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PHOTOCHEMICAL ADDITION OF 2-PROPANOL AND OF ACETONE TO 2-ACETOXY-3,4,6-TRI-*O*-ACETYL-D-GLUCAL*

YOUNOSUKE ARAKI, KAZUO SENNA, KAZUO MATSUURA, AND YOSHIHARU ISHIDO

Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152 (Japan)

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ABSTRACT

Irradiation of a solution of 2-acetoxy-3,4,6-tri-*O*-acetyl-D-glucal (**1**) in 1:200 acetone–2-propanol with a high-pressure mercury-lamp gave 4,5,6,8-tetra-*O*-acetyl-3,7-anhydro-1-deoxy-2-*C*-methyl-D-*glycero*-D-*gulo*-octitol (**2**) (51.2%), -D-*glycero*-D-*ido*-octitol (**3**) (16.2%), and -D-*glycero*-D- *galacto*-octitol (**4**) (21.0%). The irradiation of **1** in 1:1 acetone–2-propanol gave 5,6,8-tri-*O*-acetyl-3,7-anhydro-1-deoxy-4-*C*-(1-hydroxy-1-methylethyl)-2-*C*-methyl-D-*glycero*-D-(*gluco* or *manno*, *etc.*)-octitol 2,4,4[1]-orthoacetate (17%) and a 2:1:1 mixture of **2**, **3**, and **4** (64%). Moreover, the irradiation of **1** in 1:9 acetone–*tert*-butyl alcohol gave **2** (15%), **3** (9%), **4** (7%), and (4*S*)-4,5,6,8-tetra-*O*-acetyl-2,4:3,7-dianhydro-1-deoxy-2-*C*-methyl-D-*gluco*-octos-4-ulose (14%).

INTRODUCTION

The photochemical reaction of 3,4,6-tri-*O*-acetyl-D-glucal has been shown to involve an interesting solvent-effect in a series of investigations on the reaction of unsaturated sugars, *i.e.*, a (1-hydroxy-1-methylethyl) adduct was obtained selectively when the solvent was 1:9 acetone–2-propanol[1]. Cycloaddition of acetone was induced selectively when the solvent was 9:1 acetone–2-propanol[2], and higher concentrations of the unsaturated sugar in the reaction in 1:9 acetone–2-propanol also gave such products as bis(1-hydroxy-1-methylethyl) derivatives[3]. Moreover, 2-acetoxy-3,4,6-tri-*O*-acetyl-D-glucal (**1**) was found to be more reactive than 3,4,6-tri-*O*-acetyl-D-glucal in the addition reaction of 1,3-dioxolane[4]. We now report the results obtained by the photochemical addition of 2-propanol and of acetone to **1**.

RESULTS AND DISCUSSION

Based on the solvent effect found in the reaction of 3,4,6-tri-*O*-acetyl-D-glucal, the reaction of **1** in 1:9 acetone–2-propanol was examined, but separation of the

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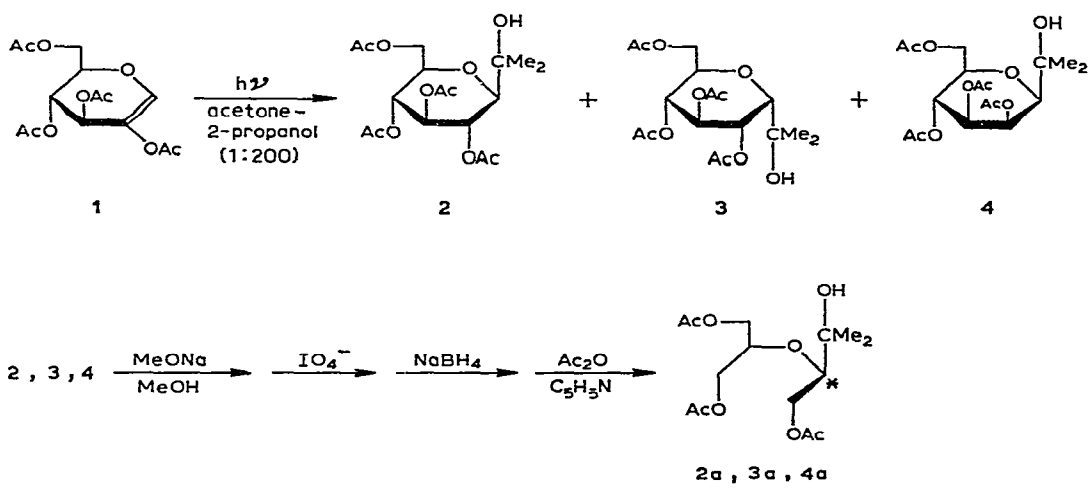
products by chromatography was impossible, because of the closeness of their R_F values. Incidentally, it has been confirmed that decrease in the proportion of acetone to 1:50 (v/v) in the solvent system made possible the minimizing of the formation of such byproducts as pinacol, and thus products could be isolated in the reaction of 3,4-di-*O*-acetyl-D-xylal[5], which has been shown to be less reactive than other unsaturated sugar derivatives. Therefore, we decreased the ratio of acetone to 2-propanol, and found that, even at a ratio of 1:200, the reaction occurred.

Consequently, compound **1** in the solvent was irradiated with a high-pressure mercury-lamp for 70 h, and the solution was evaporated. Chromatographic separation of the resulting mixture on a column of silica gel gave 4,5,6,8-tetra-*O*-acetyl-3,7-anhydro-1-deoxy-2-*C*-methyl-D-*glycero*-D-*gulo*-octitol (**2**) (51.2%), 4,5,6,8-tetra-*O*-acetyl-3,7-anhydro-1-deoxy-2-*C*-methyl-D-*glycero*-D-*ido*-octitol (**3**) (16.2%), and 4,5,6,8-tetra-*O*-acetyl-3,7-anhydro-1-deoxy-2-*C*-methyl-D-*glycero*-D-*galacto*-octitol (**4**) (21.0%); 8.3% of **1** was recovered. The D-*glycero*-D-*gulo* configuration of **2** was assigned by the n.m.r. data summarized in Table I; the coupling constants $J_{3,4}$, $J_{4,5}$, $J_{5,6}$, and $J_{6,7}$ are all 9.5 Hz, and all of the acetyl methyl signals are in the equatorial region[6]. Compound **3** was identified by comparison with an authentic specimen[3]. The configuration of C-4 of **4** was assigned as *S* on the basis that one acetyl methyl signal is at δ 2.13 (axial region[6]), and that $J_{5,6} = J_{6,7} = 10$ Hz, and $J_{4,5} = 3.0$ Hz.

The configuration of C-3 was confirmed as *R* by degrading **2**, **3**, and **4** to the corresponding (2*R* or 2*S*)-1-acetoxy-3-hydroxy-3-methylbutan-2-yl 1,3-diacetoxypropan-2-yl ethers (**2a**, **3a**, and **4a**), respectively, through a series of reactions, namely, deacetylation, oxidation with periodate, reduction with sodium borohydride, and acetylation, followed by intercomparison of the specific rotations of the products. The values of +13.4°, −9.4°, and +14.1° for **2a**, **3a***, and **4a** showed that compounds



*Compound 3a was prepared from a sample of **3** that contained a small proportion of **4**.

TABLE I

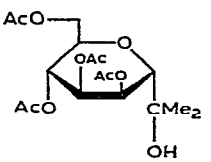
^{1}H-N.M.R. DATA FOR COMPOUNDS **2**, **4**, AND **5**

Assignment	**2** *(δ)*	**4** *(δ)*	**5** *(from ref. 7) (δ)*
H-3	3.37 (d)	3.39 (d)	3.37
H-4	5.06 } (m)	5.62 (q)	5.6
H-5,6	4.9–5.3 ∫	5.02 (q) and 5.24 (t)	4.98 and 5.25
H-7	3.68 (dt)	3.70 (dq)	3.63
H-8,8′	4.17 (bd)	4.20 (q) and 4.26 (q)	4.2
C-CH_3	1.21 (s)	1.22 (s)	1.21
	1.21 (s)	1.22 (s)	1.21
O-$COCH_3$	1.99 (s)	1.97 (s)	1.96
	2.00 (s)	2.05 (s)	2.04
	2.02 (s)	2.08 (s)	2.10
	2.06 (s)	2.13 (s)	2.11
	(Hz)	*(Hz)*	*(Hz)*
$J_{3,4}$	9.5	1.0	0.8
$J_{4,5}$	9.5[a]	3.0	3
$J_{5,6}$	9.5[a]	10.0	10.0
$J_{6,7}$	9.5	10.0	
$J_{7,8}$	4.0	3.5	
$J_{7,8'}$	4.0	5.0	
$J_{8,8'}$		11.8	

[a]This datum was calculated from the spectrum of a sample treated with <0.1 eq. of $Eu(dpm)_3$.

2 and **4** have the same configuration at C-3; that is, they have the D-*glycero*-D-*galacto* configuration.

Rosenthal and Ratcliffe[7] isolated a similar product in the photochemical addition of formamide to **1**, and assigned to it the D-*glycero*-D-*talo* configuration, as shown in formula **5**. The n.m.r. data for **5**, given adjacent to those for **4** (see Table I), are very similar to those for **4**, and their melting points are almost the same [**4**; m.p. 137° (uncorr.); **5**; m.p.[7] 139–140°]. If the structure of **5** is correct, its n.m.r. spectrum should show a favored population of $^1C_4$ conformer, because of the axially oriented (1-hydroxy-1-methylethyl) group on C-3, and the acetyl group on C-4 (in the $^4C_1$ conformation). Incidentally, the (1-hydroxy-1-methylethyl) group on C-3 of **3** causes a 53% population of the $^1C_4$ conformer [$J_{4,5} = J_{5,6} = J_{6,7} = 5.0$ Hz; the acetyl methyl signals are[3] at δ 2.10 (3 H), 2.08 (6 H), and 2.04 (3 H)]. Therefore, we decided



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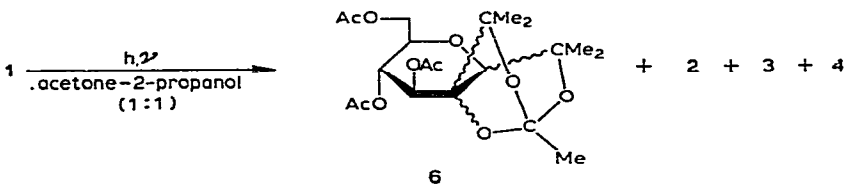
that, based on these facts, compound **5** is the same as **4**. The isolation of **4** from the reaction mixture[7] presumably arises from the fact that **4** is more readily crystallized than **2** (see Experimental section).

The reaction in acetone–2-propanol containing a higher proportion of acetone gave thin-layer and gas–liquid chromatograms involving a new spot or peak differing from those of **2**, **3**, and **4**. Reaction in 1 : 1 acetone–2-propanol for 100 h, followed by chromatographic separation, gave 5,6,8-tri-*O*-acetyl-3,7-anhydro-1-deoxy-4-*C*-(1-



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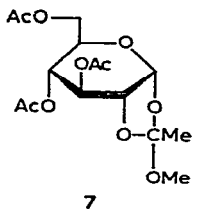
hydroxy-1-methylethyl)-2-*C*-methyl-D-*glycero*-D-(*gluco* or *manno*, *etc.*)-octitol 2,4,4^1-orthoacetate (**6**) (17%), as well as a mixture of **2**, **3**, and **4** (64%; ratios ~2:1:1). The n.m.r.- (see Table II) and i.r.-spectral evidence, and t.l.c. of **6** led us to the conclusion that **6** is an intramolecular orthoester. The n.m.r. data for **6** reveal that (*i*) C-4 bears no proton at all, (*ii*) there are three acetyl methyl signals (9 H), (*iii*) there are five *C*-methyl signals (15 H), and (*iv*) $J_{5,6}$ and $J_{6,7}$ are 5 and 7 Hz, respectively; these results suggest a considerably strained structure for **6**. The mass spectrum of **6** had a

TABLE II

^{1}H-N.M.R. DATA FOR COMPOUNDS **6** AND **10**

Assignment	**6** *(δ)*	**10** *(δ)*
H-3	3.82 (s)	4.41 (s)
H-5	5.38 (d)	5.36 (d)
H-6	4.99 (q)	5.10 (q)
H-7	3.58 (bq)	4.05–4.45 (m)
H-8,8′	4.25 (d)	
C-CH_3	1.24 (s)	1.44 (s)
	1.30 (s)	1.47 (s)
	1.41 (s)	
	1.51 (s)	
	1.55 (s)	
O-$COCH_3$	2.06 (s)	1.99 (s)
	2.09 (s)	2.01 (s)
	2.09 (s)	2.04 (s)
		2.08 (s)
	(Hz)	*(Hz)*
$J_{5,6}$	5	8.0
$J_{6,7}$	7	5.5
$J_{7,8}$	6	
$J_{7,8'}$	6	

parent peak of *m/e* 430; this may be assumed to arise from dehydration between the two (1-hydroxy-1-methylethyl) groups introduced at the double bond. An absorption band or signal corresponding to a hydroxyl group was not observed in its i.r. and n.m.r. spectra. Moreover, the R_F value (0.7) of **6** in t.l.c. is very similar to that (0.8) of **1**, and different from those of **2**, **3**, and **4** (0.4 each); the polarity of **6** is thus considered to be similar to that of **1**.



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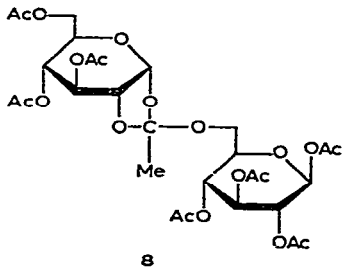

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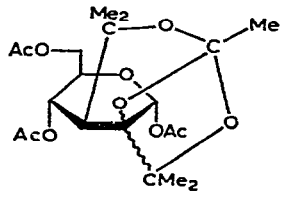

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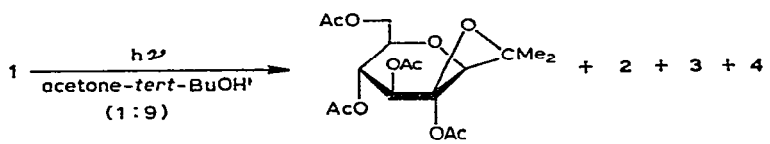
We then compared the p.m.r. and c.m.r. spectra of **6** with those[7,9] of such orthoester sugar derivatives as 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-methoxyethylidene)-α-D-glucopyranose[7] (**7**) and 3,4,6-tri-*O*-acetyl-1,2-*O*-[1-(1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranos-6-yloxy)ethylidene]-α-D-glucopyranose[8] (**8**) in order to confirm the structure of **6**. The orthoacetyl methyl signals in the p.m.r. spectra of **7** and **8** are at δ 1.71 and 1.67, respectively, and that of **6** is at δ 1.55. In their c.m.r. spectra, the orthocarbonyl carbon atoms of **7** and **8** are at δ 121.6 and 121.1, and that of **6** is at δ 117.27 (see Experimental section). The resonance of each proton and carbon nucleus of **6** at higher magnetic field may indicate that the orthoester structure is involved in a bicyclic ring structure in **6**. The chemical shifts of the orthocarbonyl carbon atom (δ 118.06) and orthoacetyl methyl protons (δ 1.55) of 1,4,6-tri-*O*-acetyl-3-deoxy-2,3-di-*C*-(1-hydroxy-1-methylethyl)-α-D-gluco- or -manno-pyranose $2,2^1,3^1$-orthoacetate[10] (**9**) presumably support the foregoing assignment of structure to **6**. We had found[3] such introduction of two (1-hydroxy-1-methylethyl) groups to one double bond in the photochemical addition of 2-propanol to 3,4,6-tri-*O*-acetyl-D-glucal, when the concentration of the unsaturated sugar was high. The enhanced concentration either of unsaturated sugar or acetone may cause the attack of two (1-hydroxy-1-methylethyl) radicals on the double bond of the unsaturated sugar.

Subsequently, we attempted to achieve the photocycloaddition of acetone to **1**. The reaction in 9:1 acetone–2-propanol, which was very effective with 3,4,6-tri-*O*-acetyl-D-glucal[2], unexpectedly resulted in almost quantitative recovery of the starting material. Hence, the reaction was performed in a potentially effective solvent, namely, 1:9 acetone–*tert*-butyl alcohol, with irradiation with a high-pressure mercury-lamp



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for 230 h, and evaporation. Chromatographic separation of the resulting mixture gave (4*S*)-4,5,6,8-tetra-*O*-acetyl-2,4:3,7-dianhydro-1-deoxy-2-*C*-methyl-D-*gluco*-octos-4-ulose (**10**) (14%), as well as **2** (15%), **3** (9%), and **4** (7%); and 17% of **1** was recovered. The structure of **10** was decided on the basis of the mechanism* of oxetane formation[1] and the n.m.r. evidence (see Table II); the H-3 signal appears at a comparatively higher field (δ 4.41), and all of the acetyl methyl signals are in the equatorial region[6]. It has already been reported that the oxetane formed from 3,4,6-tri-*O*-acetyl-D-glucal is partly susceptible to hydrolysis during column chromatography on silica gel[3]. However, such hydrolysis was not observed in this instance. The formation of the (1-hydroxy-1-methylethyl) radical adducts **2**, **3**, and **4** in the last case may arise from the hydrogen-donating effect of traces of impurities or *tert*-butyl alcohol on photo-excited acetone, as photocycloaddition of acetone to **1** was so slow as to require a long period of reaction.

EXPERIMENTAL

Acetone, 2-propanol, and *tert*-butyl alcohol were purchased, and purified as usual. 2-Acetoxy-3,4,6-tri-*O*-acetyl-D-glucal (**1**) was prepared according to a known procedure[11]. A solution of **1** was placed in a Pyrex-glass test-tube, degassed by passing argon gas through it, and the tube tightly stoppered before the photoirradiation. The irradiations were conducted externally with a 450-W, high-pressure, mercury lamp (Ushio Electric Inc.) at a distance of ~5 cm. The lamp, and each of the test tubes, was cooled with running water. T.l.c. was performed on Merck TLC aluminum sheet (Silica gel 60 F_{254}) with 9:1 benzene–methanol as the developer. G.l.c. was performed with a Hitachi Model K-53 instrument on a column (1 m) of 10% of SE-30 on Chromosorb-W (60–80 mesh) with nitrogen at 1.5 atm. as the carrier gas; the oven temperature was 200°, and the injection temperature, 300°; and the correlative retention time was recorded with reference to that of **1** as unity. Specific rotations were determined with a Carl Zeiss Photoelectric Precision Polarimeter (± 0.005°) at 546 and 578 nm, and the data were used for the calculation of $[\alpha]_D$ values from the Drude equation. N.m.r. spectra of compounds in chloroform-*d* were recorded with a Varian EM-390 instrument, with tetramethylsilane as the internal standard, and detailed analysis of the spectra was performed by means of double resonance or the INDOR technique. ^{13}C-N.m.r. spectra of compounds in chloroform-*d* were recorded with a Varian CFT-20 instrument, with tetramethylsilane as the internal standard. Mass-spectral data were obtained with a Hitachi RMU-6E spectrometer.

4,5,6,8-Tetra-O-*acetyl-3,7-anhydro-1-deoxy-2*-C-*methyl*-D-glycero-D-gulo-, -D-

*Compound **10** may be considered as being formed by intramolecular cyclization of a biradical formed by the attack of the electron-deficient, carbonyl oxygen atom of acetone in n-π^* by photoactivation on the electron-sufficient C-2 of **1**. Consequently, the 2-*O*-acetyl group may bring about a steric effect in the attack of photoexcited acetone, to make the photocycloaddition of acetone to **1** extremely difficult (and different from that to 3,4,6-tri-*O*-acetyl-D-glucal), in contrast with the trend that photochemical addition of 1,3-dioxolane or 2-propanol to **1** occurs more easily than those to the latter.

glycero-D-ido-, *and* -D-glycero-D-galacto-*octitol* (**2**, **3**, *and* **4**). — A solution of **1** (480 mg) in acetone (0.1 mL)–2-propanol (20 mL) in the test tube was irradiated for 70 h. The resulting solutions in five of the test tubes were combined and evaporated *in vacuo*. Chromatographic separation of the resulting syrup on a column (3 × 30 cm) of silica gel (Wakogel C-300) with successive elution with 997:3 benzene–methanol (1 L), 199:1 benzene–methanol (1 L), and 99:1 benzene–methanol (2 L) gave **1** (200 mg, 8.3% recovery), **2** (1.451 g, 51.2%), and a mixture of **3** and **4** containing a trace of **2**. Re-chromatography of the mixture afforded a mixture of **3** and **4** that, on allowing its solution in a small volume of diethyl ether to stand, gave crystalline **4**. Compounds **3** (460 mg, 16.2%) and **4** (597 mg, 21.0%) were thus obtained by repeating the concentration of the mother liquor and the crystallization of the resulting syrup from ether. Compound **2** crystallized on keeping the syrup for a time. Compound **2**: m.p. 95–97°, $[\alpha]_D^{22}$ +3° (*c* 1.0, acetone); compound **3**: $[\alpha]_D^{22}$ +33.4° (*c* 1.0, acetone); and compound **4**: m.p. 137° (diethyl ether), $[\alpha]_D^{22}$ −6.5° (*c* 1.0, acetone).

The ^{1}H-n.m.r. data of **2** and **4** are summarized in Table I; for those of **3**, see ref. 3; t.l.c.: R_F 0.4 (**2**, **3**, and **4**), and 0.8 (**1**); correlative retention time in g.l.c.: 2.0 (**2**), 2.2 (**3**), and 1.8 (**4**).

Anal. Calc. for $C_{17}H_{26}O_{10}$: C, 52.30; H, 6.71. Found: for **2** and **4**: C, 52.47 and 52.58; H, 6.82 and 6.62, respectively.

(R)- *or* (S)-*1-Acetoxy-4-hydroxy-3-methylbutan-2-yl 1,3-diacetoxypropan-2-yl ether* (**2a**, **3a**, *and* **4a**). — A solution of compound **2** (1.000 g) in methanol (50 mL) was treated with M sodium methoxide in methanol (5 mL) for 2 h at room temperature. The resulting solution was applied to a column of Amberlite IR-120B (H^+) resin (10 mL), and the column was washed with distilled water (200 mL). The effluent was evaporated *in vacuo* to a syrup which was then dissolved in water (20 mL) and treated with sodium metaperiodate (3 g), with stirring, for 4 days at room temperature. The inorganic precipitate was filtered off, and the filtrate was evaporated *in vacuo* to a syrup. The syrup was dissolved in water (50 mL) and treated with sodium borohydride (1.5 g) for 1.5 h at room temperature. Acetone (5 mL) was added, and the solution was then kept for 2 h at room temperature. The solution was evaporated *in vacuo* to a syrup, which was dissolved in methanol (10 mL) and evaporated; the dissolution and evaporation were repeated several times. Then, the resulting syrup was dissolved in water (50 mL), and passed through a column of Amberlite IR-120B (H^+) resin (10 mL). The column was washed with distilled water (300 mL), and the effluent was evaporated *in vacuo* to a syrup. The syrup was dissolved in ethanol (10 mL) and the solution was evaporated *in vacuo*; this procedure was repeated several times. Acetylation of the resulting syrup with acetic anhydride (10 mL) and pyridine (20 mL) gave **2a** (460 mg, 55%). Similarly, **3a** (61 mg, 69%) and **4a** (140 mg, 85%) were respectively obtained from **3** (150 mg. containing a small proportion of **4**) and **4** (200 mg); $[\alpha]_D^{22}$: **2a**, +13.4° (*c* 1.0, acetone); **3a**, −9.4° (*c* 1.0, acetone); and **4a**, +14.1° (*c* 1.0, acetone). The n.m.r. and i.r. spectra for **3a** and **4a** were superposable on that of **2a**. N.m.r. data for **2a**: δ 3.83–4.53 (m, 7 H, 2 × H-1, 2 × H-1′, H-2′, and 2 × H-3′),

3.53 (q, 1 H, $J_{1,2}$ 3 and 7 Hz, H-2), 1.20 (s, 6 H, 2 *C*-Me), and 2.07 (s, 9 H, 3 × acetyl methyl).

Anal. Calc. for $C_{14}H_{24}O_8$: C, 52.49; H, 7.55. Found (for **2a**): C, 52.28; H, 7.47.

*5,6,8-Tri-*O*-acetyl-3,7-anhydro-1-deoxy-4-*C*-(1-hydroxy-1-methylethyl)-2-*C*-methyl-*D*-glycero-*D*-(gluco *or* manno, *etc.*)-octitol 2,4,4¹-orthoacetate* (**6**). — A solution of **1** (400 mg) in acetone (12 mL)–2-propanol (12 mL) was irradiated for 100 h, evaporated, and similarly separated by chromatography on a column (3 × 20 cm) of silica gel with successive elution with 997:3 benzene–methanol (1 L), 199:1 benzene–methanol (1.5 L), and 99:1 benzene–methanol (1 L), to give **1** (a trace), **6** (89 mg, 17%), and, finally, a mixture of **2**, **3**, and **4** (350 mg, 64%; **2**:**3**:**4** = 2:1:1). Compound **6** had $[\alpha]_D^{22}$ −37.9° (*c* 1.0, acetone); R_F in t.l.c., 0.7 (**1**, 0.8); correlative retention time in g.l.c., 2.4; for ^{1}H-n.m.r. data, see Table II; ^{13}C-n.m.r. data: δ 81.79 and 82.19 (C-2 and C-1'), 75.81 and 78.88 (C-3 and C-7), 73.45 (C-4), 67.34 and 69.15 (C-5 and C-6), 64.15 (C-8), 20.72 (2 × acetyl methyl), 20.87 (acetyl methyl), 23.18 (*C*-Me), 24.47 (*C*-Me), 25.75 (*C*-Me), 25.92 (*C*-Me), 30.44 (*C*-Me), 117.27 (orthoacetyl C), 169.08 (acetyl carbonyl), 169.89 (acetyl carbonyl), and 170.61 (acetyl carbonyl); m.s.: *m/e* 430.

Anal. Calc. for $C_{20}H_{30}O_{10}$: C, 55.80; H, 7.03. Found: C, 56.04; H, 7.17.

*(4S)-4,5,6,8-Tetra-*O*-acetyl-2,4:3,7-dianhydro-1-deoxy-2-*C*-methyl-*D*-gluco-octos-4-ulose* (**10**). — A solution of **1** (360 mg) in acetone (2 mL)–*tert*-butyl alcohol (18 mL) was irradiated for 180 h. The resulting solutions (in the five tubes) were combined, and evaporated *in vacuo* to a syrup which was chromatographed on a column (3 × 30 cm) of silica gel with successive elution with 997:3 benzene–methanol (1 L), 199:1 benzene–methanol (1.5 L), and 99:1 benzene–methanol (2 L). Compounds **1** (310 mg, 17% recovery), **10** (300 mg, 14%; containing a small proportion of impurities), **2** (320 mg, 15%), **3** (200 mg, 9%), and **4** (170 mg, 7%) were obtained in turn. Compounds **2**, **3**, and **4** had n.m.r. spectra identical with those previously obtained. For compound **10**: t.l.c.: R_F 0.73 (**1** = 0.8); g.l.c.: correlative retention time, 1.7; for the ^{1}H-n.m.r. data, see Table II.

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