Stereoselective Addition of Nitromethane to Levoglucosenone; Formation and Structure of 2:1 and 1:2 Adducts[1]

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Tetramethylguanidine-catalysed addition of nitromethane to levoglucosenone affords in 98% yield a 10:1 mixture of 2:1 adducts **2** and **3**, which result from initial Michael addition of nitromethanide exclusively from the *exo* face at C-4, followed by further reaction of the nitronate anion at both faces of the 1:1 adduct **4**. In the presence of excess of levoglucosenone the major product (95%) is a pentacyclic 1:2 adduct **6**, formed by reaction of 1:1 adduct **4** with further levoglucosenone. MeOH–levoglucosenone–$MeNO_2$ adduct **12** and 2:2 adduct **7** were also formed as by-products in the corresponding diethylamine-catalysed reaction in methanol. The structure of compound **6** was established by X-ray crystallography.

Levoglucosenone (**1**, 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose) is a cellulose-derived bicyclic α-enone which is attracting considerable attention as a chiral starting material for asymmetric synthesis.[2,3] Of particular note is the high stereoselectivity of its reactions. For example, it undergoes Diels–Alder[3,4] and 1,3-dipolar[5] cycloadditions, and Michael addition with various carbon,[6–8] oxygen[4] and sulfur[9] nucleophiles, and in every instance reaction takes place at the *exo* face opposite the 1,6-anhydro bridge. We have examined its base-catalysed reactions with nitromethane and now report that the products formed depend both on the catalyst and the ratio of reactants.

Results and Discussion

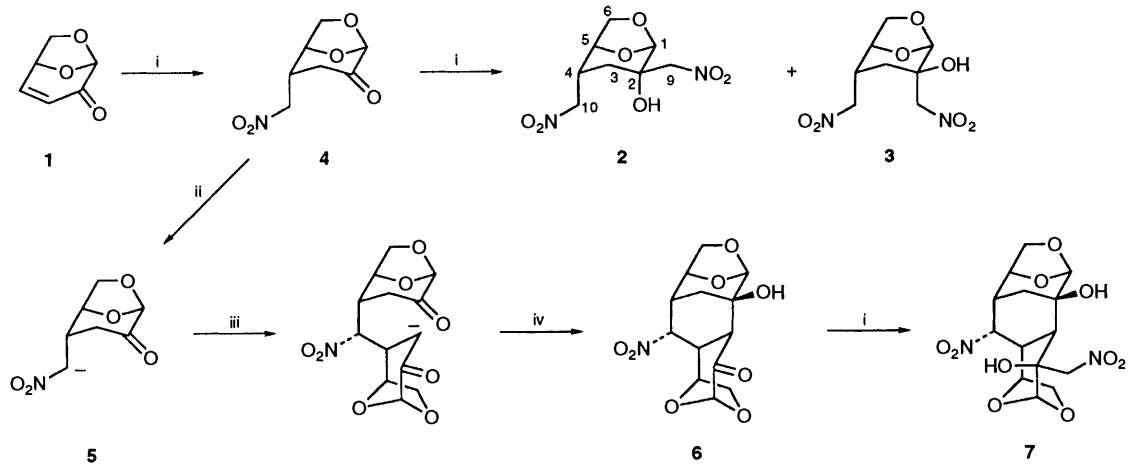
The conditions chosen for initial studies were those previously employed for the addition of nitromethane to cyclopentenones.[10] Treatment of levoglucosenone with nitromethane (1:42) in the presence of tetramethylguanidine (TMG) afforded a 10:1 mixture of two 2:1 adducts **2** and **3** in 98% combined yield. These can be attributed to the expected Michael addition of the nitromethanide anion exclusively at the 4-position from the less hindered *exo* face to give 1:1 product **4**, followed by further base-catalysed reaction of nitromethane at both faces of the carbonyl group (Scheme 1); in the second stage the selectivity is reversed and the major isomer results from *endo*-attack. The individual isomers were separated by chromatography and identified by ^1H NMR spectroscopy (Tables 1 and 2). This showed that in both cases the pyranose ring adopts the expected $^1C_4$ conformation with the nitromethyl substituent at C-4 axial. The diagnostic proton–proton couplings are compared with those for related compounds **8–10** in Table 2. The small couplings (<2 Hz) between 4-H and 5-H are consistent only with 4-H being equatorial in both isomers; the alternative arrangement with 4-H axial would be expected to give substantially larger coupling to both 5-H and 3a-H. For the *exo*, *endo* product **2** the configuration at C-2 was established using a selective heteronuclear *J*-resolved two-dimensional NMR experiment[11] to measure the $^3J_{CH}$-values between 3a-H and the carbons of the two nitromethyl groups (C-9 and C-10). The coupling of 9.1 Hz between 3a-H and C-10 of the nitromethyl substituent at the 4-position is as expected for the *trans* diaxial arrangement established above from the proton–proton couplings. In contrast the observed coupling between 3a-H and C-9 is only 2.8 Hz, which strongly supports the proposed *gauche* arrangement with the nitromethyl substituent at C-2 equatorial.[12] Epimer **3** therefore has the hydroxy group at C-2 equatorial and the nitromethyl axial. Other noteworthy features of the ^1H NMR spectrum of the major adduct **2** are W-couplings of 1.5 Hz for both 1-H–3e-H and 3e-H–5-H, and a longer range coupling across the tetrahydropyran ring between 1-H and 4-H (^5J 1 Hz).

Table 1 ^1H and ^{13}C NMR chemical shifts for compounds **2**, **3** and **12** (numbering scheme is that shown on structure **2**)

(δ/ppm)			
Proton	**2**[a]	**3**[b]	**12**[c]
1-H	5.39	5.38	5.33
3a-H	2.17	2.23	2.22
3e-H	1.68	2.05	1.78
4-H	2.61	2.74	3.30
5-H	4.58	4.62	4.65
6x-H	3.86	3.90	3.77
6n-H	4.10	4.10	3.85
9-H_2	4.49, 4.65	4.69, 4.86	4.67, 4.86
10-H_2	4.85, 5.07	4.72, 4.95	
OH	4.93	4.66	2.80
OMe			3.38
Carbon			
C-1	101.2		102.1
C-2	69.4		*d*
C-3	27.7		32.4
C-4	33.9		50.5
C-5	72.8		74.0
C-6	66.5		66.3
C-9	81.3		79.6
C-10	76.0		
OMe			75.5

[a] 360 MHz in CD_3COCD_3. [b] 200 MHz in CD_3COCD_3. [c] 200 MHz in $CDCl_3$. [d] Not detected.

When the reaction was repeated using equimolar quantities of the reactants in 1,2-dichloroethane (DCE) as solvent two products were isolated: the major 2:1 adduct **2** in 61% yield and a new crystalline solid (18%). Although elemental analysis and mass spectrometry showed that it comprised two units of levoglucosenone and one nitromethane ($C_{13}H_{15}NO_8$; *m/z* 313, M^+), its detailed structure was not readily discernible from its NMR data. The structure was fully elucidated by X-ray crystallography which showed that it was pentacyclic compound **6**. On repetition of the reaction using a 2:1 ratio of levoglucosenone to nitromethane compound **6** was the only product isolated (95%). The proposed mechanism for its

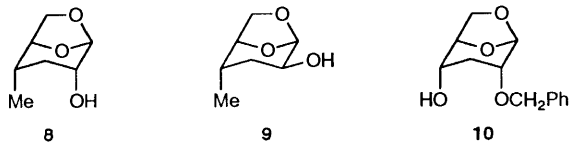


Scheme 1 *Reagents:* i, $MeNO_2$, base; ii, base; iii, **1**; iv, H^+

Table 2 ^1H NMR couplings[a] for compounds **2**, **3**, **8**–**10**, **12** (numbering scheme as on structure **2**)

J/Hz	2	3	8[b]	9[b]	10[c]	12
1,3e	1.5					1.6
1,4	1					
3a,3e	15.3	15.2	14.9	12.8		15.0
3a,4	6.9	7.4	6.9	6.1	4.5	4.4
3e,4	1.5	1.6	1.5	1.5	< 1.5	1.8
3e,5	1.5					2.0
4,5	0.9	< 1	2.0	2.0	2.8	3.3
4,10a	8.1	8.7				
4,10b	6.1	6.4				
5,6x	5.4	5.4	4.0	4.0	5.4	5.1
5,6n	1.0	0.9	2.0	2.0	0.8	1.2
6x,6n	7.7	7.7			7.7	7.9
9a,9b	11.6	12.0				12.4
10a,10b	13.8	13.8				

[a] Recorded at 200 or 360 MHz (**2** and **3** in CD_3COCD_3, **12** in $CDCl_3$). [b] Ref. 6. [c] Ref. 8.



8 **9** **10**

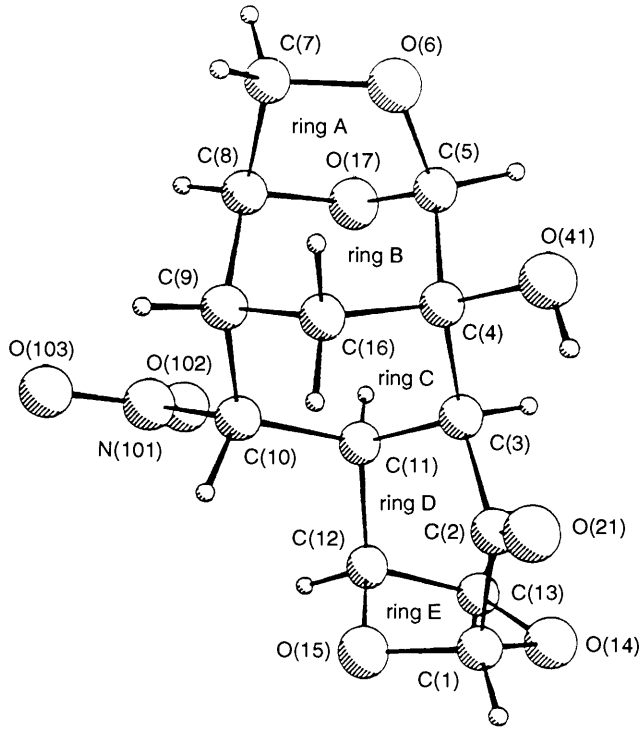


Fig. 1 X-Ray molecular structure of compound **6**

formation (Scheme 1) involves Michael addition, to a second molecule of levoglucosenone, of the nitronate anion **5** resulting from loss of a proton from the nitromethyl substituent at C–10 of the initial 1:1 adduct **4**, followed by intramolecular nucleophilic addition to the carbonyl group at C-2. The isolation of compound **6** in near quantitative yield shows that the three steps in the reaction sequence leading to its formation—two intermolecular Michael additions to levoglucoseneone and an intramolecular nucleophilic addition at carbonyl—all occur with exceptionally high *exo* face selectivity.

A stereochemical drawing of compound **6** is shown in Fig. 1 and the Cremer and Pople puckering parameters[13] are given in Table 3. The central cyclohexane ring (ring C) assumes a predominantly chair conformation $^{C\text{-}9}C_{C\text{-}3}$ (Q = 0.595 Å, θ = 156.7° and φ = 299.9°) with the nitro substituent at C-10 in the equatorial position. Tetrahydropyran ring **B**, in which all the atoms are sp^3-hybridised, assumes a conformation very close to the $^{C\text{-}5}C_{C\text{-}9}$, whereas for the other pyran ring (D) the presence of the carbonyl group at C-2 results in some distortion away from $^{C\text{-}4}C_{O\text{-}15}$. The 1,3-dioxolane rings in 1,6-anhydropyranoses[14] generally adopt a conformation between twist (3 atoms coplanar, $^{C\text{-}5}T_{O\text{-}5}$ where φ = 54°) and envelope forms (4 atoms coplanar, $E_{O\text{-}5}$ where φ = 36°). For compound **6** φ is ~40° for both five-membered rings; ring A has the $E_{O\text{-}17}$ conformation in which O-17 is 0.663 Å below the plane through C-5–C-8–C-7–O-6, and ring E is $E_{O\text{-}15}$ with O-15 0.612 Å out of the plane through C-1–C-12–C-13–O-14. The C–O bond lengths in rings A and E show deviations from the mean value typical of 1,6-anhydropyranoses.[15] As a consequence of the anomeric effect, the two outer bonds in the sequences C-8–O-17–C-5–O-6–C-7 for ring A and C-12–O-15–C-1–O-14–C-13 for ring E are long and the inner two ones are short when compared with average C–O bonds (Fig. 2). The atomic co-ordinates, bond lengths and angles and torsion angles have been deposited with the Cambridge Crystallographic Data Centre.*

* See Instructions for Authors in the January issue.

Table 3 Cremer and Pople puckering parameters[13] for compound **6**

	Ring	Q (Å)	θ(°)	φ(°)
A	C-5–O-17–C-8–C-7–O-6	0.447		41.1
B	O-17–C-5–C-4–C-16–C-9–C-8	0.660	170.7	173.4
C	C-3–C-4–C-16–C-9–C-10–C-11	0.595	156.7	299.9
D	O-15–C-1–C-2–C-3–C-11–C-12	0.630	153.8	176.7
E	C-1–O-15–C-12–C-13–O-14	0.404		39.0

Table 4 ^{1}H NMR data for 1:2 adduct **6**[a] and 2:2 adduct **7**[b] (numbering scheme follows that shown in Figs. 1 and 3)

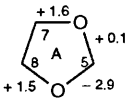
(δ/ppm)					
Proton	**6**	**7**	$J_{x,y}$/Hz	**6**	**7**
1-H	5.08	5.39	1,13		0.3
3-H	3.57	2.47	3,11	8.4	8.6
5-H	5.08	5.08	3,16e	2.4	
7x-H	3.68	3.69	5,16a	1.8	1.7
7n-H	4.03	4.04	7x,7n	7.6	7.6
8-H	4.46	4.48	7x,8	4.8	4.8
9-H	2.75	2.66	7n,8		1.3
10-H	5.12	5.18	8,9	2.6	1.8
11-H	4.40	3.70	8,16a	1.8	
12-H	4.58	4.27	9,10	4.7	4.5
13x-H	4.04	3.83	9,16e	4.5	4.0
13n-H	4.45	4.01	9,16a	2.4	2.5
16e-H	2.24	2.63	10,11	11.5	11.9
16a-H	1.78	2.10	11,12	1.5	
OH	4.67	4.69, 4.33	12,13x	5.3	5.7
C*H*HNO$_2$		4.77	12,13n	1.0	0.4
CH*H*NO$_2$		5.53	13x,13n	7.9	7.5
			16e,16a	13.3	13.3
			(CH_2NO_2)		11.4

[a] 360 MHz in CD_3COCD_3. [b] 200 MHz in CD_3COCD_3.

Table 5 NOE data for compound **6**

Irradiated protons	Enhancements (%)		
10-H	16a-H (4)	9-H (3)	
12-H	13x-H (3)	10-H (2)	11-H (4)
11-H	3-H (4)	12-H (2.5)	
13x-H(7n-H)[a]	13n-H (6)		
7n-H(13x-H)[a]	9-H (1)	7x-H (12)	16e-H (3)
7x-H	8-H (3)	7n-H (7)	
3-H	5-H (2)	13n-H (2)	
9-H	7n-H (1)	16e-H (2)	16a-H (1)
	8-H (3)	10-H (6)	
16e-H	9-H (2)	7n-H (4)	16a-H (14)
16a-H	16e-H (14)	9-H (2)	10-H (2)

[a] Overlapping signals.



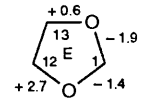


Fig. 2 Variation in C–O bond lengths (pm) for rings A and E in compound **6**

Having established the structure of compound **6** by X-ray crystallography its ^{1}H NMR spectrum was analysed and assigned using spin decoupling and steady-state NOE experiments (Tables 4 and 5). Spin decoupling of the seven non-overlapping proton multiplets allowed the assignment of each methine proton resonance and each of the resonance pairs corresponding to geminal proton pairs. The geminal proton

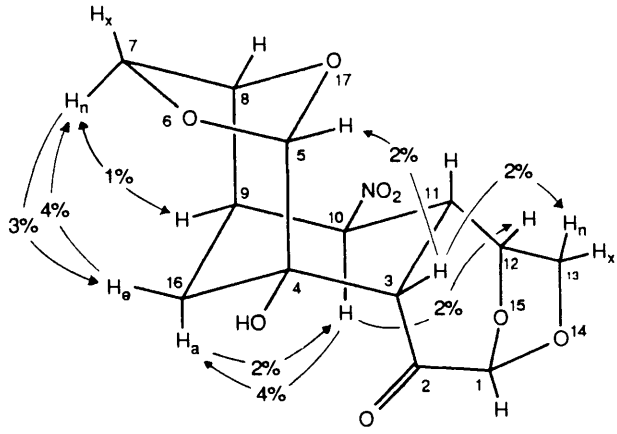


Fig. 3 NOE data observed for protons separated by more than 3 single bonds. Enhancements (%) are those obtained for the nuclei at the arrowheads on irradiating those at the arrowtails

resonances were distinguished and the other assignments confirmed by steady-state NOE measurements, whose interpretation was aided by the high degree of rigidity of the molecule. In addition to the large enhancements (>10%) between geminal protons, expected enhancements between vicinal protons were observed for all protons irradiated except between 12-H and one 13-H (which is therefore probably *endo*) and between 8-H and one 7-H (therefore also probably *endo*). These protons are no doubt relaxed by other closer protons. These assignments were confirmed by enhancement (2%) of the same 13-H on irradiation of the bridgehead proton 3-H and the enhancement (1%) of the same 7-H on irradiation of the bridgehead proton 9-H. In neither instance was the other geminal proton enhanced. Irradiation of 3-H also enhanced the anomeric proton 5-H. The axial proton 16a-H was identified by its enhancement (3%) on irradiation of the axial 10-H which also enhanced 9-H (3%) at the bridgehead between rings B and C. The equatorial proton 16e-H resonance assignment was confirmed by its enhancement on irradiation of 7n-H and *vice versa*. The absence of enhacement of 10-H or 11-H on irradiation of the other is consistent with their *trans*-diaxial orientation. The NOE enhancements for protons separated by more than three single bonds are summarised in Fig. 3.

The H–C–C–H torsion angles calculated from the crystal structure allow the relative magnitudes of the proton–proton couplings to be rationalised. Of particular note are the *trans*-diaxial coupling of 11.5 Hz between 10-H and 11-H, and the splitting pattern for the protons of the CH–O–CH bridges of dioxolane rings A and E. The ~5 Hz vicinal coupling between the *exo* protons (7x-H, 13x-H) and the adjacent bridgehead positions (8-H, 12-H), the associated <2 Hz couplings for the *endo* protons (7n-H, 13n-H), and the geminal methylene coupling of 8 Hz are all typical of 1,6-anhydroglucopyranose derivatives.[4–9] Selected H–C–C–H torsion angles are compared with observed and calculated[16] coupling constants in Table 6.

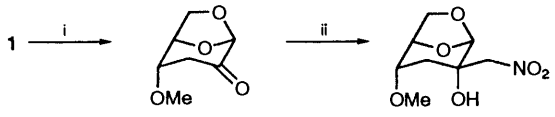
The reaction was repeated with a variety of reactant ratios, catalysts and solvents (Table 7). Changing the solvent from dichloromethane to methanol with catalytic TMG or Et_3N yielded two products: the known Michael adduct **11** of methanol and levoglucosenone and a new compound which, on the basis of its spectroscopic properties, was assigned structure **12** resulting from reaction of nitromethane at the carbonyl group of methanol adduct **11** (Scheme 2), presumably at the *endo* face; there was no indication of products derived from 1,4-addition. With diethylamine in methanol and an excess of nitromethane[17] the same MeOH–levoglucosenone–$MeNO_2$ combination product **12** was formed in 40% yield, together with traces of 2:1 adduct **2** (3%). In contrast, use of Triton-B

Table 6 Selected H–C–C–H torsion angles (θ/°) for compound **6** with observed and calculated[a] coupling constants (*J*/Hz).

	$J_{x,y}$ 3,11	8,7x	8,7n	8,9	9,10	9,16a	9,16e	10,11	11,12	12,13x	12,13n
θ	44.7	31.9	95.2	54.4	48.6	64.5	59.2	159.8	60.4	25.7	100.0
J_{calc}	4.5	6.0	1.5	3.4	4.0	2.4	2.9	12.1	2.7	6.6	1.8
J_{obs}	8.4	4.8	0	2.6	4.7	2.4	4.5	11.5	1.5	5.3	1.0

[a] $^3J = 7.76\cos^2\theta - 1.1\cos\theta + 1.4$ (ref. 16).

methoxide[18] as catalyst at 60 °C yielded substantial amounts of compound **2** (33%) and a new 2 + 2 adduct ($C_{14}H_{18}N_2O_{10}$; *m/z* 374, M^+) (22%). The latter was identified, by comparison of its ^{1}H NMR data with those of 1 : 2 adduct **6**, as having structure **7** resulting from further addition of nitromethane to the carbonyl function at C-2 of compound **6** (Scheme 1). The chemical shifts observed for most of the protons of rings A and B of compound **7** are very similar to those of ketone **6** (Table 4). There are, however, predictable differences for some of the protons of rings C, D and E associated with the change from C=O to $C(OH)CH_2NO_2$ at C-2. For example, there is a chemical-shift difference $\Delta\delta_H$ of 1.10 ppm for 3-H; smaller shifts are also observed for 13a-H (+0.44), 16e-H (−0.39), 1-H (−0.31) and 12-H (0.31 ppm). The pattern of ^3J-values is also very similar for the two compounds throughout the pentacyclic framework, indicating that they adopt broadly similar conformations. The stereochemistry at C-12 is not known but it is assumed that, as *exo* approach is partly obstructed by the cyclohexane ring fused at C-3 and C-11, the nitronate anion reacts at the less hindered *endo* face and occupies the equatorial position as indicated.



11 12

Scheme 2 *Reagents:* i, MeOH, base; ii, $MeNO_2$, base

In conclusion, the exclusive formation of *exo* Michael adducts provides further evidence for the strong influence that the 1,6-anhydro bridge has on directing the stereochemical course of reactions at the α-enone moiety of levoglucosenone.

Experimental

The instrumentation used for recording IR, ^{1}H and ^{13}C NMR, and mass spectra, and the chromatographic methods were as previously described.[19] Levoglucosenone **1** was prepared by pyrolysis of acidified cellulose according to the literature procedure.[5,20] Values for [α] are recorded in units of 10^{-1} deg cm^2 g^{-1}.

Addition of Nitromethane to Levoglucosenone.—A series of reactions were carried out using tetramethylguanidine (TMG), triethylamine, Triton-B, diethylamine and sodium methoxide as base catalysts and nitromethane, DCE or methanol as solvent. The details are given in Table 7 and a typical procedure was as follows.

To a solution of levoglucosenone **1** (0.960 g, 7.62 mmol) in DCE (50 cm^3) at 0 °C was added TMG (5 drops), followed by a solution of nitromethane (230 mg, 3.77 mmol) in DCE (10 cm^3) dropwise over a period of 30 min. After being stirred at room temperature for 4 h the mixture was washed with 1 mol dm^{-3} aq. HCl (20 cm^3), dried ($MgSO_4$), concentrated, and separated by dry flash chromatography (silica; light petroleum–ethyl acetate).

(1R,2S,4R,5S)-2,4-*Bis*(*nitromethyl*)-6,8-*dioxabicyclo*[3.2.1]-*octan*-2-*ol* **2**, clear flakes, m.p. 117–118 °C (from diethyl ether) (Found: C, 38.3; H, 4.8; N, 11.3. $C_8H_{12}N_2O_7$ requires C, 38.7; H, 4.9; N, 11.3%); $[\alpha]_D^{24}$ −72 (*c* 1.0, EtOH); ν_{max}(Nujol)/cm^{-1} 3480 (OH), 1560 and 1350 (NO_2); *m/z* (FAB, glycerol) 249 ($M + 1)^+$; for ^{1}H and ^{13}C NMR data, see Tables 1 and 2. The minor isomer (1R,2R,4R,5S)-2,4-bis(nitromethyl)-7,8-dioxabicyclo-[3.2.1]octan-2-ol **3** [m.p. 107–109 °C, *m/z* 248 (M^+)], which was isolated in low yield (9%), was identified from its NMR data (Tables 1 and 2).

(1R,2S,4R,7S,8R,9R,10R,11S,14R)-1-*Hydroxy*-9-*nitro*-5,13,-16,17-*tetraoxapentacyclo*[8.4.1.1^{4,7}.1^{11,14}.0^{2,8}]*heptadecan*-3-*one* **6**, clear needles, m.p. 244–245 °C (from ethyl acetate) (Found: C, 49.5; H, 4.7; N, 4.5. $C_{13}H_{15}NO_8$ requires C, 49.8; H, 4.8; N, 4.5%); $[\alpha]_D^{24}$ −201 (*c* 1.0, CH_2Cl_2); ν_{max}(Nujol)/cm^{-1} 3470 (OH), 1725 (C=O) and 1545 (NO_2); δ_C (50 MHz; [$^2H_6$]acetone) 103.8, 100.9, 85.2, 73.2, 73.0, 70.4 (C-1), 66.5, 66.2 (C-6, C-12), 45.6, 45.3, 38.4, 29.5 (C-15); *m/z* 313 (M^+); for ^{1}H NMR data see Table 4.

(1R,2S,4S,5R)-2-*Methoxy*-4-(*nitromethyl*)-6,8-*dioxabicyclo*-[3.2.1]*octan*-4-*ol* **12**, as mustard-coloured needles, m.p. 135 °C (from ethanol) (Found: C, 43.6; H, 6.0; N, 6.5. $C_8H_{13}NO_6$ requires C, 43.8; H, 6.0; N, 6.4%); $[\alpha]_D^{24}$ −94 (*c* 0.85, $CHCl_3$); ν_{max}(Nujol)/cm^{-1} 3390 (OH) and 1550 (NO_2); for ^{1}H and ^{13}C NMR data see Tables 1 and 2.

(1R,2RS,3S,4R,7S,8R,9R,10R,11S,14R)-9-*Nitro*-3-(*nitro-methyl*)-5,13,16,17-*tetraoxapentacyclo*[8.4.1.1^{4,7}.1^{11,14}.0^{2,8}]-*heptadecane*-1,3-*diol* **7**, m.p. 184 °C (decomp., from EtOAc) (Found: C 44.5, H, 4.4; N, 7.1. $C_{14}H_{18}N_2O_{10}$ requires C, 44.9; H, 4.8; N, 7.5%); $[\alpha]_D^{24}$ −83 (*c*. 0.06, acetone); *m/z* 374 (M^+); for ^{1}H NMR data see Table 4.

Selective Heteronuclear C–H J-Resolved 2D NMR Spectra.—These were obtained on a Bruker WH360 spectrometer using the sequence of Bax and Freeman.[11] 64 Carbon-13 FIDs (spectrum width 7692 Hz; acquisition time 0.0333 s; 512 data points; recycle delay 5 s; 8 transients) were obtained with the selective proton pulses applied at the frequency of 3-H. A heavy line-broadening (20 Hz) function was applied to the data before the first Fourier transform. Data sets corresponding to individual carbon-13 chemical shifts were then weighed with a gaussian function and zero-filled to 1 K data points before individual Fourier transformation.

Proton NOE Difference Spectra.—These were obtained on the same spectrometer by the multipoint irradiation technique during the pre-excitation delay (8 s) followed by a 90° observation pulse to minimise SPT effects. Blocks of 32 transients each preceded by 4 dummy transients were accumulated and interleaved for each irradiated multiplet to give a total of 1024 transients per site. A control spectrum was obtained with irradiation at δ_H −0.5. After zero-filling from 16K to 32K data points and Fourier transform, subtraction of the control spectrum from the site-irradiated spectra gave the enhancements quoted.

Crystal Data for Compound **6**.—$C_{13}H_{15}NO$, M = 313.22, monoclinic, space group $P2_1$, *a* = 8.640(2), *b* = 9.453(2), *c* =

Table 7 Reactions of levoglucosenone **1** with nitromethane

1 (g)	Ratio ($MeNO_2$:**1**)	Base[a]	Solvent[b] (cm^3)	Temp. (T/°C)	Time (t/h)	Products (%)
1.020	42	TMG	$MeNO_2$ (10)	~20	21	**2** (89), **3** (9)
0.072	1	TMG	DCE (5)	~20	65	**2** (61), **6** (18)
0.960	0.5	TMG	DCE (60)	0–20	4	**6** (95)
0.159	1	TMG	MeOH (5)	0–20	1	**11**[c] (13), **12** (42)
0.148	1	Et_3N	MeOH(5)	0–20	18	**11**[c] (50), **12** (25)
1.09	2	Triton B	MeOH (1.1)	60	3	**2** (33), **17** (22)
1.58	6	Et_2NH	MeOH (5)	~20	144	**2** (3), **12** (40)
1.57	2	NaOMe	MeOH (5)	~20	0.25	**6** (10), **7** (8)

[a] TMG = tetramethylguanidine. [b] DCE = 1.2-dichloroethane. [c] Ref. 7.

9.087(2) Å, β = 117.68(1)°, V = 657.2 Å^3 [from setting angles for 10 *h*0*l* and 4 0*k*0 data, 2θ = 5–36°, λ = 0.710 73 Å], Z = 2, D_{calc} = 1.583 g cm^{-3}, T = 295 K, needles, 0.8 × 0.2 × 0.08 mm, μ = 0.125 mm^{-1}, F(000) = 328.

Data Collection and Processing.—Stoë STADI-2 two-circle diffractometer, graphite-monochromated Mo-Kα X-radiation, T = 295 K, ω-scans with ω-range (1.0 + 0.5 sin μ/tan θ), 1221 unique reflections ($2\theta_{max}$ 50°, h: −10 to 10, k: 0–10, l: 0–10) giving 1098 with $|F| \geqslant 6\sigma(F)$ for use in all calculations. No significant crystal decay or movement was apparent.

Structure Solution and Refinement.—Automatic direct methods[21] located all non-hydrogen atoms which were then refined anisotropically; hydrogen atoms were located and refined positionally with fixed temperature factors of U = 0.05 Å.^{2} At final convergence, R, R_w = 0.032, 0.041 respectively, S = 1.48 for 243 refined parameters and the final difference synthesis showed no peak or trough outside ±0.2 e Å^{-3}. No extinction or absorption corrections were made. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,51\,|F|^2$ gave satisfactory agreement analyses, and in the final cycle, the maximum shift over error was 0.18. Inlaid[22] atomic scatering factors were used, molecular geometry calculations utilised CALC,[23] and Fig. 1 was produced by PLUTO.[24] The atomic coordinates, bond lengths, and angles, and torsion angles have been deposited at the Cambridge Crystallographic Data Centre. Tables of hydrogen atom coordinates, bond lengths and angles, and torsion angles involving hydrogen, and thermal parameters, have also been deposited with the CCDC.

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References

1 Preliminary communication A. C. Forsyth, R. M. Paton and A. Watt, *Tetrahedron Lett.*, 1989, **30**, 993.
2 *e.g.*, T. Ebata, K. Matsumoto, H. Yoshikoshi, K. Koseki, H. Kawakami and H. Matsushita, *Heterocycles*, 1990, **31**, 423; M. Isobe, Y. Fukuda, T. Nishikaka, P. Chabert, T. Kawai and T. Goto, *Tetrahedron Lett.*, 1990, **31**, 3327; see also Abstracts of ACS Meeting, Washington, 1992, Division of Carbohydrate Chemistry Symposium on 'Chemistry of Levoglucosenone and Levoglucosans.'
3 S. Chew, R. J. Ferrier and V. Sinnwell, *Carbohydr. Res.*, 1988, **174**, 161.
4 F. Shafizadeh, R. H. Furneaux and T. T. Stevenson, *Carbohydr. Res.*, 1979, **71**, 169.
5 A. J. Blake, A. C. Forsyth and R. M Paton, *J. Chem. Soc., Chem. Commun.*, 1988, 440; A. J. Blake, T. A. Cook, A. C. Forsyth, R. O. Gould and R. M. Paton, *Tetrahedron*, 1992, **48**, 8053.
6 P. Bhate and D. Horton, *Carbohydr. Res.*, 1985, **139**, 191.
7 F. Shafizadeh, D. Ward and D. Pang, *Carbohydr. Res.*, 1982, **102**, 217.
8 R. H. Furneaux, G. T. Gainsford, F. Shafizadeh and T. T. Stevenson, *Carbohydr. Res.*, 1986, **146**, 113.
9 M. G. Essig, *Carbohydr. Res.*, 1986, **156**, 225.
10 P. G. Baraldi, A. Barco, S. Bennetti, G. P. Pollini, D. Simoni and V. Zanirato, *Tetrahedron*, 1987, **43**, 4669.
11 A. Bax and R. Freeman, *J. Am. Chem. Soc.*, 1982, **104**, 1099.
12 *e.g.*, C. Morat, F. R. Taravel and M. R. Vignon, *Magn. Reson. Chem.*, 1988, **26**, 264 and references therein.
13 D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 1354.
14 G. A. Jeffrey and Y. J. Park, *Carbohydr. Res.*, 1979, **74**, 1.
15 G. A. Jeffrey, *American Chemical Society Symposium Series*, 1975, vol. 97, p. 1354.
16 C. A. G. Haasnoot, F. A. A. M. DeLeeuw and C. Altona, *Tetrahedron*, 1980, **36**, 2783.
17 M. C. Kloetzel, *J. Am. Chem. Soc.*, 1974, **69**, 2271.
18 E. D. Bergmann, D. Ginsburg and R. Pappo, *Org. React.*, 1954, **10**, 179.
19 A. J. Blake, I. M. Dawson, A. C. Forsyth, R. O. Gould, R. M. Paton and D. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1993, 75.
20 R. H. Furneaux, J. M. Mason and I. J. Miller, *J. Chem. Soc., Perkin Trans. 1*, 1984, 1923.
21 G. M. Sheldrick, SHELX86, Program for Crystal Structure Solution, University of Göttingen, Germany, 1986.
22 G. M. Sheldrick, SHELX76, Program for Crystal Structure Refinement, University of Cambridge, England, 1976.
23 R. O. Gould and P. Taylor, CALC, Program for Molecular Geometry Calculations, University of Edinburgh, Scotland, 1985.
24 W. D. S. Motherwell and W. Clegg, PLUTO, Program for Plotting Molecular and Crystal Structures, University of Cambridge, England, 1978.

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