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AN UNUSUAL REACTION OF 1,6-ANHYDROALDOHEXOPYRANOSE DERIVATIVES LEADING TO GLYCALS*

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ABSTRACT

Treatment of a solution of the 2-*O*-(*N*,*N*-dimethylsulfamoyl) derivative **3** of the levoglucosenone-derived carbocycle **1** in liquid ammonia at −40 to −50° with sodium metal gave 73% of the glycal derivative **4** instead of the expected 2-deoxy derivative (**2**) of **1**. Under the same conditions, the 2-*O*-(*N*,*N*-dimethylsulfamoyl) derivatives of 1,6-anhydro-3,4-dideoxy-4-*C*-methyl-β-D-*ribo*- and -*arabino*-hexopyranoses gave, after acetylation, 70% of 6-*O*-acetyl-1,5-anhydro-2,3,4-trideoxy-4-*C*-methyl-D-*erythro*-hex-1-enitol. In contrast, the 2-(*N*,*N*-dimethylsulfamates) obtained from 1,6-anhydro-3,4-*O*-isopropylidene-β-D-galacto- and -talo-pyranose gave 6-*O*-acetyl-1,5-anhydro-2-deoxy-3,4-*O*-isopropylidene-D-*lyxo*-hex-1-enitol in only low yields; the oxy substituent at C-3 may interfere with the reaction leading to the glycal.

INTRODUCTION

A sustained program in this laboratory[1–8] is concerned with chiral syntheses of functionalized carbocycles *via* thermal and Lewis-acid catalyzed cycloaddition reactions of dienes with readily available unsaturated cyclic and acyclic carbohydrate derivatives as dienophiles. In our attempts to prepare the optically pure bicyclo[2.2.1]heptane derivative **2** from the levoglucosenone-derived carbocycle[5] **1** by the deoxygenation procedure developed by Tsuchiya *et al.*[9], namely, treatment of *O*-(*N*,*N*-dimethylsulfamoyl) derivatives of carbohydrates with sodium metal in liquid ammonia, we have uncovered a new method for preparation of glycals. This report describes the advantages and limitations of this method.

RESULTS AND DISCUSSION

Numerous procedures for the deoxygenation of secondary alcohols have been developed over the past several years; these include detosyloxylation with lithium

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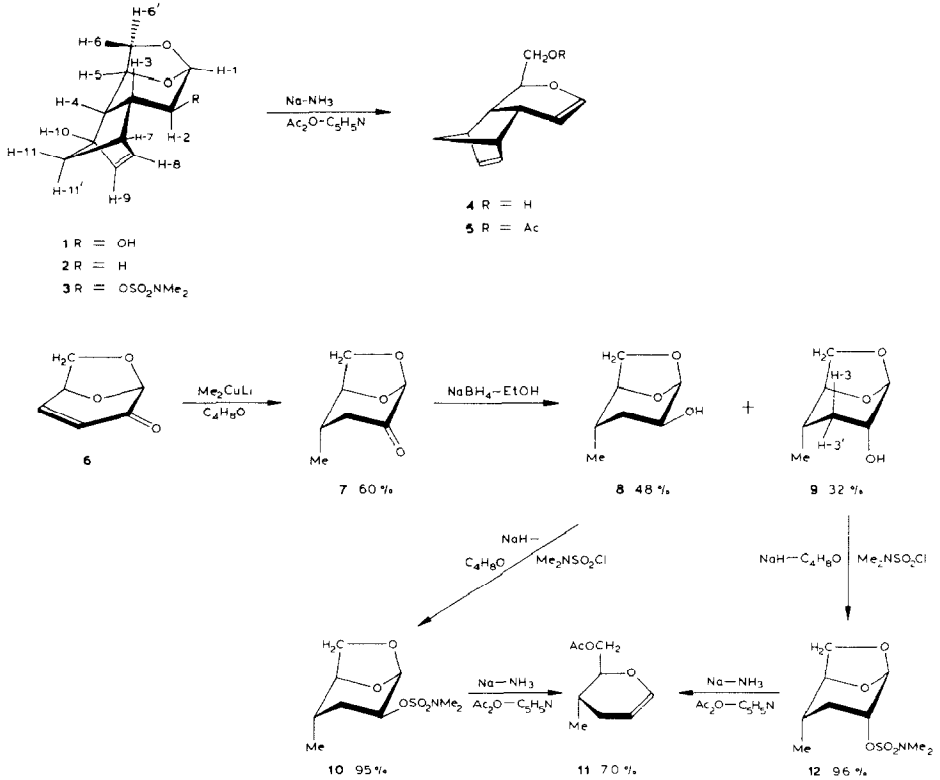
aluminium hydride[10], with lithium trimethoxyaluminohydride–Cu(I) complex[11] and with lithium triethylborohydride[12], reaction of *O*-cycloalkyl thiobenzoates and *O*-cycloalkyl *S*-methyl dithiocarbonates with tributylstannane[13], single-point reduction of sulfonic esters by use of sodium iodide–zinc powder in aprotic solvents[14], and irradiation of dimethylthiocarbamoyl[15] and thiocarbonyl[16] derivatives. In our hands, most of the aforementioned methods when applied to compound **1** either gave back the starting material or gave three to four different products.

Tsuchiya *et al.*[9] have prepared 3-deoxy analogs of several methyl α-D-glucopyranoside derivatives by treating the 3-*O*-(*N,N*-dimethylsulfamoyl) derivatives of the latter with sodium metal in liquid ammonia. When this procedure was applied to the *O*-(*N,N*-dimethylsulfamoyl) derivative* (**3**) of **1**, a single product (**4**) was obtained. The structure of **4** was determined from its 200-MHz, ^{1}H-n.m.r. spectrum (see Table I), from its i.r. spectrum, and from the 50-MHz, ^{13}C-n.m.r. spectrum of the monoacetyl derivative **5** (see Table II) that it afforded on acetylation.

The presence of the 1,5-anhydro-2-deoxyhex-1-enitol (glycal) system in **4** is evident from one-proton signals[17] at δ 6.41 (H-1) and 4.89 (H-2). The signals due to H-6 and H-6′ appear as a broad multiplet in the region δ 3.65–3.80. In the



*For a discussion of the nomenclature and numbering of this compound, see ref. 5.

TABLE I

^{1}H-N M.R CHEMICAL SHIFTS FOR COMPOUNDS **3–15**[a]

Compound	*Chemical shifts (δ)*													
	H-1	*H-2*	*H-3*	*H-3'*	*H-4*	*H-5*	*H-6*	*H-6'*	*H-7*	*H-8*	*H-9*	*H-10*	*H-11*	*H-11'*
3	5.31	4.02	2.53		2.32	4.43	3.84	3.74	3.20	6.25–6.34		2.92	1.48	1.30
	d	dd	ddd		dd	d			bs	m		bs	ddd	d
4	6.41	4.89	2.57		2.40	3.20	3.65–3.80		2.82	5.99	6.11	2.96	1.51	1.38
	dd	dd	ddd		ddd	ddd	m		bs			bs	ddd	d
5	6.40	4.89	2.58		2.36	3.29	4.32	4.11	2.96	5.99	6.11	2.86	1.51	1.38
	dd	ddd	ddd		ddd	ddd			bs			bs	ddd	d
8	5.29	3.69	1.58	1.78	1.83	4.23	3.82–3.83							
	bs	ddd	m	m	m	ddd	m							
9	5.33	3.57	2.10	1.48	1.71	4.30	3.81–3.89							
	bs	dd	ddd	m	m	m	m							
10	5.50	4.57		1.81–2.05		4.26	3.83–3.92							
	bs	ddd		m		ddd	m							
11	6.37[b]	4.69		1.64–2.08		3.71	4.33	4.19						
	ddd	ddd		m		ddd								
12	5.47	4.33[c]	2.21	1.69–1.79		4.33[b]	3.84–3.89							
	bs	m	ddd	m		m	m							
13	5.51	4.32		4.42–4.57			4.13	3.60						
	bs	d		m										
14	5.48	4.61	4.27		4.41–4.46		4.30	3.72						
	d	dd	m		m									
15	6.40	4.83	4.67		4.27	4.11	4.37–4.41							
	d	ddd	dd		d	ddd	m							

[a]For atom numbering convention, see formulas for compounds **1** and **9**. [b]$J_{1,3'}$ 1.8 Hz. In the spectra of compounds **4** and **5**, the H-8 and -9 resonances form an AB quartet with additional $J_{7,8}$ and $J_{9,10}$ coupling. In the spectra of compounds **3, 4, 11, 13,** and **15**, the H-5, -6, and -6' resonances form an ABX system. [c]Overlapping signals.

TABLE II

^{13}C-N M R CHEMICAL SHIFTS FOR COMPOUNDS **3–15**

Compound	*Chemical shifts (δ)*										
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*C-8*	*C-9*	*C-10*	*C-11*
3	97.7	78.6	40.5	47.7	74.7	71.6	45.9	136.1[a]	136.0[a]	47.8	50.2
4	143.9	108.2	33.7	41.9	75.6	65.7	47.6	135 5	134.7	45.4	49 0
8	103 1	66.6	33.2	32.6	77.4	68 8					
9	102.4	67.5	31.5	29.5	78.0	68.0					
10	100.4	75 3	29.0	33.7	77.5	69.1					
11	142.9	100.0	27.8	28.2	77.9	64.6					
12	99.7	74.1	27.2	31.0	77.5	67.9					
13	98.9	73.8	68.8	72.0[a]	76.6[a]	63.2					
14	97.8	74.7	71.4	72.95[a]	72.88[a]	65.3					
15	144.6	102.6	68.4	72.4	72.8	64 1					

[a]These assignments may be interchanged.

spectrum recorded after addition of one drop of deuterium oxide to the sample, this broad multiplet was replaced by an eight-line pattern characteristic of the AB portion of an ABX system. This information, together with the appearance of a broad band at 3400 cm^{-1} in the i.r. spectrum of **4**, indicated the presence of a hydroxyl group at C-6. Moreover, **4** was readily converted into its acetyl derivative **5** under conventional conditions. In the 200-MHz, ^{1}H-n.m.r. spectrum of **5**, the H-6 and H-6′ signals appeared at δ 4.32 and 4.11, respectively, as the characteristic AB component of an ABX system. This downfield shift of the H-6 and H-6′ resonances further establishes that the acetoxyl group is located at C-6. Finally, the presence of the glycal system is confirmed by the appearance of signals[18] at δ 143.9 (C-1) and 108.2 (C-2) in the 50-MHz, ^{13}C-n.m.r. spectrum of **5**.

In order to ascertain whether the reaction depends on the steric strain present in **3** and to investigate the effect of the configuration at C-2, the following transformations were performed on 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose (levoglucosenone, **6**). Conjugate addition of lithium dimethylcuprate in oxolane at −60° with **6** gave 1,6-anhydro-3,4-dideoxy-4-*C*-methyl-β-D-*erythro*-hexopyranos-2-ulose[19,20] (**7**) in 60% yield. Compound **7** was readily reduced by sodium borohydride in 95% ethanol at ~25°, to give a mixture of 1,6-anhydro-3,4-dideoxy-4-*C*-methyl-β-D-*ribo*-hexopyranose (**9**) (32%) and 1,6-anhydro-3,4-dideoxy-4-*C*-methyl-β-D-*arabino*-hexopyranose (**8**) (48%), readily separable by column chromatography on silica gel. The less-polar product was predictably the axial alcohol **9** (β-D-*ribo* configuration) and showed a coupling of 4.7 Hz (see Table III) between the equatorially disposed H-2 and the axially disposed H-3. On the other hand, the more-polar equatorial alcohol **8** (β-D-*arabino* configuration) displayed a coupling of 10.2 Hz, as anticipated for the diaxial disposition of H-2 and H-3.

TABLE III

^{1}H-N.M.R. COUPLING CONSTANTS FOR COMPOUNDS **3–15**

Compound	*Coupling constants (Hz)*										
	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	$J_{2,3'}$	$J_{3,3'}$	$J_{3,4}$	$J_{3',4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
3	3.1	[a]	5.1			10.1		[a]	[a]	4.3	6.8
4	6.0	2.9	2.6			9.2		9.8	3.0	6.9	[a]
5	6.0	2.9	2.6			9.3		10.1	2.9	7.2	12.0
8	1.7	[a]	10.2	6.1	12.8	7.0	1.5	2.0	2.0	4.0	[a]
9	[a]	[a]	4.7	[a]	14.9	6.9	1.5	2.0	2.0	4.0	[a]
10	1.6	[a]	10.0	6.3	[a]	[a]	[a]	[a]	[a]	[a]	[a]
11	6.1	1.8	2.6	4.7	[a]	[a]	[a]	8.4	2.9	6.0	12.0
12	[a]	[a]	5.0	[a]	15.5	6.6	[a]	[a]	[a]	[a]	[a]
13	[a]	[a]	7.3			[a]		[a]	[a]	5.2	7.7
14	2.5	[a]	6.1			[a]	[a]	[a]	[a]	[a]	7.7
15	6.2	[a]	2.9			6.2		1.4	4.9	7.4	[a]

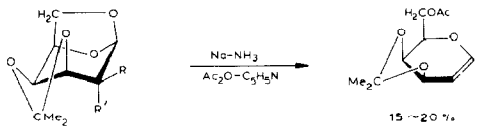
[a]No observable coupling.

Both alcohols were colorless, crystalline solids and were converted[9] in excellent yields into their crystalline 2-*O*-(*N*,*N*-dimethylsulfamoyl) derivatives **10** and **12** by treatment with sodium hydride and *N*,*N*-dimethylsulfamoyl chloride in oxolane. Treatment of either **10** or **12** with sodium metal in liquid ammonia, followed by acetylation of the product with acetic anhydride in pyridine, gave 6-*O*-acetyl-1,5-anhydro-2,3,4-trideoxy-4-*C*-methyl-D-*erythro*-hex-1-enitol (**11**) in 70% yield. The presence of the glycal system in **11** is evident from one-proton signals at δ 6.37 (H-1) and 4.69 (H-2) in its 200-MHz, ^{1}H-n.m.r. spectrum, as well as from signals at δ 142.9 (C-1) and at 100.0 (C-2) in its 50-MHz, ^{13}C-n.m.r. spectrum.

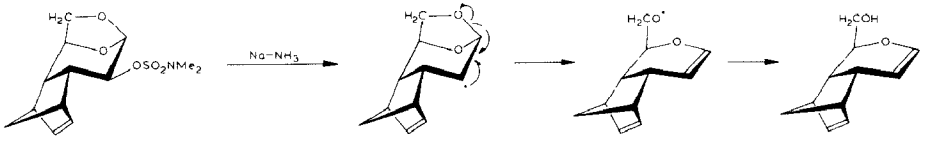
In order to investigate the effect of an oxygen substituent at C-3, 1,6-anhydro-3,4-*O*-isopropylidene-2-*O*-(*N*,*N*-dimethylsulfamoyl)-β-D-galactopyranose (**13**) and the corresponding *talo* 2-epimer **14** were prepared. These compounds were each treated with sodium metal in liquid ammonia, and the product acetylated conventionally. In both instances, a glycal (**15**) was obtained, but in only low yield (~20%); the reaction gave mainly a mixture of very polar products that were not characterized.

The introduction of the glycal system, together with selective protection of the hydroxyl groups, make compound **15** a very attractive intermediate for further synthetic transformations. The low yield may be attributable to the oxygen substituent at C-3 and is a disadvantage; the use of different protecting groups in 1,6-anhydro-β-D-galactopyranose might be advantageous, but this aspect has not been explored in detail.

A possible mechanism for this unusual transformation is shown in Scheme 1. The non-dependence of the course of the reaction on the configuration at C-2 supports a radical pathway as has been suggested[9] for such reactions. A pathway involving formation of a carbanion at C-2, followed by O-6–C-1 bond cleavage, could



13 R = H, R′ = OSO_2NMe_2
14 R = OSO_2NMe_2, R′ = H



Scheme 1

also account for this transformation. Cleavage of the 1,6-anhydro ring system under acidic conditions is well known. To the best of our knowledge, this is the first time that this system has been cleaved under nonacidic conditions. Moreover, the product of this reaction belongs to the versatile family of glycals. Preparation of such glycals as **11** from levoglucosenone (**6**) by using the transformations described here is attractive, as the initial conjugate addition to the enone system is stereospecific. Thus, a variety of carbon nucleophiles may be employed to provide branched-chain glycals. Of particular interest is the conjugate addition of hydrogen azide to provide amino glycals, since an azido group has been shown[9] to be convertible to an amino group under these conditions. Details of these and related investigations will be reported separately.

EXPERIMENTAL

General methods. — Evaporation of solvents was performed under diminished pressure at a bath temperature <50°. Melting points were determined by using a Thomas–Hoover Unimelt apparatus and are uncorrected. A Perkin–Elmer Model 141 polarimeter and 1-dm tubes were used for measurement of specific rotations at room temperature (~25°); solutions were in chloroform. T.l.c. was performed on precoated glass plates (0.25 mm) of Silica Gel 60F-254 (E. Merck); zones were detected by spraying the plates with 10% (v/v) H_2SO_4 solution, with subsequent heating. Silica Gel 60 (E. Merck) was used for column chromatography. Microanalyses were performed by Atlantic Microlab Inc., Atlanta, Georgia. I.r. spectra were recorded with a Perkin–Elmer Model 283B i.r. spectrophotometer. Solids were dispersed in KBr and syrups were placed between two NaCl discs. ^{1}H-N.m.r. spectra were recorded at 200 MHz with a Bruker WP-200 spectrometer operating in the Fourier-transform mode at ~25°. The assignments were confirmed by decoupling experiments. ^{13}C-N.m.r. spectra were

recorded at 50.3 MHz with a Bruker WP-200 spectrometer operating in the Fourier-transform mode at ~35°. Most assignments were confirmed by heteronuclear decoupling experiments. Unless otherwise noted, samples for ^1H- and ^{13}C-n.m.r. spectroscopy were dissolved in chloroform-*d* containing tetramethylsilane as the internal standard. Mass spectra were recorded by C. R. Weisenberger with a KRATOS MS-30 double-focusing, double-beam, high-resolution, electron-impact spectrometer operating at 70 eV and an accelerating potential of 4 kV. The source temperature (direct-inlet system) was 120°. All reactions of organometallic reagents and other air- and moisture-sensitive materials were performed in flame-dried glassware under an atmosphere of N_2. Solutions of these materials were transferred with hypodermic needles. Oxolane was distilled from dark-blue or dark-purple solutions of sodium benzophenone radical anion or dianion under an atmosphere of N_2.

2-O-(N,N-Dimethylsulfamoyl) derivative (**3**) *of* **1**. — To sodium hydride (250 mg, 50% dispersion in oil; 2.60 mmol) was added hexane (~2 mL) and the mixture was stirred for a few min at ~25°. The suspension was allowed to settle and the hexane decanted. This procedure was repeated four times. Oxolane (~10 mL) was added and to the resulting suspension was added dropwise a solution of compound[5] **1** (250 mg, 1.29 mmol) in oxolane (~3 mL) containing a few crystals (~1 mg) of imidazole. After the evolution of H_2 gas had ceased, the mixture was stirred for 20 min at ~25°. *N,N*-Dimethylsulfamoyl chloride (373 mg, 2.60 mmol) was added and the resulting mixture boiled under reflux for 2 h, when t.l.c. (1:1 hexane–ethyl acetate) indicated that **1** was absent. The mixture was cooled to ~25° and quenched with an excess of methanol. Water (~10 mL) was added and the resulting solution was extracted (3 × 15 mL) with diethyl ether. The combined organic phases were washed with a saturated solution of NaCl (~5 mL), dried ($MgSO_4$), and evaporated to give **3** (330 mg, 85%) as a syrup; $[\alpha]_D^{25}$ −72.0° (*c* 1.9); ν_{max}^{film} 3060 (CH=CH cis), 1350, and 1160 cm^{-1}(-SO_2-OR); *m/z* (rel. intensity): 235 (5, $M^+ - C_5H_6$), 193 (6, $M^+ - C_2H_6NO_2S$), 177 (27, $M^+ - C_2H_6NO_3S$), 131 (43, $M^+ - H$, $C_2H_6NO_3S$, HCO_2), 127 (25, 193 − C_5H_6), 117 (28, 131 − CH_2), 111 (62, 177 − C_5H_6), 110 (12, 111 − H), 108 (67, $M^+ - C_{11}H_{13}O_3$), 105 (36, $M^+ - H_2CO_2$, $C_4H_8NO_3S$), 91 (47, 105 − CH_2), 81 (100, 110 − CH_2O), 66 (86, $M^+ - C_8H_{13}NO_5S$), 65 (27, 131 − C_5H_6), 44 (47, 108 − SO_3), and 43 (31, 44 − H).

Anal. Calc. for $C_{13}H_{19}NO_5S$ (301.35): C, 51.81; H, 6.35; N, 4.65; S, 10.64. Found: C, 51.91; H, 6.40; N, 4.61; S, 10.67.

Conversion of **3** *into glycal* **5**. — Ammonia (~15 mL) was condensed into a flask maintained between −50 and −60° and fitted with a Dry Ice–acetone condenser. A solution of the *exo* sulfamate **3** (200 mg, 660 μmol) in oxolane (~2 mL) was added. To the resulting homogeneous solution were added small pieces of metallic Na until the solution turned dark blue. The mixture was stirred for 45 min, during which time the deep-blue color of the solution was maintained by addition of metallic Na as necessary. The ammonia was gradually evaporated and water (~10 mL) was added. The resulting mixture was extracted with three 15-mL por-

tions of diethyl ether. The organic phase was washed with saturated aqueous NaCl (~5 mL), dried ($MgSO_4$), and evaporated. The residue was dissolved directly in dry pyridine (~10 mL) and treated with an excess (~2 mL) of acetic anhydride at 0°, and the mixture was stirred overnight at ~25°. Water (~10 mL) was added and the resulting mixture was extracted with three 5-mL portions of dichloromethane. The organic phase was washed with saturated aqueous NaCl (~5 mL), dried ($MgSO_4$) and evaporated to afford **5** (166 mg, 73%) as an oil, $[\alpha]_D^{25}$ +10.3° (*c* 1); ν_{max}^{film} 3060 (CH=CH *cis*), 1740 (C=O), 1230 (CH_3CO_2R), 1080 cm^{-1} (C-O-C); *m/z* (rel. intensity): 154 (10, $M^+ - C_5H_6$), 95 (18, 154 − $C_2H_3O_2$), 94 (100, 154 − $C_2H_4O_2$), and 43 (76, $M^+ - C_{11}H_{13}O_2$).

Compound **5** decomposed rapidly and a satisfactory elemental analysis for it was not obtained.

*1,6-Anhydro-3,4-dideoxy-4-C-methyl-β-*D-ribo-*hexopyranose* (**9**) *and 1,6-anhydro-3,4-dideoxy-4-C-methyl-β-*D-arabino-*hexopyranose* (**8**). — To a solution at ~25° of 1,6-anhydro-3,4-dideoxy-4-*C*-methyl-β-D-*erythro*-hexopyranos-2-ulose* (**7**) (1.00 g, 7.04 mmol) in 95% ethanol (15 mL) was added a solution of $NaBH_4$ (200 mg, 5.28 mmol) in water (~2 mL) containing one drop of 40% aqueous KOH. The mixture was stirred for 2 h at ~25°; t.l.c. (1:1 hexane–ethyl acetate) then indicated the absence of **7**. Acetone (~1 mL) was added, to decompose the excess of borohydride, and the mixture was made neutral (to pH 7) with regenerated Dowex 50W-4S cation-exchange resin, requiring 500 mg of the resin. Decantation of the solution followed by evaporation afforded a syrup that contained (t.l.c., 1:1 hexane–ethyl acetate) two components, namely **9** (R_F 0.45) and **8** (R_F 0.25). Chromatography on a column of silica gel with 1:1 hexane–ethyl acetate afforded **9** (325 mg, 32%) and **8** (490 mg, 48%), both as colorless solids.

The less-polar (axial) alcohol **9** had m.p. 48–49°, $[\alpha]_D^{25}$ −96.8° (*c* 0.9); ν_{max}^{KBr} 3420 (O–H), 1140 (C–O–C), and 1050 cm^{-1} (C–O); *m/z* (rel. intensity): 98 (21, $M^+ - H_2CO_2$), 83 (14, 98 − CH_3), 71 (35, $M^+ - C_3H_5O_2$), 70 (8, 71 − H), 69 (25, $M^+ - CH_2O$, HCO_2), 56 (5, 71 − CH_3), 55 (100, 98 − C_2H_3O), 54 (24, 98 − C_2H_4O), 53 (8, 83 − CH_2O), 44 (25, 98 − C_4H_7), 43 (30, $M^+ - C_5H_8O_2$), and 41 (26, 71 − CH_2O).

Anal. Calc. for $C_7H_{12}O_3$ (144.17): C, 58.32; H, 8.39. Found: C, 58.15; H, 8.38.

The more-polar (equatorial) alcohol **8** had m.p. 64–66°, $[\alpha]_D^{25}$ −169° (*c* 0.95); ν_{max}^{KBr} 3460 (O–H), 1150 (C–O–C), and 1050 cm^{-1} (C–O); *m/z* (rel. intensity): 98 (22, $M^+ - H_2CO_2$), 83 (16, 98 − CH_3), 71 (33, $M^+ - C_3H_5O_2$), 70 (8, 71 − H), 69 (21, $M^+ - CH_2O$, HCO_2), 56 (8, 71 − CH_3), 55 (100, 98 − C_2H_3O), 54 (25, 98 − C_2H_4O), 53 (7, 83 − CH_2O), 44 (19, 98 − C_4H_7), 43 (35, $M^+ - C_5H_8O_2$), and 41 (25, 71 − CH_2O).

*Compound **7** was prepared in 60% yield by conjugate addition of lithium dimethylcuprate to levoglucosenone (**6**) at −40° in oxolane and had physical constants and spectral data in good agreement with those concurrently reported by Mori *et al.*[20]

Anal. Calc. for $C_7H_{12}O_3$ (144.17): C, 58.32; H, 8.39. Found: C, 58.27; H, 8.39.

1,6-Anhydro-3,4-dideoxy-2-O-(N,N-dimethylsulfamoyl)-4-C-methyl-β-D-ribo-hexopyranose (**12**). — Treatment of **9** (250 mg, 1.75 mmol) with NaH (84 mg, 3.50 mmol) and *N,N*-dimethylsulfamoyl chloride (500 mg, 3.50 mmol) in oxolane (15 mL) according to the procedure described for the preparation of **3**, afforded **12** (414 mg, 95%) as a pale-yellow solid.

For analytical purposes, compound **12** was recrystallized from 95% ethanol; m.p. 90–91°, $[\alpha]_D^{25}$ −51.1° (*c* 1); ν_{max}^{KBr} 1360, 1170 cm^{-1} (–SO_2–OR); *m/z* (rel. intensity): 143 (50, $M^+ - C_2H_6NO_2S$), 127 (38, $M^+ - C_2H_6NO_3S$), 108 (51, $M^+ - C_7H_{11}O_3$), 97 (90, 127 − CH_2O), 71 (40, 127 − C_3H_4O), 69 (100, $M^+ - C_3H_7NO_3S$, HCO_2), 55 (18, $M^+ - C_4H_9NO_3S$, HCO_2), 44 (21, $M^+ - C_7H_{11}O_3S$), and 41 (77, 71 − CH_2O).

Anal. Calc. for $C_9H_{17}NO_5S$ (251.30): C, 43.02; H, 6.82; N, 5.57; S, 12.76. Found: C, 43.09; H, 6.86; N, 5.56; S, 12.76.

1,6-Anhydro-3,4-dideoxy-2-O-(N,N-dimethylsulfamoyl)-4-C-methyl-β-D-arabino-hexopyranose (**10**). — Treatment of **8** (504 mg, 3.50 mmol) with NaH (170 mg, 7.00 mmol) and *N,N*-dimethylsulfamoyl chloride (1.00 g, 7.00 mmol) in oxolane (30 mL) according to the procedure described for the preparation of **3**, afforded **10** (810 mg, 92.2%) as a colorless solid.

For analytical purposes, **10** was recrystallized from 95% ethanol; m.p. 90–91°, $[\alpha]_D^{25}$ −94.5° (*c* 1.6); ν_{max}^{KBr} 1370, 1170 cm^{-1} (–SO_2–OR); *m/z* (rel. intensity): 143 (53, $M^+ - C_2H_6NO_2S$), 127 (33, $M^+ - C_2H_6NO_3S$), 108 (51, $M^+ - C_7H_{11}O_3$), 97 (89, 127 − CH_2O), 71 (39, 127 − C_3H_4O), 69 (100, $M^+ - C_3H_7NO_3S$, HCO_2), 55 (16, $M^+ - C_4H_9NO_3S$, HCO_2), 44 (17, $M^+ - C_7H_{11}O_3S$), and 41 (59, 71 − CH_2O).

Anal. Calc. for $C_9H_{17}NO_5S$ (251.30): C, 43.02; H, 6.82; N, 5.57; S, 12.76. Found: C, 43.18; H, 6.87; N, 5.52; S, 12.70.

*6-O-Acetyl-1,5-anhydro-2,3,4-trideoxy-4-C-methyl-*D-erythro-*hex-1-enitol* (**11**). — Treatment of **10** (480 mg, 1.91 mmol) with NaH in liquid NH_3 (~20 mL), followed by acetylation of the product according to the procedure described for the preparation of **5**, afforded the glycal **11** (230 mg, 70%) as an oil. Treatment of **12** under the same conditions afforded **11** (68%) that was identical in all respects to **11** obtained from **10**.

For analytical purposes, compound **11** was distilled in a Kugelrohr apparatus at 100–110° and 10–20 Pa; $[\alpha]_D^{25}$ +95.8° (*c* 1); ν_{max}^{film} 3060 (CH=CH), 1740 (C=O), and 1250 (CH_3CO_2R); *m/z* (rel. intensity): 170 (7, M^+), 110 (29, $M^+ - C_2H_4O$), 109 (8, 110 − H), 97 (16, $M^+ - C_3H_5O_2$), 95 (19, 97 − H_2), 84 (6, $M^+ - C_2H_3O_2$, C_2H_3), 71 (12, M^+ − CO, CH_2O, C_2H_2), 57 (8, 71 − CH_2), 43 (100, $CH_3C\,O+$), and 41 (22, $M^+ - C_4H_6O_3$, C_2H_2, H).

Anal. Calc. for $C_9H_{14}O_3$ (170.21): C, 63.51; H, 8.29. Found: C, 63.58; H, 8.34.

1,6-Anhydro-2-O-(N,N-dimethylsulfamoyl)-3,4-O-isopropylidene-β-D-galactopyranose (**13**). — Treatment of 1,6-anhydro-3,4-*O*-isopropylidene-β-D-galac-

topyranose[21] (750 mg, 3.71 mmol) with NaH (180 mg, 7.50 mmol) and *N,N*-dimethylsulfamoyl chloride (1.08 g, 7.50 mmol) in oxolane (50 mL) according to the procedure described for the preparation of **3**, afforded **13** (1.10 g, 96%) as a colorless solid. This product was recrystallized from 95% ethanol and had m.p. 80–81°, $[\alpha]_D^{25}$ −36.1° (*c* 0.8); ν_{max}^{KBr} 1350, 1170 cm^{-1} (–SO_2–OR); *m/z* (rel. intensity): 294 (28, $M^+ - CH_3$), 201 (42, 294 − CH_3NO_2S), 143 (65, 201 − C_3H_6O), 127 (13, $M^+ - C_2H_6NO_3S$, C_3H_6O), 108 (61, $M^+ - C_9H_{13}O_5$), 69 (100, $M^+ - CH_3$, $C_2H_6NO_2S$, HCO, CH_3CO, HCO_2), 57 (36, $M^+ - H$, CH_2O, $C_7H_{11}NO_5S$), 55 (37, 143 − CH_2O, $C_2H_2O_2$), 44 (26, $M^+ - C_9H_{13}O_3S$), 43 (84, 127 − $C_4H_4O_2$), and 41 (32, $M^+ - H$, $C_8H_{13}NO_7S$).

Anal. Calc. for $C_{11}H_{19}NO_7S$ (309.33): C, 42.71; H, 6.19; N, 4.53; S, 10.36. Found: C, 42.79; H, 6.23; N, 4.52; S, 10.42.

1,6-Anhydro-2-O-(N,N-dimethylsulfamoyl)-3,4-O-isopropylidene-β-D-talopyranose (**14**). — Treatment of 1,6-anhydro-3,4-*O*-isopropylidene-β-D-talopyranose[22] (250 mg, 1.24 mmol) with NaH (60 mg, 2.50 mmol) and *N,N*-dimethylsulfamoyl chloride (360 mg, 2.50 mmol) in oxolane (15 mL) according to the procedure described for the preparation of **3**, afforded **14** (375 mg, 98%) as a pale-yellow solid. It was recrystallized from 95% ethanol and had m.p. 137–139°, $[\alpha]_D^{25}$ −65.3° (*c* 0.9); ν_{max}^{KBr} 1370, 1165 cm^{-1} (–SO_2–OR); *m/z* (rel. intensity): 294 (24, $M^+ - CH_3$), 201 (36, 294 − CH_3NO_2S), 143 (68, 201 − C_3H_6O), 127 (12, $M^+ - C_2H_6NO_3S$, C_3H_6O), 108 (65, $M^+ - C_9H_{13}O_5$), 69 (100, $M^+ - CH_3$, $C_2H_6NO_2S$, HCO, CH_3CO, HCO_2), 57 (46, $M^+ - H$, CH_2O, $C_7H_{11}NO_5S$), 55 (47, 143 − CH_2O, $C_2H_2O_2$), 44 (26, $M^+ - C_9H_{13}O_3S9$, 43 (74, 127 − $C_4H_4O_2$), and 41 (37, $M^+ - H$, $C_8H_{13}NO_7S$).

Anal. Calc. for $C_{11}H_{19}NO_7S$ (309.33): C, 42.71; H, 6.19; N, 4.53; S, 10.36. Found: C, 42.89; H, 6.23; N, 4.48; S, 10.43.

*6-O-Acetyl-1,5-anhydro-2-deoxy-3,4-O-isopropylidene-*D-lyxo-*hex-1-enitol* (**15**). — Treatment of **13** (1.00 g, 3.24 mmol) with Na in liquid ammonia (~40 mL), followed by acetylation of the product according to the procedure described for the preparation of **5** afforded **15** (150 mg, 20%) as an oil. Treatment of **14** under the same conditions afforded **15** (22%) that was identical in all respects to **15** obtained from **13**.

For analytical purposes, compound **15** was distilled in a Kugelrohr apparatus at 120–130° and 10–20 Pa; $[\alpha]_D^{25}$ +13.1° (*c* 1); ν_{max}^{film} 1740 (C=O) and 1230 (CH_3CO_2R); *m/z* (rel. intensity): 213 (6, $M^+ - CH_3$), 153 (12, 213 − $C_2H_4O_2$), 111 (31, 153 − C_2H_2O), and 43 (100, CH_3CO^+).

Anal. Calc. for $C_{11}H_{16}O_5$ (228.25): C, 57.89; H, 7.07. Found: C, 57.71; H, 7.09.

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