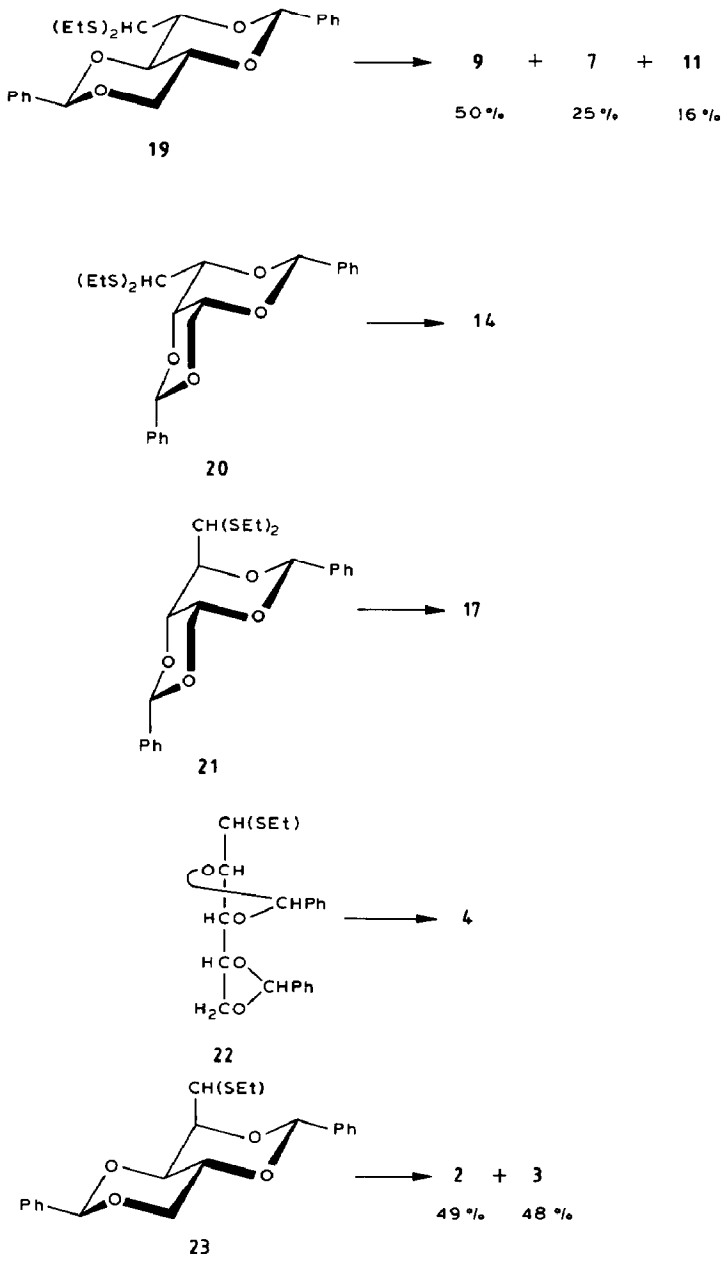




9 R = Bn,R′ = H 13 R = R′ = H 16 R = R′ = H
10 R = Bn,R′ = Ac 14 R = Bn,R′ = H 17 R = H,R′ = Bn
11 R = H,R′ = Bn 15 R = Bn,R′ = Ac 18 R = Ac,R′ = Bn
12 R = Ac,R′ = Bn

of the two 1,3-dioxane rings in **21** has an axial substituent at C-4 or C-6[11,18]. Thus, 2,4:3,5-di-*O*-benzylidene-D-lyxose diethyl dithioacetal also formed its *cis*-2,4,6,8-tetraoxa-3,7-diphenylbicyclo[3.3]decane ring system in an "O"-inside conformation.

The results obtained are shown in Scheme 1. Two often conflicting factors, both previously recognized, appear to be sufficient to explain all but one of these results. The reaction is thought to proceed by complexation of aluminium trichloride to an oxygen atom, opening the bond to the acetal carbon atom, and reduction of the resulting carbocation[1]. The factor normally considered most important in determining the regiochemistry of the reaction for carbohydrates[5] is steric hindrance of initial complexation by aluminium trichloride. If steric effects are not predominant, cleavage of a bond from a secondary oxygen atom to an acetal center is known to proceed more rapidly than one from a primary oxygen atom to the acetal center[2]. For the current work, it was possible to rationalize the sequence and regiochemistry of all reductions only if the latter factor is considered highly significant. Thus, the following tentative outline is based mainly on the importance of the second factor.

For each compound, the two benzylidene rings are cleaved sequentially. For **20**, the equatorial $CH(SEt)_2$ group shields O-2 and O-3. The only secondary oxygen atom available is O-4. Aluminium trichloride complexes with O-4 resulting in a 2-*O*-benzyl derivative. The large $CH(OBn)CH(SEt)_{2\text{-}3}$ group is now free to rotate and shields O-3



Scheme 1. The reduction of di-*O*-benzylidene pentose diethyl dithioacetals **19–23** with $LiAlH_4$–$AlCl_3$.

from aluminium trichloride. Therefore, the subsequent reduction gave a 3-*O*-benzyl derivative.

For **21**, the initial cleavage occurred for the O-3–acetal carbon bond, rather than for the O-4–acetal carbon bond for reasons that are not evident but are probably related to the axial $CH(SEt)_2$ substituent on the 2,4-*O*-benzylidene ring. Complexation at O-2 is

presumably blocked by this large axial group. The released equatorial CH_2OBn group protects O-4 from complexation more effectively than the axial $CH(SEt)_2$ group protects O-2. Thus, the 4,5-di-*O*-benzyl derivative is obtained.

The *trans*-fused systems produced more complicated mixtures of products. For **23**, the axial $CH(SEt)_2$ group protects O-2, but initial complexation resulting in ring cleavage occurs equally at O-3 and O-4. The large groups released protect the adjacent secondary oxygen atoms so that the 2,3- and 4,5-di-*O*-benzyl derivatives were obtained.

For the D-ribose derivative **19**, the major two products appeared to arise from initial cleavage of the O-4–acetal carbon bond resulting in the 2-*O*-benzyl ether. The equatorial $CH(SEt)_2$ group shields both O-2 and O-3. The large group released protects O-3 from complexation, but only partially. Although 50% of the product was obtained by cleavage of the O-5–acetal carbon bond, the greater ease of cleavage of the secondary O–acetal carbon bond resulted in the 2,5-isomer being produced in 25% yield. The other product arose from cleavage of the 3,5-*O*-benzylidene ring first; opening the O-3 bond releases a large group which protects O-4 and resulted in the 4,5-di-*O*-benzyl derivative.

The sample of 2,3:4,5-di-*O*-benzylidene-D-arabinose diethyl dithioacetal (**22**) reduced was obtained by crystallization of the crude di-*O*-benzylidene product from methanol and dichloromethane. The ^{13}C-n.m.r. spectrum of **22** suggested that only a single diastereomer was present, although four are possible. It is not obvious at this time why only the 2,5-di-*O*-benzyl derivative was obtained on reduction of **22**.

Conformational analysis of products. — The conformations assumed by the di-*O*-acetyl-di-*O*-benzyl pentose diethyl dithioacetals are interesting. It is clear that the effects of *O*-benzyl groups are large in comparison to those of *O*-acetyl groups. For instance, all of the acyclic derivatives having the *arabino*-configuration that have been studied previously assume the planar zig-zag conformation in solution[13,19–23]. The compounds studied included D-arabinose diethyl dithioacetal in di($^2H_3$)methyl sulfoxide[13] and ($^2H_4$)methanol[19] and its peracetate in (^2H)chloroform solutions[20]. In contrast, the vicinal coupling constants (Table III) from the ^1H-n.m.r. spectrum of the 3,4-di-*O*-acetyl-2,5-di-*O*-benzyl derivative **5** showed that it is present in (^2H)chloroform solution as a mixture of conformers of which the planar zig-zag conformation probably constitutes less than 50%.

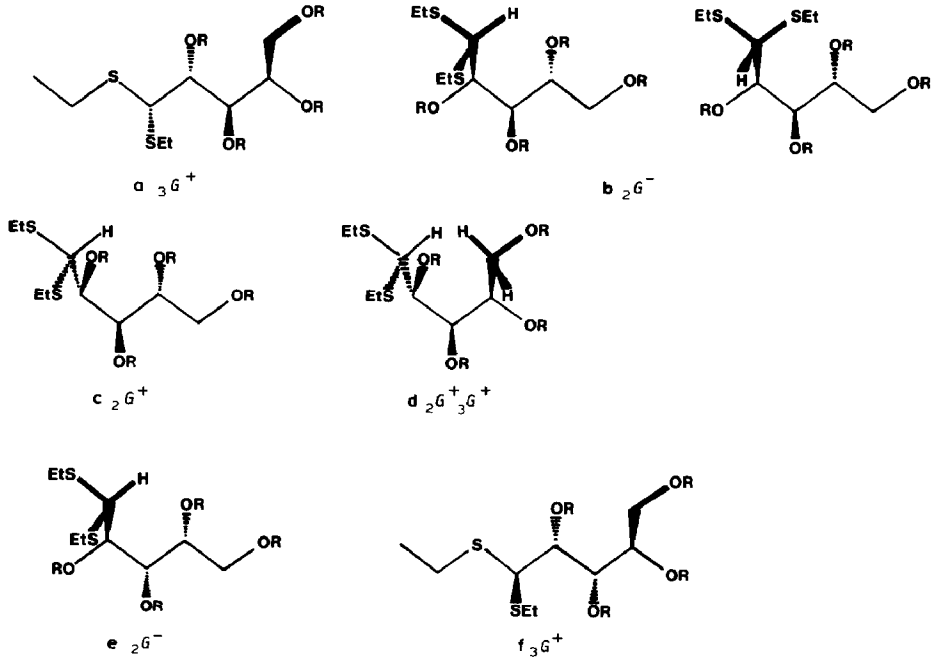
The ^1H-n.m.r. coupling constants of two of the D-ribose diethyl dithioacetyl derivatives (**8** and **10**) indicated that these compounds are mainly present in one sickle conformation*, ${}_3G^+$. This conformation had only been observed previously for the diphenyl dithioacetal[19] and its peracetate[24].

The other D-ribose derivative (**12**) yielded coupling constants similar to those observed for compounds considered to be present in another sickle conformation[19], ${}_2G^-$. We believe that a conformation with two butane *gauche* relationships, ${}_2G^+{}_3G^+$, is more in accord with the coupling constants observed for **12**. The coupling constants observed for D-ribose diethyl dithioacetal in ($^2H_4$)methanol also fit this conformation

* The nomenclature used for sickle conformations is that developed by Horton and Wander[19]; a ${}_3G^+$ conformation is obtained from the planar zig-zag conformation by a 120° counterclockwise rotation of the remote atom along the C-3–C-4 bond.

better[19]. A $_2G^-$ conformation has H-3 and H-4 *anti* and $J_{3,4}$ should be 7 Hz or larger if this conformation is the most populated. The values obtained were 5.2 Hz here and 3.6 Hz for **6**[19]. Furthermore, it is difficult to understand the reason for a large $J_{1,2}$ value for the $_2G^-$ conformation. Only two of the rotamers about the C-1–C-2 bond in the $_2G^-$ conformation (**b** in Scheme 2) will be significantly populated. Of these two, the one with H-1 and H-2 *anti* (on the right in **b** in Scheme 2) is destabilized by a large S–C-4 1,3-interaction (S || C-4), and a S,O *gauche* interaction (S/O), whereas the second has a H-1 || C-4 interaction, a S/O interaction and two S/C interactions. Angyal *et al.*[23] have suggested that S/O interactions have very small effects and the S/C interaction should also be small. Thus, a conformational mixture about the C-1–C-2 bond that is rich in the second rotamer is expected, and $J_{1,2}$ should have a value of 5 Hz or less.

In the $_2G^+$ conformation, the rotamer about the C-1–C-2 bond with H-1 and H-2 *anti* can be shown to be much more stable than the other two rotamers. This conformation has C-1 || O-4, H-1 || C-4, and S/O interactions and should be marginally less stable than the $_2G^-$ conformation. In order for the observed small value of $J_{3,4}$ to be reconciled with the $_2G^+$ conformation, it is necesary that another *gauche* relationship in the carbon skeleton be added, because the $_2G^+$ conformation also has H-3 and H-4 *anti*. Adding the $_3G^+$ relationship to the $_2G^+$ conformation replaces a 1,3-interaction between C-1, which is conformationally restricted by the two SEt groups, and O-4 with a probably less



Scheme 2. Possible conformations of derivatives of compounds **6** and **13** (R = H): (**a**) The $_3G^+$ conformation of **6**, (**b**) two $_2G^-$ conformations of **6** differing in the conformation about the C-1–C-2 bond, (**c**) the $_2G^+$ conformation of **6**, (**d**) the $_2G^+{}_3G^+$ conformation of **6**, (**e**) the $_2G^-$ conformation of **13**, and (**f**) the $_3G^+$ conformation of **13**.

severe O-2 || C-5 interaction. It has recently been shown that the C || O interaction is only slightly more destabilizing than an O || O interaction[23,25]. Thus, this $_2G^+{}_3G^+$ conformation is probably the most important conformer present for **5** or **6**.

The D-xylose derivative **15** had a pattern of coupling constants similar to that of **13** in ($^2H_4$)methanol[19]. The large value for $J_{2,3}$ showed that H-2 and H-3 are *anti*, consistent with a $_2G^-$ conformation. The coupling constants reported[19] for **13** and for the peracetate of D-xylose diphenyl dithiacetal[26] did not fit the assigned $_3G^+$ conformation[19] but did fit the $_2G^-$ conformation. Compound **18** is present mainly in its normally more stable planar zig-zag conformation.

The unusual conformations reported here must be caused by the *O*-benzyl groups. For the D-ribose derivatives **8** and **9** having 2-*O*-benzyl groups, the conformation adopted is the same as that previously adopted only by *ribo* derivatives having large substituents at C-1, such as the diphenyl acetal derivatives. This observation suggested that *gauche* interactions with the SEt groups are important. The 2-*O*-benzyl group in the planar zig-zag conformations of **5** is *gauche* between an SEt group and O-3, and this conformation of **5** is clearly less stable relative to other possible conformations than normal for *arabino* derivatives. However, **5** apparently adopts a conformation with the 2-*O*-benzyl group *gauche* to two SEt groups. These results emphasized the small energy differences between conformations of acyclic derivatives, even those of classes of compounds, such as the *arabino* derivatives, that are usually considered to be present in one major conformation.

EXPERIMENTAL

General methods. — Melting points were determined with a Fischer–Johns melting-point apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer 141 polarimeter. ^{1}H-N.m.r. spectra of acetates were recorderd for (^{2}H)-chloroform solutions containing tetramethylsilane at 361.06 Hz with a Nicolet NT-360 NB spectrometer; other ^{1}H-n.m.r. spectra were recorderd at 60 MHz with a Varian EM-360L spectrometer. ^{13}C-N.m.r. spectra were recorderd for (^{2}H)chloroform solutions at 20 or 90.8 MHz with a Varian CFT-20 or Nicolet NT-360 NB spectrometer, respectively. Assignments for **1** and **13** were taken to be the same as those for ($^2H_3$)-dimethyl sulfoxide solutions[13]. Those for **6** and **16** were made by heteronuclear, single-frequency decoupling of the attached ^{1}H signals, that were in turn assigned by decoupling experiments for the ^{1}H-n.m.r. spectra. Assignments for other compounds were made by considering the incremental shift effects of substituents. Most accurate mass measurements were made with a Dupont CEC 21-110B mass spectrometer; that for **3** was done with a VG 7070 mass spectrometer. As correct values for elemental analysis of dithioacetals are difficult to obtain, elemental composition was determined by mass spectrometry.

General procedure for benzylidenation, illustrated for the benzylidenation of D-ribose diethyl dithioacetal (**6**). — Compound **6** (20.0 g) was stirred with freshly distilled benzaldehyde (100 mL) and Amberlite IR-120 (H^+) cation-exchange resin (20 g) for

18 h. The mixture was filtered, and the filtrate diluted with methanol (300 mL), and then stored at 5° for several h. The thick, colorless precipitate of 2,4:3,5-di-*O*-benzylidene-D-ribose diethyl dithioacetal (**19**) was isolated by filtration and crystallized from 4:1 methanol–dichloromethane (yield 16 g, 47%), m.p. 121–122°, lit.[8] 122–123°.

General procedure for reduction, illustrated for the reduction of compound **19**. — Lithium aluminium hydride (3.5 g, 92 mmol) was added slowly to a stirred solution of **19** (10 g, 23 mmol) in anhydrous ether (75 mL) and dichloromethane. After 5 min, a solution of $AlCl_3$ (10 g, 75 mmol) in anhydrous ether (20 mL) was added dropwise over 5 min. The mixture was stirred for 90 min, and then ethyl acetate (20 mL) was added, followed by water (50 mL). The aqueous layer was separated and then extracted with ether (3 × 50 mL). The combined organic layers were washed with water (4 × 100 mL), dried ($MgSO_4$), and then fractionated by column chromatography on silica gel using 4:1 petroleum ether(30–60°)–ethyl acetate as eluent. 4,5-Di-*O*-benzyl-D-ribose diethyl dithioacetal (**11**; 1.6 g, 16%) was eluted first, followed by 2,5-di-*O*-benzyl-D-ribose diethyl dithioacetal (**7**; 2.5 g, 25%), and 2,3-di-*O*-benzyl-D-ribose diethyl dithioacetal (**9**; 5.0 g, 50%); for spectral constants, see Table II. Compound **9** was a syrup, $[\alpha]_D$ + 32° (*c* 1.7, chloroform).

Anal. Calc. for $C_{23}H_{32}O_4S_2$: Mol.wt. 436.1744. Found, 436.175.

Compound **7** was a syrup, $[\alpha]_D$ + 29° (*c* 2.6, chloroform).

Anal. Calc. for $C_{23}H_{32}O_4S_2$: Mol. wt. 436.1744. Found, 436.174.

Compound **11** was a syrup, $[\alpha]_D$ −17° (*c* 1.9, chloroform).

Anal. Calc. for $C_{23}H_{32}O_4S_2$: Mol. wt., 436.1744. Found, 436.174.

*Reduction of 2,3:4,5-di-*O*-benzylidene-*D*-arabinose diethyl dithioacetal* (**22**). — Reduction of compound **22** (2 g) was performed as described above. The product, 2,5-di-D-benzyl-D-arabinose diethyl dithioacetal (**4**), was a syrup (yield 1.95 g, 98%), $[\alpha]_D$ + 12° (*c* 2.1, chloroform).

Anal. Calc. for $C_{23}H_{32}O_4S_2$: Mol. wt. 436.1744. Found, 436.174.

*Reduction of 2,4:3,5-di-*O*-benzylidene-*D*-arabinose diethyl dithioacetal* (**23**). — Compound **23** (0.1 g) was reduced as described above to give a mixture of 2,3-di-*O*-benzyl- (**3**) and 4,5-di-*O*-benzyl-D-arabinose diethyl dithioacetal (**2**). For ^{13}C-n.m.r. data shifts, see Table II (yields 0.046 g, 48%; and 0.049 g, 49%, respectively).

Anal. Calc. for $C_{23}H_{32}O_4S_2$: Mol. wt., 436.1744. Found (**3**) 436.1730.

*Reduction of 2,4:3,5-di-*O*-benzylidene-*D*-xylose diethyl dithioacetal* (**20**). — Compound **20** (1 g) was reduced as described above to give 2,3-di-*O*-benzyl-D-xylose diethyl dithioacetal (**14**) as a syrup (yield 0.95 g, 95%), $[\alpha]_D$ + 20° (*c* 2.1, chloroform).

Anal. Calc. for $C_{23}H_{32}O_4S_2$: Mol.wt. 436.1744. Found, 436.175.

*Reduction of 2,4:3,5-di-*O*-benzylidene-*D*-lyxose diethyl dithioacetal* (**21**). — Compound **21** (2 g) was reduced as described above to 2,3-di-*O*-benzyl-D-lyxose diethyl dithioacetal (**17**) as a syrup (yield 1.88 g, 94%), $[\alpha]_D$ + 6.2° (*c* 1.5, chloroform).

Anal. Calc. for $C_{23}H_{32}O_4S_2$: Mol.wt. 436.1744. Found, 436.175.

Acetates of the di-*O*-benzyl derivatives were prepared in the standard way by reaction with acetic anhydride in dry pyridine.

ACKNOWLEDGMENTS

T.B.G. thanks NSERC for an operating grant. The authors thank the Atlantic Region Magnetic Resonance Centre for time on the Nicolet spectrometer and the Atlantic Research Laboratories for use of their polarimeter. They are very grateful to Dr. L. Ramaley for performing most of the mass measurements, and to Dr. Brian Gregory for performing that of **3**.

REFERENCES

1 For a review, see J. Gelas, *Adv. Carbohydr. Chem. Biochem.*, 39 (1981) 71–156.
2 B. E. Leggetter and R. K. Brown, *Can. J. Chem.*, 42 (1964) 990–1004; U. E. Diner and R. K. Brown, *ibid.*, 45 (1967) 1297–1299.
3 S. S. Bhattacharjee and P. A. J. Gorin, *Can. J. Chem.*, 47 (1969) 1195–1206; 1207–1215.
4 P. A. J. Gorin and A. J. Finlayson, *Carbohydr. Res.*, 18 (1971) 269–279; P. A. J. Gorin, *ibid.* 18 (1971) 281–288.
5 A. Lipták, I. Jodál, and P. Nánási, *Carbohydr. Res.*, 44 (1975) 1–11; A. Lipták, P. Fugedi, and P. Nánási, *ibid.*, 68 (1979) 151–154; A. Lipták, J. Imre, J. Harangi, and P. Nánási, *Tetrahedron*, 38 (1982) 3721–3729.
6 E. L. Eliel, *Rec. Chem. Prog.*, 23 (1961) 129–145.
7 H. Zinner and H. Banz, *J. Prakt. Chem.*, 314 (1972) 428–436.
8 H. Zinner and E. Wittenburg, *Chem. Ber.*, 94 (1961) 1298–1303.
9 H. Zinner, K.-H. Rohde, and A. Mattheus, *Jnstus Liebigs Ann. Chem.*, 677 (1964) 160–165.
10 H. Zinner, W. Rehder, and H. Schmandke, *Chem. Ber.*, 95 (1962) 1805–1811.
11 T. B. Grindley, S. Kusuma, T. S. Cameron, and A. Kumari, *Carbohydr. Res.*, 159 (1987) 171–183.
12 A. Lipták, I. Jodál, J. Harangi, and P. Nánási, *Acta Chim. Hung.*, 113 (1983) 415–422.
13 G. W. Schnarr, D. M. Vyas, and W. A. Szarek, *J. Chem. Soc., Perkin Trans. 1*, (1979) 496–503.
14 J.-P. Joseleau, M. Lapeyre, M. Vignon, and G. S. Dutton, *Carbohydr. Res.*, 67 (1978) 197–212; K. Bock and C. Pedersen, *Adv. Carbohydr. Chem. Biochem.*, 41 (1983) 27–66.
15 R. U. Lemieux and J. Howard, *Can. J. Chem.*, 41 (1963) 393–398.
16 J. F. Stoddart, *Stereochemistry of Carbohydrates*, Wiley, New York, 1971, p. 210.
17 A. B. Foster, A. H. Haines, and J. Lehmann, *J. Chem. Soc.*, (1961) 5011–5014.
18 T. B. Grindley and V. Gulasekharam, *Carbohydr. Res.*, 74 (1979) 7–30.
19 D. Horton and J. D. Wander, *J. Org. Chem.*, 39 (1974) 1859–1863.
20 D. Horton and J. D. Wander, *Carbohydr. Res.*, 10 (1969) 279–288.
21 D. Velasco, J. Castells, F. López-Calahorra, and C. Jaime, *J. Org. Chem.*, 55 (1990) 3526–3530.
22 M. Blanc-Muesser, J. Defaye, and D. Horton, *Carbohydr. Res.*, 87 (1980) 71–86.
23 S. J. Angyal, J. K. Saunders, C. T. Grainger, R. Le Fur, and P. G. Williams, *Carbohydr. Res.*, 150 (1986) 7–21.
24 D. Horton and J. D. Wander, *Carbohydr. Res.*, 15 (1970) 271–284.
25 D. Lewis and S. J. Angyal, *J. Chem. Soc., Perkin Trans. 2*, (1989) 1763–1765.
26 D. Horton and J. D. Wander, *Carbohydr. Res.*, 13 (1970) 33–47.