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STEREOSELECTIVE SYNTHESIS OF FUNCTIONALIZED CARBOCYCLES BY CYCLOADDITION TO LEVOGLUCOSENONE*

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ABSTRACT

Levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose) undergoes [4 + 2] addition with cyclopentadiene from the α face to give 65% of *endo*-alkene (**2**) and 16% of *exo*-alkene (**3**) adducts. Reduction of **2** with sodium borohydride gave 53% of the *endo* alcohol **4**, and 39% of the *exo* alcohol **5**. Oxidation of **5** with *m*-chloroperoxybenzoic acid gave the expected oxirane, whereas **4** gave an alcohol (**6**) resulting from oxirane ring-opening by HO-2. Reduction of adduct **3** with sodium borohydride gave 74% of the *exo* alcohol and 22% of the *endo* alcohol. The structure of **6** was confirmed by X-ray crystallography.

INTRODUCTION

Work in this laboratory[2–4] has demonstrated that addition of cyclopentadiene to suitable acyclic, *trans*-unsaturated sugar derivatives may be used to afford crystalline bicyclo[2.2.1]hept-2-ene derivatives in good yield under stereochemical control. These offer convenient access to optically pure, tetra-*C*-substituted cyclopentane derivatives of defined stereochemistry that are of interest in the synthesis of prostaglandin analogs. In the present work, we have employed the cyclic, unsaturated sugar derivative 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose (levoglucosenone, **1**) as the dienophile, and have prepared crystalline and optically pure bicyclo[2.2.1]heptane derivatives in good yields. The products have been fully characterized by ^{1}H- and ^{13}C-n.m.r. spectroscopy.

The structure of compound **1**, a product obtained by pyrolysis of acid-treated cellulose, was elucidated by Broido and his co-workers[5], and Shafizadeh *et al.* have described its preparation from waste paper[6] and have studied several of its reactions[7–11], including its conversion into a crystalline adduct with cyclopentadiene[9]. Brimacombe and co-workers[12] prepared **1** by pyrolysis of microgranular cellulose powder pretreated with potassium hydrogensulfate, and used it in a synthesis of

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2,6-diamino-2,3,4,6-tetradeoxy-D-*erythro*-hexose (purpurosamine C), a component of the aminocyclitol antibiotic gentamicin C_{1a}. Addition of cyclopentadiene to other hex-2-enopyranosides has been reported by Fraser-Reid *et al.*[13].

RESULTS AND DISCUSSION

Although levoglucosenone was successfully prepared from microgranular cellulose as described by Brimacombe and co-workers[12], we experienced experimental difficulties in proper maintenance of the vacuum, in uneven heat-transfer, and in clogging of the receiving tube, and these problems discouraged routine use of the method. An attractive feature of this method is its simplicity in employing a Bunsen burner, rather than the electrically heated tube-furnace employed by Chin and Shafizadeh[6].

We now describe a relatively inexpensive apparatus for pyrolysis (see Fig. 1) that is simple to operate and which may be readily assembled from standard laboratory equipment. The acid-treated paper is pyrolyzed under nitrogen in a rotating quartz tube heated by a Meker burner. This apparatus was used to prepare ~75 g of **1** from waste newspaper in a net yield of 1.5–2%.

It has been reported[9] that Diels–Alder reaction of **1** with cyclopentadiene, conducted in an excess of refluxing dicyclopentadiene, affords 47.8% of a crystalline adduct **2** and a trace of an unidentified hydrocarbon. We have conducted the reaction between **1** and cyclopentadiene at 133–137° in boiling chlorobenzene, and have isolated a syrupy adduct **3** (16.5%), in addition to the crystalline adduct **2** (65%). The latter had the same m.p. and ^{1}H-n.m.r. spectrum as the product reported by Ward and Shafizadeh[9]. The structure of **3** was determined from its 200-MHz, ^{1}H-n.m.r. spectrum (see Table I). No coupling was observed between H-4 and H-5 in the spectrum of either **2** or **3**, indicating that H-4 and H-5 are approxi-

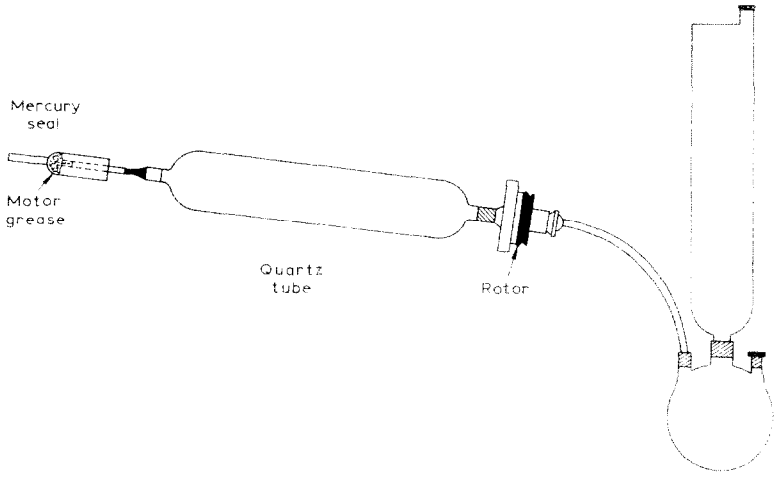


Fig. 1. Apparatus for pyrolysis. (The quartz tube is 25 cm long and 6 cm wide.)

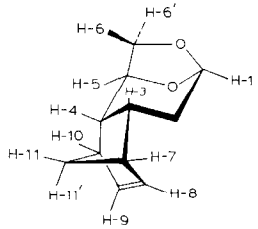


TABLE 1

PROTON-N.M.R.-SPECTRAL DATA FOR COMPOUNDS **2–10**

Compound[a]	*Chemical shifts (δ) (coupling constants, Hz, in parentheses)*														
	H-1 ($J_{1,2}$)	*H-2* ($J_{2,3}$)	*H-3* ($J_{3,4}$)	($J_{3,7}$)	*H-4* ($J_{4,10}$)	*H-5* ($J_{5,6'}$)	*H-6'* ($J_{6,6'}$)	*H-6*	*H-7* ($J_{7,8}$)	*H-8* ($J_{8,9}$)	*H-9* ($J_{9,10}$)	*H-10* ($J_{10,11}$)	*H-11* ($J_{11,11'}$)	($J_{7,11}$)	*H-11'* ($J_{10,11'}$)	($J_{7,11'}$)
2[b]	4.80s	—	3.00dd		2.38dd	4.63d	3.79	3.83	3.39bs	6.02	6.24	3.03bs	1.46ddd		1.30d	
			(9.2)	(4.4)	(3.3)	(4.4)	(7.0)		(2.9)	(5.0)	(2.8)	(2.0)	(8.6)	(2.0)		
3	5.05s	—	2.26d		1.66d	4.81d	3.87	3.81	3.30bs	6.21	6.32	2.89bs	1.73d		1.26ddd	
			(8.6)	(2.5)	(2.5)	(4.6)	(6.8)		(2.9)	(5.6)	(3.2)		(9.0)		(2.0)	(2.0)
4	5.08s	3.83dd	2.77ddd		2.12dd	4.32d	3.77	3.88	3.08bs	6.34	6.24	2.92bs	1.89ddd		1.26d	
		(10.5)	(10.5)	(4.0)	(4.0)	(4.0)	(6.5)		(2.7)	(5.5)	(3.2)	(1.5)	(8.0)	(2.0)	(1.5)	
5	5.14d	3.17[c]	2.23[c]		2.23[c]	4.42d	3.71	3.76	3.12[c]	6.18	6.29	2.89bs	1.44ddd		1.28d	
	(3.4)					(3.9)	(6.8)		(2.9)	(5.7)	(2.9)	(2.0)	(7.8)	(2.0)		
6	5.37d	3.88dd	2.49ddd		1.67dd	4.62[c]	3.84	3.78	2.78ddd	4.10d	4.60[c]	2.24bs	2.02ddd		1.35dd	
	(2.2)	(5.5)	(10.2)	(5.1)	(3.5)	(4.9)	(7.0)		(4.9)			(1.8)	(10.4)	(1.8)		(1.8)
7	5.33d	3.66ddd	2.06[c]		2.06[c]	4.59d	3.79	3.75	2.77bs	3.29	3.43	2.63bs	1.44ddd		0.69d	
	(3.7)	(1.8)				(4.2)	(7.1)			(3.6)		(2.0)	(10.0)	(2.0)		
8	5.37d	3.85dd	2.54[c]		1.81dd	4.63d	3.85	3.77	2.76dd	4.86–4.89		2.56[c]	2.23ddd		1.65d	
	(2.3)	(5.4)	(10.3)	(5.4)	(3.4)	(5.0)	(7.1)		(5.0)			(2.0)	(11.0)	(2.0)		
9	5.31d	3.23ddd	1.46[c]		1.46[c]	4.60d	3.80	3.71	2.85bs	6.07	6.22	2.65bs	1.61d		1.30ddd	
	(3.4)	(2.7)				(4.9)	(7.1)		(2.9)	(5.6)	(2.9)		(8.8)		(1.7)	(1.7)
10	5.26s	3.86bs	1.93ddd		1.30dd	4.54dd	←3.71d→		3.05bs	6.11	6.25	2.68bs	1.70d		1.38ddd	
		(10.1)	(10.0)	(1.8)	(2.0)	(2.5)	$J_{5,6}$ 2.5		(3.0)	(5.6)	(3.0)		(8.5)		(1.7)	(1.7)

[a]For atom-numbering convention, see accompanying, generalized formula. [b]Data at 90 MHz have been reported[9] for this compound. [c]Overlapping signals. In the spectra of all compounds, except **6** and **8**, the H-8 and H-9 resonances form an AB quartet with additional $J_{7,8}$ and $J_{9,10}$ coupling. In those of all compounds, except **10**, the H-5, H-6, and H-6′ resonances form an ABX system with $J_{5,6}$ = zero.

mately diequatorial in both compounds (β-D-*ribo* configuration) and that both adducts arise from attack at the lower (α) face of the dienophile **1**. Assuming that the crystalline, major adduct **2** is the *endo*-alkene, as described by Ward and Shafizadeh[9] (and conclusively established here by X-ray crystallography of a transformation product), the minor, syrupy adduct **3** is the *exo*-alkene*. Compounds **2** and **3** thus differ only in the configuration** at C-7 and C-10, being 7(*S*),10(*R*) in **2**, and 7(*R*),10(*S*) in **3**.

The adduct **2** was readily reduced by sodium borohydride in 95% ethanol at ~25°, to give a mixture of the *endo* alcohol **4** (53%) and *exo* alcohol **5** (39%), readily separable by column chromatography on silica gel. The less-polar product was predictably the *endo* alcohol (**4**, β-D-*allo* configuration) and showed zero $J_{1,2}$ coupling, as anticipated for the diquasiequatorial disposition of H-1 and H-2; the more-polar, *exo* alcohol **5** (β-D-*altro* configuration) displayed a coupling of 3.4 Hz between H-1 and the quasiaxially disposed H-2.

Both alcohols were colorless, crystalline solids whose structures were confirmed chemically by subjecting them to oxidation with *m*-chloroperoxybenzoic acid. The *endo* alcohol **4** (*allo* configuration) has the 2-hydroxyl group situated in close proximity for rearside, intramolecular attack at C-8 on an intermediate oxirane, to form a five-membered, cyclic ether[14] having an *exo*-hydroxyl group at C-9. On the other hand, the *exo* alcohol **5** (*altro* configuration), would be expected to yield a stable oxirane.

The results were in accord with expectations. Treatment of **4** with *m*-chloroperoxybenzoic acid in chloroform at ~25° gave the polycyclic alcohol **6** (97%) as colorless crystals, whereas, under similar conditions, **5** gave the crystalline oxirane **7** (84%). Furthermore, treatment of **4** with iodine in ethanol at ~25° afforded the crystalline iodide **8** (97%), whose 200-MHz, ^{1}H-n.m.r. spectrum was similar to that of **6**. The ^{13}C-n.m.r. spectrum of **8** (see Table II) was very similar to that of **6**, except for a marked, upfield shift of the signal for C-9.

The structure of **6** was confirmed by X-ray crystallographic analysis[15], and that of **7**, by comparing the 200-MHz, ^{1}H-n.m.r. spectra of the two compounds. An AB quartet in the δ-3.3–3.5 region, showing a coupling constant of 3.6 Hz, was observed in the spectrum of **7**, indicating the presence of an oxirane ring having *cis*-hydrogen atoms. In contrast, $J_{8,9}$ for **6** was found to be zero, indicating that the two hydrogen atoms are *trans*-disposed. The marked, upfield shift of the signal for H-

*Since this manuscript was submitted, Shafizadeh *et al.*[9a] have described the isolation, in 3% yield, of a compound, identified as **3**, having constants in good agreement with those reported here.

**No suitable, carbohydrate-based nomenclature has been devised for such carbocyclic derivatives as those reported here. The Ring Index names utilize numbering that differs from conventional carbohydrate numbering, and makes relation to the carbohydrate precursors difficult. The numbering used here for the Diels–Alder adducts is that given in ref. 9; it retains the standard system for the sugar ring, and uses 7, 8, 9, 10, and 11 for the cyclopentane ring, starting from the atom attached to the lowest-numbered asymmetric atom (C-3) of the sugar ring. The formulas herein arbitrarily depict idealized chair conformations for the pyranoid ring. It is recognized that the *cis*-fused, 5-membered ring may cause distortion of the pyranoid ring to non-chair conformations.

TABLE II

CARBON-13 N.M.R.-SPECTRAL DATA FOR COMPOUNDS **2–10**

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*
2	99.5	200.1	47.0	42.6	75.0	70.4	47.0	135.7	134.2	46.5	49.6
3	99.3	201.1	45.0	42.0	77.0	70.0	47.0	139.5	136.4	48.3	44.6
4	102.1	68.0	39.6	42.3	74.5	71.3	46.5	137.8	132.9	47.7	50.0
5	100.0	69.9	47.0[a]	44.2[a]	74.4	71.1	46.3	←135.8→		47.9	50.4
6	99.5	77.1	34.2	40.9	73.9	69.0	47.1	89.4	75.4	45.2	32.6
7	99.7	66.7	42.5[a]	44.1[a]	73.5	71.3	39.4	49.9	49.5	42.2	26.9
8	99.3	76.7	34.0	42.5	73.8	69.1	49.0	91.3	33.1	48.2	37.5
9	99.7	73.7	44.5[a]	41.2[a]	76.4	70.9	47.6	139.0	135.4	46.4	44.3
10	102.3	70.9	41.4	42.8	76.5	67.7	47.4	139.6	136.6	46.0	33.9

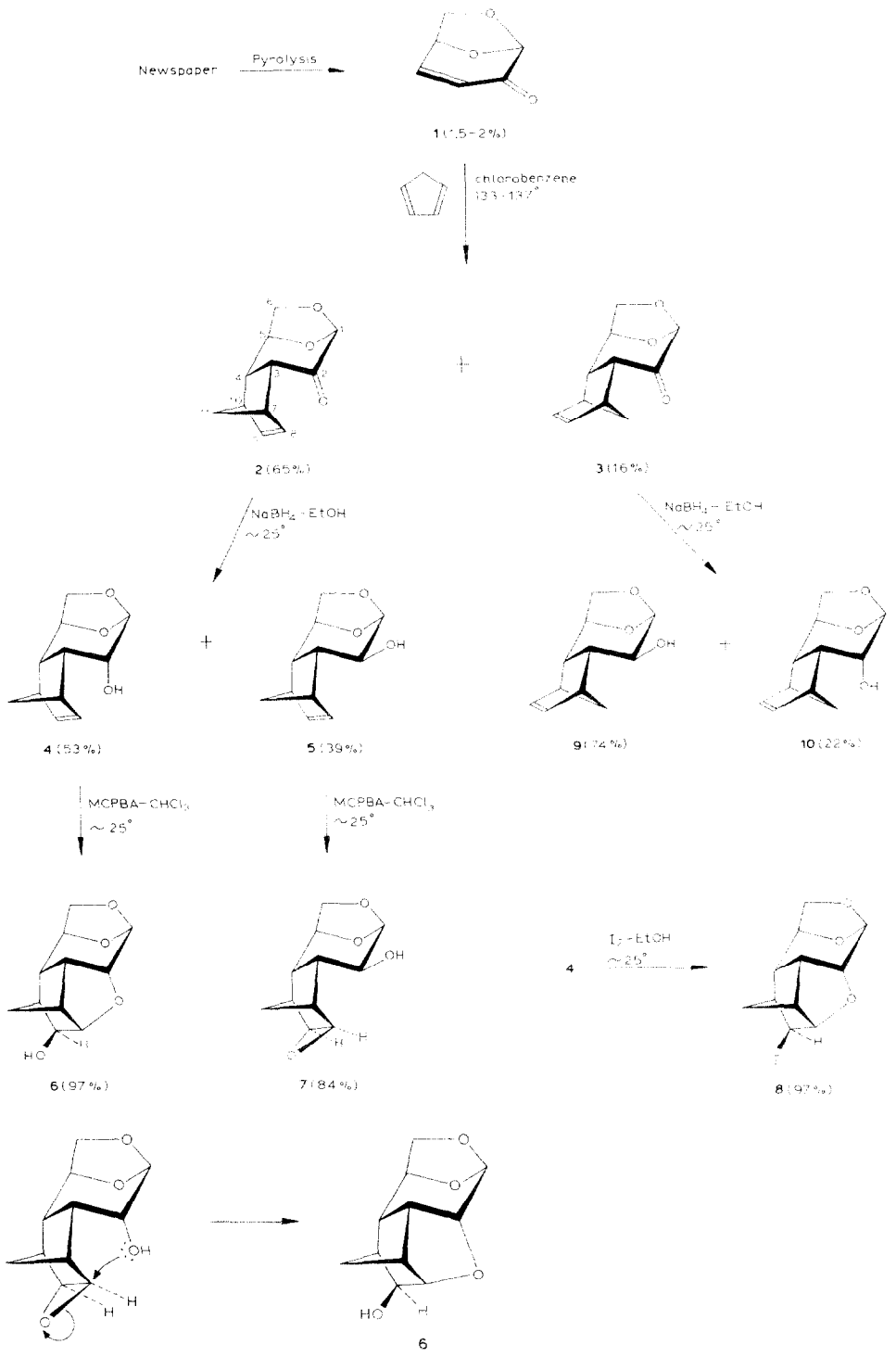
[a]These assignments may have to be interchanged.

11′ in **7**, relative to that for the other compounds in this study, further confirms the anticipated, *exo* disposition of the epoxide group in **7**.

The 200-MHz, ^{1}H-n.m.r. spectrum of the *exo* alcohol **5** corresponds closely to those of 1,6-anhydro-β-D-altropyranose derivatives, in that H-1 resonates as a doublet[16–21]. However, the value of $J_{1,2}$ (3.4 Hz) is significantly greater than that (1.2–2.2 Hz) reported in those examples. The ^{1}H-n.m.r. spectrum of the *endo* alcohol **4** resembles those of 1,6-anhydro-β-D-allopyranose derivatives, but the H-1 signal is observed as a singlet, rather than a narrow doublet. A similar observation was made by Pedersen and co-workers in their study of benzoxonium ions derived from 1,6-anhydro-2,3-*O*-benzylidene-β-D-hexopyranoses having the *altro* and *galacto* configurations[22]. A probable reason for this diminished $J_{1,2}$ value is perturbation of the molecular framework through the additional rigidity imposed on the structure by the bicyclo[2.2.1]hept-2-ene system. It is noteworthy that, in the 200-MHz, ^{1}H-n.m.r. spectrum of the polycyclic alcohol **6**, H-1 resonates as a doublet, with $J_{1,2}$ = 2.2 Hz, indicating a change in the geometry in the vicinity of C-2 as a result of the formation of the five-membered, cyclic ether.

Reduction of the minor adduct **3** with sodium borohydride in 95% ethanol at ~25° afforded a mixture of the (more polar) *exo* alcohol **9** (74%) and (less polar) *endo* alcohol **10** (22%), readily separable as colorless, crystalline solids by column chromatography on silica gel. The structures were clearly established from their 200-MHz, ^{1}H-n.m.r. spectra. Once again, H-1 for **9** appears as a doublet, with $J_{1,2}$ = 3.4 Hz, indicative of the *altro* configuration, whereas the H-1 signal for **10** is a singlet, demonstrating that **10** has the *allo* configuration.

The product distribution in the reduction of **2** differs from that observed with **3**. The *endo*-alkene adduct **2** gives the *endo* alcohol as the major product, whereas the *exo*-alkane **3** gives mainly the *exo* alcohol. Axial attack by borohydride is more hindered in **2** than in **3**, because the carbonyl group is *endo* to the


Newspaper
Pyrolysis
1 (1.5–2%)
chlorobenzene
133–137°
2 (65%)
3 (16%)
NaBH4 – EtOH
~25°
NaBH4 – EtOH
~25°
4 (53%)
5 (39%)
9 (74%)
10 (22%)
MCPBA – CHCl3
~25°
MCPBA – CHCl3
~25°
6 (97%)
7 (84%)
4
I2 – EtOH
~25°
8 (97%)
6

bicyclo[2.2.1]hept-2-ene system in **2**, whereas it is *exo* in **3**. Thus, *endo* attack of the borohydride (resulting in the formation of the *exo* alcohol) is favored for the *exo*-alkene **3**.

EXPERIMENTAL

General methods. — Evaporations were performed under diminished pressure at a bath temperature below 50°. Melting points were determined with a Thomas–Hoover apparatus and are uncorrected. A Perkin–Elmer Model 141 polarimeter and 1-dm tubes were used for measurement of specific rotations. 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% sulfuric acid, with subsequent heating. Silica Gel 60 (E. Merck) was used for column chromatography. Microanalyses were performed by Dr. Ole Mols. I.r. spectra were recorded with a Perkin–Elmer Model 457 grating i.r. spectrophotometer, with solids dispersed in potassium bromide, and syrups as films on sodium chloride 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, confirmed by decoupling experiments, are listed in Table I. ^{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, and are listed in Table II. Unless otherwise noted, samples for ^{1}H-n.m.r. and ^{13}C-n.m.r. study were dissolved in chloroform-*d* containing tetramethylsilane as the internal standard. Mass spectra for compounds **7**, **9**, and **10** 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°. Mass spectra for the remaining compounds were recorded by C. R. Weisenberger with an AEI MS-9 double-focusing, high-resolution spectrometer operating at an ionizing potential of 70 eV and an accelerating potential of 8 kV; the source temperature (direct-inlet system) was 120°. X-Ray powder diffraction data give interplanar spacings, Å, for CuKα radiation. The camera diameter was 114.59 mm. Relative intensities were estimated visually: m, moderate; s, strong; v, very; w, weak. The strongest lines are numbered (1, strongest); double numbers indicate approximately equal intensities.

*1,6-Anhydro-3,4-dideoxy-β-*D-glycero-*hex-3-enopyranos-2-ulose* (*levoglucosenone;* **1**). — Shredded newspaper was pretreated with 1% phosphoric acid[6] and pyrolyzed, in 20–25-g batches, in the apparatus illustrated in Fig. 1, consisting of a quartz tube, one end of which was connected to a rotor, and the other, to a mercury seal containing motor-grease as the sealant. Pyrolysis was conducted in an atmosphere of nitrogen, which was passed through the mercury seal. A Meker burner was used for heating. The pyrolyzates were treated as described in ref. 6. The brown, oily product was distilled at a pressure of 13.3 Pa (0.1 torr), and the

fraction distilling in the range of 50–60° was collected. The ^{1}H-n.m.r. spectrum of this fraction was essentially identical to that reported by Broido *et al.*[5]. About 75 g of **1** was prepared, and the yield was 1.5–2%, based on the weight of paper used. The levoglucosenone thus obtained, $[\alpha]_D^{25}$ −503° (*c* 1, chloroform) (lit.[7] $[\alpha]_D^{25}$ −530°), was suitable for the following synthetic transformations.

Major (**2**) *and minor* (**3**) *adducts of levoglucosenone* (**1**) *with cyclopentadiene.* — A mixture of **1** (3.00 g), dicyclopentadiene (6.00 g), and chlorobenzene (9 mL) was boiled for 9 h under reflux (134–137°); t.l.c. with 5:1 toluene–ethyl acetate then indicated that the reaction was complete. Evaporation of the solution afforded a yellow syrup, t.l.c. (5:1 toluene–ethyl acetate) of which exhibited a major component, **2** (R_F 0.54), and a minor one, **3** (R_F 0.62). Chromatography of the syrup on a column of silica gel with 5:1 toluene–ethyl acetate afforded 3.01 g (65%) of **2** as a pale-yellow solid, and 750 mg (16%) of syrupy **3**.

For analytical purposes, the major adduct **2** was recrystallized from 1:1 ether–hexane; m.p. 62–63° (lit.[9] m.p. 61.5–62.5°), $[\alpha]_D^{25}$ −222° (*c* 1, choroform); X-ray powder diffraction data: 7.16 w, 5.90 m (2), 5.39 s (1), 5.18 vw, 4.95 w, 4.78 w, 3.90 w, 3.34 w, and 2.97 vw.

The minor adduct **3** had $[\alpha]_D^{25}$ −220°(*c* 1, chloroform); ν_{max}^{KBr} 3000 (CH=CH *cis*), 1760 (C=O), and 1100 cm^{-1} (C–O–C); *m/z* (rel. intensity): 192 (14, M^+), 164 (8, $M^+ - CO$), 119 (11, 164 − HCO_2), 118 (69, 164 − H_2CO_2), 117 (78, 118 −H·), 105 (30, 164 − CH_2O, CO, H·), 92 (49, 118 − C_2H_2), 91 (77, 92 − H·), 78 (11, 92 − CH_2), 77 (15, 91 − CH_2), and 66 (100, $M^+ - C_6H_6O_3$).

Anal. Calc. for $C_{11}H_{12}O_3$ (192.21): C, 68.73; H, 6.30. Found: C, 69.06; H, 6.08.

Reduction of major adduct **2** *to* endo (**4**) *and* exo (**5**) *alcohols.* — To a solution at ~25° of adduct **2** (2.00 g, 10.4 mmol) in 95% ethanol (20 mL) was added a solution of sodium borohydride (320 mg, 8.45 mmol) in water (3 mL) containing one drop of 40% potassium hydroxide solution. The mixture was stirred for 2 h at ~25°; t.l.c. (1:2 toluene–ethyl acetate) then indicated the absence of **2**. 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 1.07 g of the resin. Decantation of the solution, followed by evaporation, afforded a syrup that contained (t.l.c., 1:2 toluene–ethyl acetate) two components, namely **4** (R_F 0.64) and **5** (R_F 0.44). Chromatography on a column of silica gel with 1:2 toluene–ethyl acetate afforded **4** (1.06 g, 52.8%) and **5** (790 mg, 39.2%), both as colorless solids that were recrystallized from 1:1 ether–hexane.

The less-polar (*endo*) alcohol **4** had m.p. 85–86°, $[\alpha]_D^{25}$ +36.6° (*c* 1, chloroform); ν_{max}^{KBr} 3500 (O–H), 1140 (C–O–C), and 1040 cm^{-1} (C–O); *m/z* (rel. intensity): 119 (9, $M^+ - CH_2O$, C_2H_2, H_2O, H·), 92 (6, $M^+ - CH_2O$, C_2H_2, H_2O, CO), 91 (16, 119 − CO), 77 (6, 91 − CH_2), 66 (100, $M^+ - C_6H_8O_3$); X-ray powder diffraction data: 8.30 m, 6.15 s (1,1), 5.68 vw, 5.09 s (1,1), 4.75 w, 4.24 m, 3.98 w, 3.79 w, 3.67 vw, 3.44 vw, 3.31 vw, 2.80 w, 2.31 vw, and 1.96 m.

Anal. Calc. for $C_{11}H_{14}O_3$ (194.22): C, 68.00; H, 7.27. Found: C, 68.10; H, 7.21.

The more-polar (*exo*) alcohol **5** had m.p. 71–72°, $[\alpha]_D^{25}$ −79.0° (*c* 1, chloroform); ν_{max}^{KBr} 3400 (O–H), 1090 (C–O–C), and 1070 cm^{-1} (C–O); *m/z* (rel. intensity): 119 (11, $M^+ - CH_2O$, C_2H_2, H_2O, H·), 91 (14, 119 − CO), 77 (5, 91 − CH_2), 66 (100, $M^+ - C_6H_8O_3$); X-ray powder diffraction data: 12.74 m, 7.60 m, 6.39 s (2), 5.69 m, 5.44 vw, 5.13 vs (1), 4.84 s, 4.70 m, 4.38 w, 4.23 m, 3.97 w, 3.76 m, 3.03 w, 2.86 vw, 2.79 vw, 2.62 w, 2.55 w, 2.49 vw, 2.41 w, and 2.35 w.

Anal. Calc. for $C_{11}H_{14}O_3$ (194.22): C, 68.00; H, 7.27. Found: C, 68.23; H, 7.13.

Conversion of endo *alcohol* **4** *into polycyclic alcohol* **6**. — To a solution of **4** (200 mg, 1.03 mmol) in chloroform (10 mL) was added a solution of *m*-chloroperoxybenzoic acid (80% purity; 232 mg, 1.08 mmol) in chloroform (5 mL) at ~25°. The mixture was stirred for 2 h at ~25°, when t.l.c. with 2:5 toluene–ethyl acetate indicated that **4** was absent. Saturated sodium hydrogencarbonate solution (10 mL) was added, and the mixture was vigorously stirred for 0.5 h. The aqueous phase was separated, extracted with three 5-mL portions of chloroform, and the organic phases combined, and evaporated, to afford essentially pure **6** (211 mg, 97%) as a colorless solid which was recrystallized from 95% ethanol; m.p. 120°, $[\alpha]_D^{25}$ +17.5° (*c* 1, chloroform); ν_{max}^{KBr} 3430 (O–H), 1100 (C–O–C), and 1060 cm^{-1} (C–O); *m/z* (rel. intensity): 210 (17, M^+), 192 (14, $M^+ - H_2O$), 181 (5, $M^+ - HCO$), 164 (17, 192 − CO), 146 (10, 192 − H_2CO_2), 135 (14, 181 − H_2CO_2), 109 (9, 135 − C_2H_2), 105 (11, 164 − CH_2O, CO, H·), 92 (11, 192 − CO, H_2CO_2, C_2H_2), 91 (12, 92 − H·), 81 (29, $M^+ - C_5H_7O_2$, CH_2O), 78 (5, 92 − CH_2), 77 (13, 91 − CH_2), and 69 (100, $M^+ - CH_2O$, $C_4H_5O_2$, C_2H_2); X-ray powder diffraction data: 11.04 vw, 7.46 w, 6.33 m (2,2), 5.85 m, 5.46 m (2,2), 4.74 vs (1), 4.47 w, 3.94 m, 3.65 w, 3.49 vw, 3.30 w, 3.16 w, 3.04 vw, and 2.84 m.

Anal. Calc. for $C_{11}H_{14}O_4$ (210.22): C, 62.81; H, 6.71. Found: C, 62.88; H, 6.79.

Epoxidation of exo *alcohol* **5** *to oxirane* **7**. — To a solution of **5** (134 mg, 0.69 mmol) in chloroform (10 mL) was added a solution of *m*-chloroperoxybenzoic acid (80% purity; 155 mg, 0.73 mmol) in chloroform (5 mL) at ~25°. The mixture was stirred for 2 h at ~25°, when t.l.c. with 2:5 toluene–ethyl acetate indicated that **5** was absent. Saturated sodium hydrogencarbonate solution (10 mL) was added, and the mixture was vigorously stirred for 0.5 h. The aqueous phase was separated, and extracted with three 5-mL portions of chloroform. Evaporation of the combined organic phases afforded **7** (121 mg, 83.4%) as a colorless solid which was recrystallized from 95% ethanol; m.p. 119–121°, $[\alpha]_D^{25}$ −71.8° (*c* 1, chloroform); ν_{max}^{KBr} 3440 (O–H), 1090, 1080 (C–O–C), and 1020 cm^{-1} (C–O); *m/z* (rel. intensity): 135 (34, $M^+ - CH_2O$, HCO_2), 121 (59, $M^+ - CH_2O$, $C_2H_3O_2$), 111 (10, $M^+ - OH$, C_5H_6O), 108 (42, $M^+ - C_4H_6O_3$), 95 (55, 121 − C_2H_2), 82 (100, $M^+ - C_6H_8O_3$), 69 (94, $M^+ - C_2H_2$, $C_5H_7O_3$), 66 (96, 108 − C_2H_2O), 55 (46, 108 − C_4H_5), 53 (64, 135 − C_5H_6O), 43 (57, $M^+ - CH_2O$, $C_8H_9O_2$), 42 (10, 82 − C_3H_4), 40 (23, 82 −

C_2H_2O); X-ray powder diffraction data: 6.17 w, 5.75 m, 5.45 vs (1), 5.17 s (2,2), 4.55 m, 4.25 s (2,2), 4.05 w, and 3.80 w.

Anal. Calc. for $C_{11}H_{14}O_4$ (210.22): C, 62.81; H, 6.71. Found: C, 62.94; H, 6.53.

Conversion of endo *alcohol* **4** *into polycyclic iodide* **8**. — A solution of iodine (132 mg, 0.52 mmol) in 95% ethanol (5 mL) was added dropwise to a solution of compound **4** (100 mg, 0.52 mmol) in 95% ethanol (5 mL), stirred at ~25° at a rate such that the mixture remained colorless. Evaporation of the mixture afforded **8** (156 mg, 97.6%) as a colorless, crystalline solid; m.p. 126–127°, $[\alpha]_D^{25}$ +69.5° (*c* 1, chloroform); ν_{max}^{KBr} 3460 (O–H) and 1080 cm^{-1} (C–O–C); *m/z* (rel. intensity): 320 (7.9, M^+), 193 (100, $M^+ - I$), 147 (10.5, 193 − H_2CO_2), 117 (15.8, 147 − CH_2O), 91 (26.8, 117 − C_2H_2), and 66 (14.7, 193 − $C_6H_7O_3$).

Anal. Calc. for $C_{11}H_{13}IO_3$ (319.99): C, 41.27; H, 4.09. Found: C, 41.34; H, 4.19.

Reduction of the minor adduct **3** *to* exo (**9**) *and* endo (**10**) *alcohols*. — To a solution of compound **3** (112 mg, 583 μmol) in 95% ethanol (5 mL) at ~25° was added a solution of sodium borohydride (17 mg, 453 μmol) in 1 mL of water containing one drop of 20% potassium hydroxide solution. The mixture was processed as for the preparation of **4** and **5**. T.l.c. (1:2 toluene–ethyl acetate) exhibited one major product, **9** (R_F 0.65), and a minor, less-polar one, **10** (R_F 0.77), plus a trace of a third product (R_F 0.81). Chromatography on a column of silica gel with 2:3 toluene–ethyl acetate afforded **9** (83 mg, 73.6%) and **10** (25 mg, 22%), both as colorless solids.

The *exo* alcohol **9** had m.p. 72–73°, $[\alpha]_D^{25}$ −104° (*c* 1, chloroform); ν_{max}^{KBr} 3430 (O–H), 110 (C–O–C), and 1060 cm^{-1} (C–O); *m/z* (rel. intensity): 148 (50, $M^+ - H_2CO_2$), 147 (8, 148 − H·), 118 (9, 148 − CH_2O), 117 (38, 147 − CH_2O), 104 (33, 118 − CH_2), 103 (17, 117 − CH_2), 92 (44, $M^+ - CH_2O$, C_2H_2, H_2O, CO), 91 (77, $M^+ - CH_2O$, C_2H_2, H_2O, H·, CO), 82 (83, 148 − C_5H_6), 81 (86, 147 − C_5H_6), 78 (28, 104 − C_2H_2), 77 (54, 91 − CH_2), and 66 (100, $M^+ - C_6H_8O_3$); X-ray powder diffraction data: 8.11 s (3,3), 6.78 vw, 5.94 m, 5.51 s (3,3), 5.12 s, 4.93 vs (1), 4.73 s (2), 3.97 w, 3.82 w, 3.58 w, 3.42 w, 3.29 vw, 2.99 w, 2.81 m, 2.36 w, and 2.22 vw.

Anal. Calc. for $C_{11}H_{14}O_3$ (194.22): C, 68.00; H, 7.27. Found: C, 67.71; H, 7.23.

The *endo* alcohol **10** had m.p. 109–110°, $[\alpha]_D^{25}$ −36.3° (*c* 1, chloroform); ν_{max}^{KBr} 3420 (O–H), 1160 (C–O–C), and 1070 cm^{-1} (C–O); *m/z* (rel. intensity): 148 (42, $M^+ - H_2CO_2$), 147 (7, 148 − H·), 118 (8, 148 − CH_2O), 117 (34, 147 − CH_2O), 104 (28, 118 − CH_2), 103 (14, 117 − CH_2), 92 (36, $M^+ - CH_2O$, C_2H_2, H_2O, CO), 91 (75, $M^+ - CH_2O$, C_2H_2, H_2O, H·, CO), 82 (83, 148 − C_5H_6), 81 (85, 147 − C_5H_6), 78 (21, 104 − C_2H_2), 77 (75, 91 − CH_2), and 66 (100, $M^+ - C_6H_8O_3$); X-ray powder diffraction data: 10.97 s, 7.82 w, 6.65 vs (1), 5.73 m, 5.48 m, 4.87 s (2), 4.62 m, 4.25 m, 3.91 w, 3.67 m, 3.36 w, and 3.20 w.

Anal. Calc. for $C_{11}H_{14}O_3$ (194.22): C, 68.00; H, 7.27. Found: C, 67.76; H, 7.21.

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