261. Deoxy-nitrosugars

9th Communication[1])

Chain Elongation of 1-*C*-Nitroglycosyl Halides by Substitution with Some Weakly Basic Carbanions

by **Bernard Aebischer, Roger Meuwly** and **Andrea Vasella***

Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH–8057 Zürich

(8.X.84)

Summary

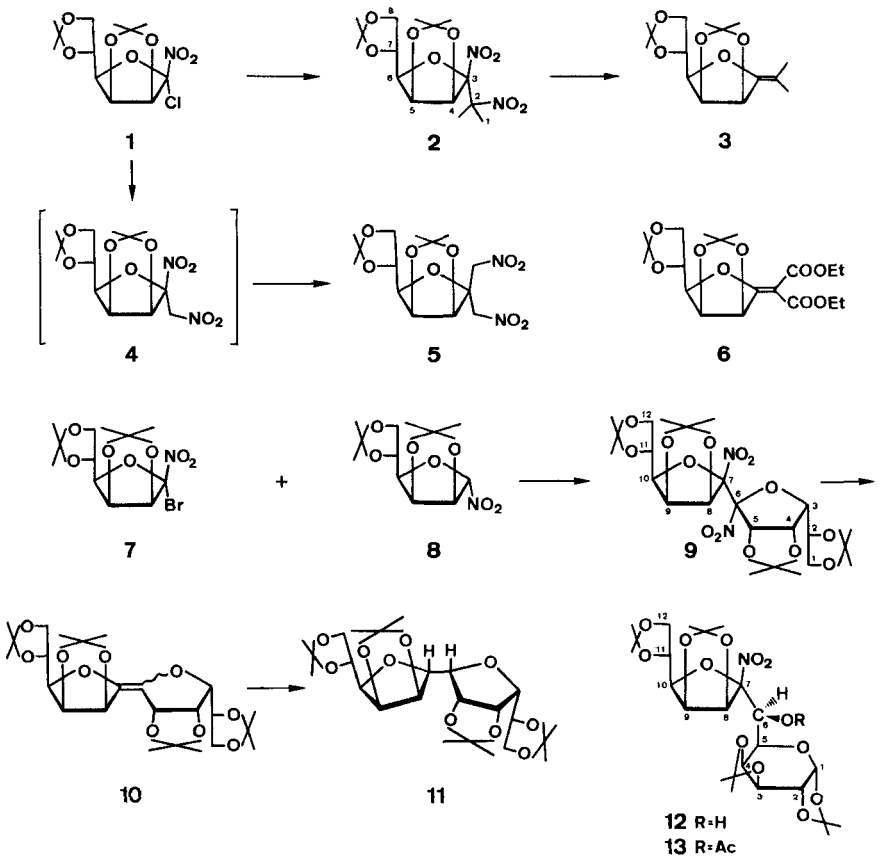
The 1-*C*-nitroglycosyl chloride **1** reacted with the anions from 2-nitropropane, nitromethane, and diethyl malonate, to give the chain-extended products **2** (81%), **5** (72%), and **6** (83%), respectively. Treatment of the 1-*C*-nitroglycosyl bromide **7** by the lithium salt obtained from **8** gave the dodecodiulose derivative **9** (76%). The β-D-configuration of **2** and **9** was inferred from their NMR and CD spectra. Treatment of **2** and **9** with sodium sulfide gave the enol ethers **3** (96%) and **10** (92%), respectively. The (*Z*)-configuration of **10** was deduced from the configuration of its hydrogenation product **11**.

Introduction. – The 1-*C*-nitroglycosyl chlorides [1] and bromides [2] are easily available from sugar oximes. Apart from their transformation into 1-deoxy-1-nitroaldoses [2], little is known about their reactivity, but they might be useful intermediates for the preparation of chain-extended sugars. The halogen substituent in geminal halonitroalkanes can indeed be substituted by various nucleophiles [3–7] by what appears to be a radical-chain mechanism ('$S_{RN}1$ reaction') [8–11], proceeding *via* a nitroalkyl radical. By analogy, 1-alkoxy-1-halo-1-nitroalkanes (halonitro ethers) such as 1-*C*-nitroglycosyl halides may give rise to alkoxynitro radicals which should be more stable than simple nitroalkyl radicals ('captodative stabilization' [12]). They may, therefore, not be suitable for radical chain substitutions. To determine if useful yields of chain extended substitution products can be obtained from halonitro ethers, we examined the reaction of 1-*C*-nitroglycosyl halides with the weakly basic anions derived from nitromethane, 2-nitropropane, diethyl malonate and the 1-deoxy-1-nitroaldose **8** [2].

Results. – Treatment of the protected 1-*C*-nitromannosyl chloride **1** [1] with the potassium salt of 2-nitropropane in DMF under irradiation (60-W lamp) gave the expected vicinal dinitrosugar **2** (81%) as a single diastereoisomer *(Scheme)*. The same compound was obtained in a similar way from the reaction of the sodium salt of **8** with

[1]) 8th Communication: [1].

Scheme



2-chloro-2-nitropropane in DMSO (85%)[2]). Reduction of **2** with Na_2S according to *Kornblum et al.* [13] gave the enol ether **3** (96%), which showed a relatively strong IR band at 1709 cm^{-1}. The reaction of **1** with the potassium salt of nitromethane gave the disubstitution product **5** (72%), presumably *via* the monosubstitution product **4**. This may react further either *via* β-elimination of HNO_2 followed by a *Michael* addition of nitromethane or *via* a radical substitution of the tertiary NO_2-group (*cf.* [14]). A β-elimination product **6** (83%) was obtained from the reaction of **1** with the potassium salt of diethyl malonate [4]. The three compounds **2**, **5**, and **6** thus represent three types of products that may result from monosubstitution, from monosubstitution followed by elimination, or from a (formal) disubstitution. The coupling of two glycosyl moieties was realized by treating the bromonitro derivative **7** with the lithium salt of the 1-deoxy-1-nitromannose **8**. The dimeric nature of the crystalline product **9** (76%) was evident from its mass spectrum which showed a $M^+ - 15$ peak at m/z 561. The configuration of **2** and **9** was inferred from the NMR and CD spectra[3]) (*cf. Table 1* and *2*).

[2]) This experiment was performed by Dr. *S. Mirza.*

[3]) We thank Prof. Dr. G. *Snatzke,* Ruhr-Universität Bochum, for the CD spectra.

Table 1. *Molecular Rotation and Spectroscopic Data of Nitrosugars*

Compound	$[M]_D^{25}$	IR ($\nu_{as}(NO_2)$) [cm^{-1}]	^{1}H-NMR δ [ppm]	^{13}C-NMR δ [ppm]
2	−114.8°	1550 1570	5.83 (*d*, *J* = 5.8, H–C(4)); 4.05–4.3 (*m*, H–C(6))	120.99 C(3)
8	+ 52.9°	1565	5.03 (*d*, *J* = 5.7, H–C(2)); 4.11–4.57 (*m*, H–C(4))	110.54 C(1)
9	+342.5°	1585	5.77 (*d*, *J* = 6.2, H–C(5 and 8)); 4.23 (*dd*, *J* = 9.0, 4.8, H–C(3 and 10))	118.16 C(6 and 7)
12	− 83.2°	1565	5.32 (*d*, *J* = 5.9, H–C(8)); 4.43 (*dd*, *J* = 7.9, 4.5, H–C(10))	108.99–115.75 C(7)
13	− 58.4°	1578	5.12 (*d*, *J* = 6.0, H–C(8)); 4.06–4.25 (*m*, H–C(10))	108.98–115.0 C(7)

Table 2. *CD Spectra of Nitrosugars*

Compound (c [mmol/l] in CH_3CN)	CD λ[nm]	$\Delta\varepsilon$	Compound (c [mmol/l] in CH_3CN)	CD λ[nm]	$\Delta\varepsilon$
2 (1.1)	242	+0.52	**9** (0.7)	241	+1.97
	287	+1.63		283	+5.77
	325	−0.42		326	−0.46
5 (0.9)	222	+0.72	**12** (0.5)	231	+1.37
	270	+0.45		278	+2.09
	317	−0.17		319	−0.61
8 (1.2)	284	+0.77	**13** (0.3)	227	+1.34
				280	+2.55
				317	−0.39

The two glycosyl moieties of **9** are homotopic (single set of signals in the ^{1}H- and ^{13}C-NMR spectrum); hence the two anomeric centers have the same configuration. H–C(4) in **2** and the corresponding H–C(5 and 8) in **9** appear at a very similar chemical shift. A comparison of H–C(2) in **8** and of the corresponding H–C(8) in **12**[4]) shows the previously observed shielding effect of a *cis*-NO_2-group on the vicinal H-atom [2] and a comparison of the H–C(8) signals of **12** and **13** [15] show the shielding effect on H–C(8) of a 1,3-related AcO-group. A similar but inverse (deshielding) effect of the 1,3-related NO_2-groups in **2** and in **9** may account for the extreme chemical shift of H–C(4) in **2** and of H–C(5 and 8) in **9** (corresponding to H–C(2) in **8**), consistent with a β-D-configuration. The NO_2-groups in the vicinal dinitroalkanes prefer a synclinal arrangement [16] [17] ('attractive *gauche* effect'). Vicinal nitro ethers prefer a synclinal arrangement of the NO_2- and the RO-groups [2] [15] [18]; this factor would lead to an antiperiplanar arrangement of the NO_2-groups in the compounds **2** and **9**. Hence, the conformers with a synclinal and with an antiperiplanar arrangement of the two NO_2-groups should be preferred. In the (+)-*sc*- and the *ap*- conformations (**2**), the C(2)-nitro group may adopt a conformation (rotation around the C(2)–N bond) which brings H–C(4) into the deshielding cone of the C(2)-nitro group [19]. Similar considerations hold for compound **9**.

The compounds listed in *Table 2* show very similar CD spectra. The bands at 275–295 nm show a small $\Delta\varepsilon$ for **8** and a much stronger one for the other compounds. Significantly, the $\Delta\varepsilon$ of the dimeric product **9** is approximatively twice as large as the one of the β-D-configurated **12**. The remaining data, while more difficult to interpret are also consistent with a β-D-configuration of **2** and **9**, as expected from a sterically preferred *'exo'*-attack.

[4]) Structure secured by X-ray analysis [15].

Treatment of **9** with Na_2S [13] gave the enediol diether **10** (92%), which again has two homotopic glycosyl moieties. This is consistent with either the (E) or the (*Z*)-configuration, since both diastereoisomers have a C_2 axis. Hydrogenation (Pd/C) of **10** gave **11** (79%)[5]) which had two diastereotopic glycosyl moieties. Although cases are known, where Pd catalysis leads to a *trans*-addition of H_2[6]) [20], we assume a more common *cis*-hydrogenation. The formation of a hydrogenation product with diastereotopic glycosyl moieties is then a proof for the (*Z*)-configuration of **10**, since a *cis*-addition destroys the C_2 axis of (*Z*)-**10**, but not the one of its (*E*)-diastereoisomer.

We thank the *Swiss National Science Foundation* and *Sandoz AG*, Basle, for generous support.

Experimental Part

General. See [21]. Nitromethane, 2-nitropropane and diethyl malonate *(Fluka)* were distilled before use. DMF and DMSO were distilled from CaH_2. ^{1}H-NMR spectra were measured with a *Varian-FT-80A* (80 MHz), a *Varian-EM-390* (90 MHz), or with a *Varian-XL-200* spectrometer (200 MHz). ^{13}C-NMR spectra were recorded at 25.2 MHz with a *Varian XL-100* spectrometer.

*1,2,3-Trideoxy-4,5:7,8-di-*O*-isopropylidene-2-methyl-2,3-dinitro-β-*D*-manno-3-octulofuranose* (**2**). *A.* A solution of 500 mg (1.5 mmol) of **1**, 330 mg (3 mmol) of *t*-BuOK and 270 mg (3 mmol) of 2-nitropropane in 4 ml of dry DMF was stirred and irradiated (60-W lamp, 30 cm from the reaction flask) at 70° under N_2 for 3 h. The mixture was cooled to r.t. and poured into H_2O. Normal workup with EtOAc gave a residue which was purified by flash chromatography (50 g SiO_2, EtOAc/hexane 1:4) yielding 470 mg (81%) of **2** as a colourless solid, which was recrystallized from CH_2Cl_2/hexane. M.p. 174–5°, $[\alpha]_D^{25} = -30.5°$ ($c = 1.06$). IR: 2980*m*, 2935*w*, 2883*w*, 1570*s*, 1550*s*, 1458*w*, 1397*w*, 1374*m*, 1345*m*, 1322*w*, 1248*m*, 1140*s*, 1068*s*, 1042*m*, 987*m*, 970*w*, 953*m*, 883*w*, 854*m*, 838*m*. ^{1}H-NMR (80 MHz): 5.83 (*d*, $J = 5.8$, H–C(4)); 5.03 (*dd*, $J = 5.8$ and 4.5, H–C(5)); 4.68 (*dt*, $J = 7.8$, 4.5 and 4.5, H–C(7)); 4.30–4.05 (*m*, H–C(6), H–C(8) and H′–C(8)); 1.98 (*s*, CH_3); 1.63 (*s*, CH_3); 1.44 (*s*, CH_3); 1.39 (*s*, 3 CH_3). ^{13}C-NMR ((D_6)acetone): 120.99 (*s*); 115.26 (*s*); 109.74 (*s*); 90.49 (*s*); 85.63 (*d*); 83.72 (*d*); 80.52 (*d*); 73.42 (*d*); 66.93 (*t*); 27.08 (*q*); 25.58 (2*q*); 24.54 (*q*); 23.62 (*q*); 22.68 (*q*). MS: 362 (2), 361 (10), 303 (3), 285 (3), 284 (7), 227 (7), 167 (5), 151 (13), 141 (13), 137 (6), 125 (8), 109 (9), 101 (90), 97 (10), 72 (13), 71 (11), 70 (12), 69 (19), 59 (16), 43 (100). Anal. calc. for $C_{15}H_{24}N_2O_9$ (376.37): C 47.86, H 6.43, N 7.43; found: C 48.04, H 6.23, N 7.46.

B[2]). A solution of **8** (300 mg, 1.05 mmol) in dry DMSO (2 ml) was added dropwise to a stirred suspension of NaH (24 mg, 1 mmol) in dry DMSO (4 ml) at 0°, under Ar, and stirred for 15 min. Then, 2-chloro-2-nitropropane (156 mg, 1.26 mmol) was added dropwise to the mixture at 0°. The resulting mixture was irradiated (60-W lamp) and allowed to warm to r.t. within 30 min. Normal workup gave an oil which was chromatographed on silica (EtOAc/hexane 1:2) to furnish 332 mg (85%) of **2** as a white crystalline solid, identical with the sample prepared before.

*3,6-Anhydro-1,2-dideoxy-4,5:7,8-di-*O*-isopropylidene-2-methyl-*D*-manno-oct-2-enitol* (**3**). A solution of 600 mg (1.6 mmol) of **2** and 960 mg (4 mmol) of $Na_2S \cdot 9H_2O$ in 15 ml of dry DMF was stirred and irradiated (60-W lamp) at r.t. for 4 h and then poured into H_2O. Normal workup with EtOAc gave a residue which was purified by chromatography (50 g SiO_2, EtOAc/hexane 1:4) yielding 435 mg (96%) of **3** as a colourless oil, $[\alpha]_D^{25} = +181.7°$ ($c = 0.65$). IR: 2990*m*, 2935*m*, 2885*m*, 1709*w*, 1452*w*, 1382*s*, 1372*s*, 1169*s*, 1148*s*, 1128*s*, 1068*s*, 1029*m*, 970*m*, 953*w*, 941*w*, 882*m*, 868*m*, 840*m*. ^{1}H-NMR (80 MHz): 5.18 (*d*, $J = 6.0$, H–C(4)); 4.71 (*dd*, $J = 6.0$ and 3.8, H–C(5)); 4.40 (*ddd*, $J = 7.2$, 5.6 and 4.7, H–C(7)); 4.20–4.00 (*m*, H–C(8) and H′–C(8)); 3.80 (*dd*, $J = 7.2$ and 3.8, H–C(6)); 1.70 (*s*, CH_3); 1.63 (*s*, CH_3); 1.45 (*s*, 2 CH_3); 1.38 (*s*, 2 CH_3). ^{13}C-NMR: 147.40 (*s*); 112.41 (*s*); 109.03 (*s*); 107.70 (*s*); 81.43 (*d*); 79.04 (*d*); 77.94 (*d*); 73.37 (*d*); 66.56 (*t*); 26.83 (*q*); 26.37 (*q*); 25.42 (*q*); 25.36 (*q*); 18.10 (*q*); 17.02 (*q*). MS: 285 (4), 284 (23), 169 (4), 167 (4), 152 (4), 151 (40), 141 (5), 133 (5), 129 (5), 127 (5), 125 (8), 120 (26), 109 (20), 108 (10), 107 (100), 105 (15), 101 (98), 79 (49), 77 (23), 43 (87). Anal. calc. for $C_{15}H_{24}O_5$ (284.37): C 63.35, H 8.51; found: C 63.43, H 8.30.

---

[5]) In addition to **11**, 21% of a saturated diol was obtained.

[6]) Hydrogenation in the presence of Pt or Rh catalysts was unsuccessful.

*2,5-Anhydro-1-deoxy-3,4:6,7-di-*O*-isopropylidene-1-nitro-2-(nitromethyl)-*D-manno-*heptitol* (**5**). A solution of 500 mg (1.5 mmol) of **1**, 660 mg (6 mmol) of *t*-BuOK and 360 mg (6 mmol) of nitromethane in 4 ml of dry DMF was stirred and irradiated (60-W lamp) at 40° under N_2 for 5 h. After cooling the mixture was poured into H_2O. Normal workup with EtOAc gave a residue which was purified by chromatography (EtOAc/hexane 1:3) yielding 398 mg (72%) of **5**, which was crystallized from CH_2Cl_2/hexane. M.p. 103–104°, $[\alpha]_D^{25} = +43.9°$ ($c = 1.35$). IR: 3020*w*, 2980*m*, 2937*m*, 2882*w*, 1558*s*, 1450*w*, 1430*w*, 1412*m*, 1375*s*, 1335*w*, 1250*m*, 1155*m*, 1112*m*, 1090*s*, 1063*s*, 1025*m*, 995*w*, 970*m*, 939*w*, 912*w*, 878*m*, 853*m*, 838*m*. ^{1}H-NMR (200 MHz): 5.08 and 4.67 (*AB*, $J = 12.3$, 2H); 4.96 (*dd*, $J = 5.8$ and 3.6, H–C(4)); 4.94 and 4.72 (*AB*, $J = 15.5$, 2H); 4.73 (*d*, $J = 5.8$, H–C(3)); 4.37 (*ddd*, $J = 8.0$, 6.0 and 4.4, H–C(6)); 4.03 (*dd*, $J = 9.0$ and 6.0, H–C(7)); 3.95 (*dd*, $J = 8.0$ and 3.6, H–C(5)); 3.90 (*dd*, $J = 9.0$ and 4.4, H′–C(7)). ^{13}C-NMR: 113.81 (*s*); 109.46 (*s*); 83.60 (*d*); 81.99 (*s*); 81.13 (*d*); 80.62 (*d*); 74.44 (*t*); 72.82 (*t*); 72.35 (*d*); 66.81 (*t*); 26.73 (*q*); 25.42 (*q*); 25.04 (*q*); 24.04 (*q*). MS: 348 (6), 347 (34), 213 (2), 200 (3), 153 (3), 145 (7), 139 (29), 123 (3), 115 (4), 111 (4), 102 (4), 101 (53), 69 (12), 59 (12), 55 (11), 43 (100). Anal. calc. for $C_{14}H_{22}N_2O_9$ (362.3): C 46.40, H 6.12, N 7.72; found: C 46.28, H 5.94, N 7.45.

*Ethyl 3,6-Anhydro-2-deoxy-2-(ethoxycarbonyl)-4,5:7,8-di-*O*-isopropylidene-*D-manno-*oct-2-enonate* (**6**). A solution of 1 g (3 mmol) of **1**, 1 g (9 mmol) of *t*-BuOK and 144 mg (9 mmol) of diethyl malonate in 8 ml of dry DMF was stirred and irradiated (60-W lamp) under N_2 at r.t. for 5 h. The mixture was then poured into H_2O. Normal workup with EtOAc gave a residue which was purified by chromatography (100 g SiO_2, EtOAc/hexane 1:3) yielding 1.01 g (83%) of **6**, which was crystallized from CH_2Cl_2/hexane. M.p. 92–93°, $[\alpha]_D^{25} = +219°$ ($c = 1.18$). IR: 2985*m*, 2936*m*, 2900*w*, 1720*s*, 1648*m*, 1470*w*, 1463*w*, 1452*w*, 1445*w*, 1383*s*, 1372*s*, 1340*m*, 1300*s*, 1275*s*, 1186*s*, 1153*m*, 1123*s*, 1090*s*, 1070*s*, 1052*s*, 1040*m*, 968*m*, 953*m*, 922*w*, 892*m*, 868*m*, 840*m*. ^{1}H-NMR (200 MHz): 5.78 (*d*, $J = 5.6$, H–C(4)); 4.86 (*dd*, $J = 5.6$ and 3.8, H–C(5)); 4.52 (*ddd*, $J = 7.4$, 5.5 and 4.5, H–C(7)); 4.40–4.05 (*m*, 7H); 1.45 (*s*, CH_3); 1.44 (*s*, CH_3); 1.41 (*s*, CH_3); 1.39 (*s*, CH_3); 1.29 (*t*, CH_3); 1.28 (*t*, CH_3). ^{13}C-NMR: 170.76 (*s*); 164.01 (*s*); 163.93 (*s*); 113.53 (*s*); 109.50 (*s*); 103.70 (*s*); 84.52 (*d*); 81.06 (*d*); 76.91 (*d*); 72.76 (*d*); 66.10 (*t*); 60.80 (*t*); 26.77 (*q*); 25.88 (*q*); 25.30 (*q*); 14.12 (*q*); 14.01 (*q*). MS: 385 (12), 355 (4), 293 (3), 285 (5), 253 (7), 239 (18), 196 (10), 187 (6), 101 (58), 98 (5), 87 (10), 69 (14), 59 (15), 43 (100). Anal. calc. for $C_{19}H_{28}O_9$ (400.45): C 56.99, H 7.05; found: C 57.22, H 7.21.

*6,7-Dideoxy-1,2:4,5:8,9:11,12-tetra-*O*-isopropylidene-6,7-dinitro-*α*-*D*-manno-*β*-*D*-manno-dodeco-3,6-furano-6,7-diulo-7,10 furanose* (**9**). A solution of 578 mg (2 mmol) of 1-deoxy-2,3:5,6-di-O-isopropylidene-1-nitro-α-D-mannofuranose [2] in 6 ml of MeOH was treated with freshly prepared LiOMe (1.1M in MeOH, 2 ml). After concentration and drying under high vacuum for 2 h, the residue was again taken up in 8 ml of dry DMSO and treated under N_2 with 736 mg (2 mmol) of 7 in 8 ml of dry DMSO. The mixture was stirred at r.t., irradiated (60-W lamp) for 2 h and then poured into H_2O. Normal workup with EtOAc gave a residue which was purified by chromatography (30 g SiO_2, EtOAc/hexane 1:3) yielding **9** which was crystallized from CH_2Cl_2/hexane to give 995 mg of **9** which contained CH_2Cl_2 (m.p. 218–220° with loss of solvent at 130°). The CH_2Cl_2 was eliminated by heating at 80°/0.01 Torr to give 876 mg (76%) of **9**. M.p. 219–220°, $[\alpha]_D^{25} = +59.4°$ (c = 1.2). IR: 3000*s*, 2955*m*, 2900*w*, 1585*s*, 1485*w*, 1469*m*, 1440 (sh), 1385*s*, 1379*s*, 1370 (sh), 1355 (sh), 1329*m*, 1160*s*, 1155 (sh), 1130*s*, 1075*s*, 1049*m*, 1032*m*, 991*s*, 890*m*, 870*m*. ^{1}H-NMR (90 MHz): 5.77 (*d*, $J = 6.2$, H–C(5) and H–C(8)); 5.13 (*dd*, $J = 6.2$ and 4.8, H–C(4) and H–C(9)); 4.73 (*ddd*, $J = 9.0$, 5.4 and 4.5, H–C(2) and H–C(11)); 4.23 (*dd*, $J = 9.0$ and 4.8, H–C(3) and H–C(10)); 4.19 (*dd*, $J = 9.1$ and 5.4, H–C(1) and H–C(12)); 4.07 (*dd*, $J = 9.1$ and 4.5, H′–C(1) and H′–C(12)); 1.44 (*s*, 2 CH_3); 1.40 (*s*, 6 CH_3). ^{13}C-NMR: 118.16 (*s*); 116.10 (*s*); 109.78 (*s*); 86.24 (*d*); 85.00 (*d*); 79.75 (*d*); 72.29 (*d*); 66.70 (*t*); 27.05 (*q*); 25.23 (2*q*); 24.37 (*q*). MS: 563 (5), 562 (20), 561 (80), 485 (6), 484 (6), 442 (6), 400 (13), 155 (8), 141 (8), 102 (6), 101 (100), 98 (5), 97 (7), 85 (6), 81 (6), 73 (5), 72 (9), 69 (8), 59 (9), 43 (32). Anal. calc. for $C_{24}H_{36}N_2O_{14}$ (576.55): C 50.00, H 6.29, N 4.86; found: C 50.04, H 6.30, N 4.86.

*3,6:7,10-Dianhydro-1,2:4,5:8,9:11,12-tetra-*O*-isopropylidene-*D-manno-D-manno-*docec-6-enitol* (**10**). A solution of 576 mg (1 mmol) of **9** and 600 mg (2.5 mmol) of $Na_2S \cdot 9H_2O$ in 10 ml of dry DMF was irradiated (60 W lamp) at r.t. for 6 h and then poured into H_2O. Normal workup with EtOAc and drying of the residue afforded 487 mg of crystalline product. Recrystallization from CH_2Cl_2/hexane and chromatography of the mother-liquor gave 446 mg (92%) of **10**. M.p. 262–264°, $[\alpha]_D^{25} = +288.4°$ ($c = 1.0$). IR: 3000*s*, 2950*m*, 2900*m*, 1748*w*, 1481*w*, 1457*m*, 1386*s*, 1376*s*, 1321*w*, 1290 (sh), 1160*s*, 1120*s*, 1070*s*, 990 (sh), 972*s*, 968 (sh), 940*m*, 920*m*, 885*m*, 867*s*. ^{1}H-NMR (90 MHz): 5.42 (*d*, $J = 5.7$, H–C(5) and H–C(8)); 4.80 (*dd*, $J = 5.7$ and 3.7, H–C(4) and H–C(9)); 4.47 (*ddd*, $J = 7.8$, 5.5 and 4.4, H–C(2) and H–C(11)); 4.13 (*d*, $J = 5.0$, $H_2C(1)$ and $H_2C(12)$); 3.97 (*dd*, $J = 7.8$ and 3.7, H–C(3) and H–C(10)); 1.47 (*s*, 2 CH_3); 1.43 (*s*, 2 CH_3); 1.39 (*s*, 4 CH_3). ^{13}C-NMR: 135.21 (*s*); 113.09 (*s*); 109.29 (*s*); 82.94 (*d*); 78.89 (*d*); 78.28 (*d*); 73.02 (*d*); 66.66 (*t*); 26.98 (*q*); 25.71 (*q*); 25.26 (*q*). MS: 486 (6), 485 (31), 484 (100), 469 (15), 411 (6), 293 (5), 156 (6), 151 (5), 127 (5), 126 (8), 101 (36), 99 (6), 98 (10), 72 (5), 59 (6), 43 (7). Anal. calc. for $C_{24}H_{36}O_{10}$ (484.54): C 59.49, H 7.49; found: C 59.30, H 7.57.

3,6:7,10-Dianhydro-1,2:4,5:8,9:11,12-tetra-O-*isopropylidene*-β-D-manno-β-D-manno-*dodecitol* (**11**). A mixture of 484 mg (1 mmol) of **10** (finely powdered) and 25 mg of 10% Pd/C in 25 ml of EtOH was stirred under H_2 for 14 h. After filtration on *Celite*, the filtrate was concentrated and the residue was purified by chromatography (30 g SiO_2, EtOAc/$CHCl_3$ 1:9) to afford 383 mg (79%) of **11** as a colourless foam, $[\alpha]_D^{25} = -21.6°$ ($c = 0.9$). IR: 3000*s*, 2945*m*, 2890*m*, 1605*w*, 1482*w*, 1458*m*, 1389*s*, 1379*s*, 1355 (sh), 1168*s*, 1153 (sh), 1120*s*, 1070*s*, 996 (sh), 980*m*, 960*w*, 952*w*, 898*m*, 865*m*. ^{1}H-NMR (90 MHz): 5.02 (*d*, $J = 6.1$, H–C(5)); 4.85–4.60 (*m*, 3H); 4.53–4.27 (*m*, 3H); 4.21–4.00 (*m*, 4H); 3.90 (*dd*, $J = 7.1$ and 3.6, 1H); 3.67–3.47 (*m*, 2H); 1.50, 1.43, 1.37 and 1.33 (4*s*, 24H). ^{13}C-NMR: 112.59 (*s*); 112.18 (*s*); 108.92 (2*s*); 82.96 (*d*); 81.93 (2*d*); 80.98 (*d*); 80.84 (2*d*); 79.98 (*d*); 73.47 (*d*); 72.95 (*d*); 66.81 (*t*); 66.46 (*t*); 27.01 (*q*); 26.86 (*q*); 26.06 (*q*); 25.31 (2*q*); 25.10 (*q*); 24.53 (*q*); 23.94 (*q*). MS: 473 (3), 472 (5), 471 (21), 414 (3), 413 (3), 219 (5), 205 (4), 193 (5), 185 (5), 177 (5), 155 (5), 127 (10), 123 (11), 101 (57), 97 (11), 95 (11), 86 (60), 85 (13), 84 (100), 83 (16), 81 (15), 73 (14), 71 (10), 69 (22), 57 (14), 51 (37). Anal. calc. for $C_{24}H_{38}O_{10}$ (486.56): C 59.25, H 7.87; found: C 59.09, H 7.77.

REFERENCES

[1] *R. Meuwly & A. Vasella*, Helv. Chim. Acta *67*, 1568 (1984).
[2] *B. Aebischer, A. Vasella & H.P. Weber*, Helv. Chim. Acta *65*, 621 (1982).
[3] *G.A. Russell, R.K. Norris & E.J. Panek*, J. Am. Chem. Soc. *93*, 5839 (1971).
[4] *R. Beugelmans, A. Lechevallier & H. Rousseau*, Tetrahedron Lett. *24*, 1787 (1983).
[5] *G.A. Russell & J. Hershberger*, J. Chem. Soc., Chem. Commun. *1980*, 216.
[6] *W.R. Bowman & G.D. Richardson*, Tetrahedron Lett. *22*, 1551 (1981).
[7] *G.A. Russell, M. Jawdosink & M. Mahosza*, J. Am. Chem. Soc. *101*, 2355 (1979).
[8] *N. Kornblum*, Angew. Chem. *87*, 797 (1975).
[9] *R.K. Norris & R.J. Smyth-King*, Tetrahedron *38*, 1051 (1982).
[10] *G.A. Russell, M. Jawdosink & F. Ros*, J. Am. Chem. Soc. *101*, 3378 (1979).
[11] *M.C.R. Symons & W.R. Bowman*, Tetrahedron Lett. *22*, 4549 (1981).
[12] *H.G. Viehe, R. Merenyi, L. Stehle & Z. Janousek*, Angew. Chem. *91*, 982 (1979).
[13] *N. Kornblum, S.D. Boyd, H.W. Pinnick & R.G. Smith*, J. Am. Chem. Soc. *93*, 4316 (1971).
[14] *N. Kornblum & A.S. Erickson*, J. Org. Chem. *46*, 1037 (1981).
[15] *B. Aebischer, J. Bieri, R. Prewo & A. Vasella*, Helv. Chim. Acta *65*, 2251 (1982).
[16] *A.O. Diallo*, Spectrochim. Acta, Part A *30A*, 1505 (1974).
[17] *Y. Kai, P. Knochel, S. Kwiatkowsky, J.D. Dunitz, J.F.M. Oth, D. Seebach & H.O. Kalinowski*, Helv. Chim. Acta *65*, 137 (1982).
[18] *C.A. Kingsbury, A.E. Sopchik, G. Underwood & S. Rajan*, J. Chem. Soc., Perkin Trans. 2 *1982*, 867.
[19] *G. Kresze, N.M. Mayer & J. Winkler*, Justus Liebigs Ann. Chem. *747*, 172 (1971).
[20] *H.O. House*, in 'Modern Synthetic Reactions', 2nd edn., W.A. Benjamin, Menlo Park, p. 19.
[21] *B. Aebischer, H. Hanssen, A. Vasella & W. Schweizer*, J. Chem. Soc., Perkin Trans. 1 *1982*, 2139.