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Note

Synthesis of branched-chain sugars with methiniminium salts

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Branched-chain sugars have been found in many types of antibiotics[1]. Synthesis of branched-chain monosaccharides can be achieved by the reaction of carbon nucleophiles with suitable uloses[2–5], sugar oxiranes[6,7], and unsaturated sugars[8,9]. Recently, stereocontrolled radical reactions have been used increasingly for this purpose[10,11]. There are only a few examples in the literature reporting electrophilic reactions on carbohydrates, to form branches[12–14].

Following our own investigations on the reaction of deoxyhexopyranosiduloses with carbon disulfide[15], we now describe a method for the preparation of monosaccharides with an exocyclic C_3-unit by using β-chlorovinylmethiniminium perchlorates. The resulting sugar derivatives, with push–pull functionality[16,17], may serve as precursors for the synthesis of potential biologically active monosaccharides bearing an amino group in the branching.

The readily accessible β-chlorovinylmethiniminium perchlorates[18] can be attacked easily by nucleophiles at C-1. Thus, the reaction with acidic CH compounds in the presence of a base yields push–pull-butadienes[18,19] or push–pull-hexatrienes[20].

Following this idea, the hexopyranosiduloses **2** and **7** were treated with 3-chloro-3-phenylprop-2-enylidenedimethyliminium perchlorate (**1**) at low temperatures.

By using BuLi as a proton acceptor (see Table I), the preferred reaction, unfortunately, was a nucleophilic attack on the carbonyl function by the butyl group of the base. The NMR data confirmed the formation of compounds **5**, **6**, and **10**, respectively. Only **5** had been mentioned in the literature[21] until now, but the description of it was incomplete. To yield the butyl branched-chain sugars exclusively, **2** and **7** were each treated with only BuLi at −40°C in THF. In the case of

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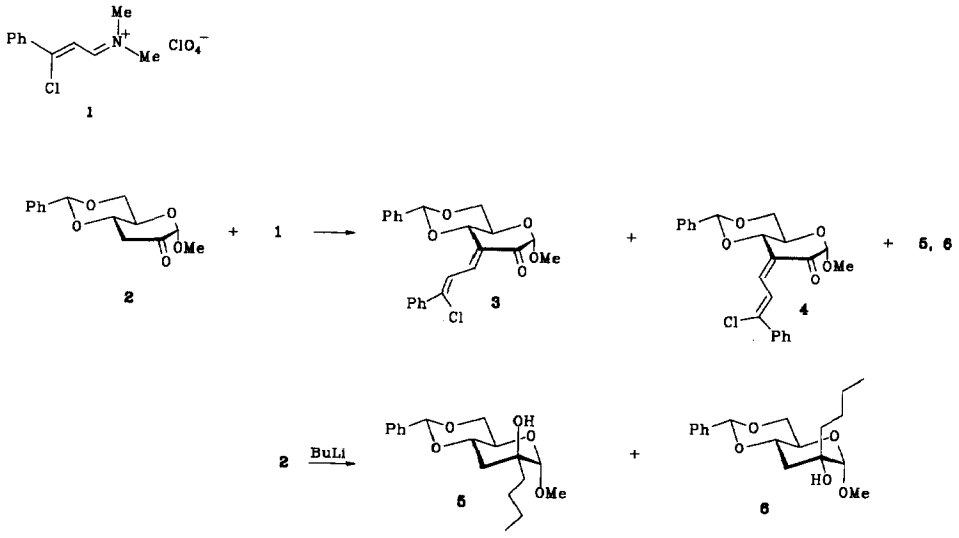
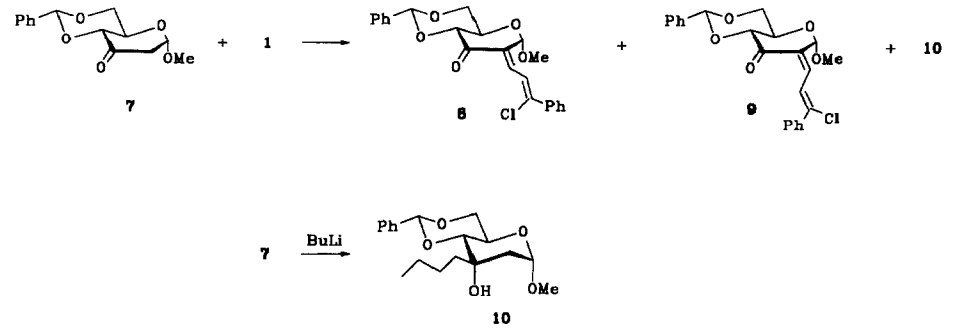


Scheme 1.

2, besides some starting material, the *C*-butyl derivatives **5** and **6** could be separated in a ratio of 3.1 : 1 (total yield 65.1%). As expected, the product with an axially arranged OH function was formed in excess. After shaking with D_2O, the chemical resonances of the OH signals, which were visible only in Me_2SO-d_6, could be determined unequivocally. The OH signal of **5** appeared at higher field (δ 4.51) compared with that of **6** (δ 4.65). Consequently, **5** bears an axially orientated OH function and **6** an equatorial one. In contrast to this, in the reaction of **7** with BuLi, only one product was formed and it seems probable that the butyl group adopts the equatorial position.

It was not possible to suppress this undesired reaction by metal exchange[13] (conversion of the Li enolate into the Zn enolate). The problems were solved by



Scheme 2.

TABLE I

Reaction [a] of the hexopyranosiduloses **2** and **7** with the β-chlorovinylmethiniminium perchlorate **1**

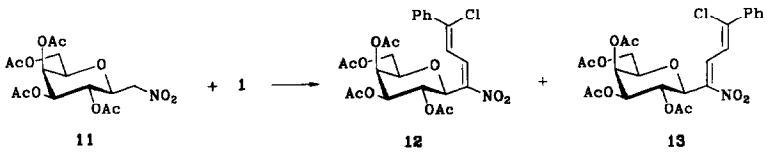
Ulose	Base	Solvent	Products (% yield)	(*E*):(*Z*)
2	BuLi	THF	**3**, **4** (19.2) [b]	2:1
			5, **6** (55.0) [c]	
2	DBU	DMF	**3**, **4** (36.2) [b]	2.8:1
2	LDA	THF	**3**, **4** (19.2) [b]	1.8:1
7	BuLi	THF	**8**, **9** (17.7) [b]	2.9:1
			10 (40.6)	
7	DBU	DMF	**8**, **9** (42.0) [b]	1.1:1

[a] Compound **1** and the base were always added 1.1 molar; temperature, −40°C. [b] Total yield [(*E*)+(*Z*) product]. [c] Total yield.

use of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a bulky, non-nucleophilic base; **2** and **7** then yielded in the reaction with the β-chlorovinylmethinimonium perchlorate **1**, the expected chloropropenylidenehexopyranosiduloses. Lithium diisopropylamide (LDA) as base gave poorer results (Table I). The (*E*)–(*Z*)-mixtures of **3**, **4** and **8**, **9**, respectively, could be separated by column chromatography. No byproducts, besides decomposed material, could be detected.

Mass spectroscopic investigations of these compounds confirmed the formation of (*E*)–(*Z*)-isomers due to the observed identical $[M + H]^+$ peaks of *m/z* 413. For the analysis of configurations, NOE experiments on H-1′ and H-2′ worked as a powerful tool. Due to the observable $^4J_{1',4}$ or $^4J_{1',1}$ coupling constants, the H-1′ and H-2′ resonances of **3** (H-1′, δ 7.88; H-2′, δ 7.79), **4** (H-1′, δ 7.21; H-2′, δ 7.94; solvent $CDCl_3$–Me_2SO-d_6), **8** (H-1′, δ 7.89; H-2′, δ 6.85), and **9** (H-1′, δ 7.06; H-2′, δ 7.99) could be assigned. For the unambiguous assignment of the other ^1H and ^{13}C signals, ^{13}C–^1H COSY measurements were necessary. When the H-2′ resonances of **3**, **4**, **8**, and **9** were saturated, each of the resulting spectra showed an increased signal in the region of the aromatic resonances. Thus, it could be concluded that the substituents at the double bond beginning at C-2′ are always arranged in a (*Z*) configuration. Since the ^{13}C NMR spectrum of **1** showed only one isomer, the starting compound already existed in this configuration.

Likewise, a strong NOE for the H-1 signals of **8** and **9** was observed by irradiation at H-2′ (compound **8**) and H-1′ (compound **9**), respectively. As the only possible conclusion, we formulate for **9** the (*Z*) and for **8** the (*E*) configuration for the substituents attached at the C-2–C-1′ double bond. ^1H NMR measurements of **4** in $CDCl_3$ did not allow the assignment of the δ value for H-1′ since this signal was hidden by aromatic resonances. After the addition of some Me_2SO-d_6, the H-1′ signal was shifted upfield out of the aromatic area and could be identified. Unfortunately, selective irradiation of the H-1′ resonances in **3** and **4** showed no enhancement of the H-4 signals and consequently no information was available about the stereochemistry at the exocyclic double bond. Due to deshielding by the neighbouring carbonyl group, we found in the side chain of **8** and **9** that the



Scheme 3.

hydrogen atom which points in the direction of the carbonyl group (H-1′ in **8** and H-2′ in **9**) resonated approximately 1 ppm downfield compared with the other hydrogen atom of the branching (compound **8**: H-1′, δ 7.89; H-2′, δ 6.85; compound **9**: H-2′, δ 7.99; H-1′, δ 7.06). This effect was also observed for **3** and **4**; the side chain of **3** showed a downfield shifting of H-1′ (H-1′, δ 7.88; H-2′, δ 7.79) and compound **4** showed a downfield-shifted signal for H-2′ (H-2′, δ 8.02; H-1′, δ 7.38–7.46). Therefore, the side chain of **3** must have a 3(*E*)–2′(*Z*) and that of **4** a 3(*Z*)–2′(*Z*) configuration.

The β-chlorovinylmethiniminium perchlorate **1** can also be used for a C_3 extension of sugar chains. In preliminary experiments, the anhydronitroheptitol **11** was treated with **1** in the presence of DBU, yielding an (*E*)–(*Z*) mixture of the anhydronitrodecenitols **12** and **13** (39%), which was not separated.

EXPERIMENTAL

General methods.—Melting points were determined on a Leitz SM Lux microscope. Optical rotations were measured with a Perkin–Elmer 241 MC polarimeter (10-cm cell). All reactions were monitored by TLC on Silica Gel 60 F_{254} (Merck) with detection by charring with sulfuric acid. Column chromatography was performed as flash chromatography on Silica Gel 60 (Merck 230–400 mesh). NMR spectra ($CDCl_3$, internal Me_4Si) were recorded with a Bruker AC 300 and a Bruker WM 300 spectrometer (^1H, 300 MHz; ^{13}C, 75.5 MHz). 2D experiments and *N*OE measurements were performed by means of a Bruker program on the AC 300. Mass spectra were obtained with a Varian MAT 311 A spectrometer (CI, isobutane). The reported MH^+ ions of the chlorine-containing compounds are those due to the ^{35}Cl isotope.

*Methyl 4,6-O-benzylidene-3[(1E,2Z)-3-chloro-3-phenylprop-2-enylidene]-3-deoxy-α-*D-erythro-*hexopyranosid-2-ulose* (**3**) *and methyl 4,6-O-benzylidene-3-[(1Z,2Z)-3-chloro-3-phenylprop-2-enylidene]-3-deoxy-α-*D-erythro-*hexopyranosid-2-ulose* (**4**).—To a solution of methyl 4,6-*O*-benzylidene-3-deoxy-α-D-*erythro*-hexopyranosid-2-ulose[22] (**2**; 350 mg, 1.32 mmol) and 3-chloro-3-phenylprop-2-enylidenedimethyliminium perchlorate (**1**; 427 mg, 1.45 mmol) in anhydrous DMF (5 mL) at −40°C was added DBU (221 mg, 1.45 mmol). After stirring for 3 h at this temperature, the reaction was quenched by the rapid addition of satd aq NH_4Cl. Then the mixture was poured into water (50 mL) and extracted with $CHCl_3$ (3 × 20 mL).

The combined extracts were washed with water (3 × 15 mL), dried (Na_2SO_4), and concentrated. Column chromatography (benzene) of the solid residue yielded three main products with R_f values of 0.36, 0.22, and 0.15 (starting material **2**, 35 mg, 10.0%). The component with R_f 0.22 could be identified by NMR as **3** (146 mg, 26.7%): yellow needles, mp 212–215°C, $[\alpha]_D^{20}$ −278° (*c* 1.01, $CHCl_3$). NMR data: ^1H, δ 3.53 (s, 3 H, OCH_3), 3.90 (dd, 1 H, $J_{5,6a}$ 10.2, $J_{6a,6e}$ 10.4 Hz, H-6a), 4.29 (ddd, 1 H, H-5), 4.45 (dd, 1 H, $J_{5,6e}$ 5.0 Hz, H-6e), 4.79 (dd, 1 H, $J_{4,5}$ 9.8, $J_{4,1'}$ 2.5 Hz, H-4), 4.79 (s, 1 H, H-1), 5.72 (s, 1 H, PhC*H*), 7.21–7.60 (m, 10 H, 2 Ph), 7.79 (d, 1 H, $J_{1',2'}$, 11.6, Hz H-2'), 7.88 (dd, 1 H, H-1'); NOE: enhancement of the intensity during irradiation at δ 7.79, δ 7.44; ^{13}C, δ 56.2 (OCH_3), 63.2 (C-5), 69.4 (C-6), 79.2 (C-4), 99.8 (C-1), 101.6 (Ph*C*H), 121.4 (C-2'), 131.5 (C-3'), 135.2 (C-1'), 126.3, 126.8, 128.4, 129.3, 130.0, 137.0, 137.1 (2 Ph), 143.5 (C-3), 191.0 (C-2). Mass spectrum: *m/z* 413 $[M + H]^+$. Anal. Calcd for $C_{23}H_{21}ClO_5$ (412.9): C, 66.91; H, 5.13. Found: C, 66.91; H, 4.96.

The product with R_f 0.36 was **4** (52 mg, 9.5%): yellow needles, mp 165–167°C, $[\alpha]_D^{20}$ −117° (*c* 1.01, $CHCl_3$). NMR data: ^1H ($CDCl_3$–Me_2SO-d_6), δ 3.51 (s, 3 H, OCH_3), 3.91 (dd, 1 H, $J_{5,6a} = J_{6a,6e}$ = 10.2 Hz, H-6a), 4.10 (ddd, 1 H, H-5), 4.40 (dd, 1 H, $J_{5,6e}$ 4.9 Hz, H-6e), 4.60 (dd, 1 H, $J_{4,5}$ 9.6 $J_{4,1'}$ 2.4 Hz, H-4), 4.75 (s, 1 H, H-1), 5.76 (s, 1 H, PhC*H*), 7.30 (dd, 1 H, $J_{1',2'}$ 11.2 Hz, H-1'), 7.36–7.74 (m, 10 H, 2 Ph), 7.94 (d, 1 H, H-2'); NOE: enhancement of the intensity during irradiation at δ 7.94, δ 7.72; ^1H $CDCl_3$), δ 3.53 (s, 3 H, OCH_3), 3.86 (dd, 1 H, $J_{5,6a} = J_{6a,6e}$ = 10.2 Hz, H-6a), 4.20 (ddd, 1 H, H-5), 4.45 (dd, 1 H, $J_{5,6e}$ 4.9 Hz, H-6e), 4.53 (dd, 1 H, $J_{4,5}$ 9.6, $J_{4,1}$, 2.4 Hz, H-4), 4.75 (s, 1 H, H-1), 5.73 (s, 1 H, PhC*H*), 7.38–7.46 (dd, 1 H, H-1'), 7.38–7.76 (m, 10 H, 2 Ph), 8.02 (d, 1 H, $J_{1',2'}$ 11.2 Hz, H-2'); ^{13}C ($CDCl_3$), δ 56.2 (OCH_3), 63.7 (C-5), 69.3 (C-6), 78.7 (C-4), 100.6 (C-1), 101.4 (Ph*C*H), 121.3 (C-2'), 131.5 (C-1'), 132.8 (C-3'), 126.3, 127.1, 128.4, 128.5, 129.2, 129.9. 137.0, 137.1 (2 Ph), 142.8 (C-3), 192.0 (C-2). Mass spectrum: *m/z* 413 $[M + H]^+$. Anal. Calcd for $C_{23}H_{21}ClO_5$ (412.9): C, 66.91; H, 513. Found: C, 66.81; H, 4.89.

*Methyl 4,6-O-benzylidene-2-C-butyl-3-deoxy-α-*D-arabino-*hexopyranoside* (**5**) *and methyl 4,6-O-benzylidene-2-C-butyl-3-deoxy-α-*D-ribo-*hexopyranoside* (**6**).—Compound **2** (350 mg, 1.32 mmol) was dissolved in ahyd THF (15 mL) and a solution of butyllithium in hexane (1.6 M, 1.0 mL, 1.6 mmol) was added under Ar with stirring at −40°C. After stirring for 3 h at this temperature, the reaction mixture was worked up following the procedure described for **3**. Column chromatography (benzene–EtOAc, 13 : 1) of the syrupy residue gave two new products besides some starting material (R_f 0.39, 80 mg, 22.9%). The product with R_f 0.35 was **5** (211 mg, 49.4%): syrup, $[\alpha]_D^{20}$ +28° (*c*, 1.04, $CHCl_3$). NMR data: ^1H (Me_2SO-d_6), δ 0.90 (t, 3 H, $J_{3',4'}$ 6.9 Hz, H-4'), 1.21–1.64 (m, 6 H, H-1', 2', 3'), 1.72 (dd, 1 H, $J_{3a,3e}$ 11.5, $J_{3a,4}$ 11.4 Hz, H-3a), 1.86 (dd, 1 H, $J_{3e,4}$ 4.0 Hz, H-3e), 3.35 (s, 3 H, OCH_3), 3.47–3.66 (m, 2 H, H-4,5), 3.72 (dd, 1 H, $J_{5,6a} = J_{6a,6e}$ = 10.0 Hz, H-6a), 4.12 (dd, 1 H, $J_{5,6e}$ 4.2 Hz, H-6e), 4.20 (s, 1 H, H-1), 4.51 (s, 1 H, OH), 5.59 (s, 1 H, PhC*H*), 7.32–7.45 (m, 5 H, Ph); ^{13}C, δ 14.0 (C-4'), 23.1 (C-3'), 24.6 (C-2'), 35.9, 36.6 (C-3, C-1'), 55.3 (OCH_3), 64.4 (C-5), 69.4 (C-6), 72.2 (C-2), 75.8 (C-4), 101.8 (C-1), 102.6

(PhCH), 126.2, 128.2, 129.0, 137.4 (Ph). Mass spectrum: m/z 422 $[M + H]^+$. Anal. Calcd for $C_{18}H_{26}O_5$ (322.4): C, 67.06; H, 8.17. Found: C, 66.63; H, 7.89.

The component with R_f 0.19 was **6** (67 mg, 15.7%): white solid, mp 121–124°C, $[\alpha]_D^{20}$ +79° (c 1.00, $CHCl_3$). NMR data: ^1H (Me_2SO-d_6), δ 0.84 (t, 3 H, $J_{3',4'}$ 6.8 Hz, H-4'), 1.18–1.48 (m, 6 H, H-1',2',3'), 1.54 (dd, 1 H, $J_{3a,3e} = J_{3a,4} = 11.9$ Hz, H-3a), 1.84 (dd, 1 H, $J_{3e,4}$ 4.2 Hz, H-3e), 3.33 (s, 3 H, OCH_3), 3.54 (ddd, 1 H, $J_{4,5}$ 5.2 Hz, H-5), 3.74 (dd, 1 H, $J_{5,6a} = J_{6a,6e} = 10.2$ Hz, H-6a), 3.97 (ddd, 1 H, H-4), 4.15 (dd, 1 H, $J_{5,6e}$ 4.8 Hz, H-6e), 4.24 (s, 1 H, H-1), 4.65 (s, 1 H, OH), 5.61 (s, 1 H, PhC*H*), 7.34–7.46 (m, 5 H, Ph); ^{13}C, δ 12.6 (C-4'), 21.7 (C-3'), 22.6 (C-2'), 35.0, 36.8 (C-3, C-1'), 53.7 (OCH_3), 63.1 (C-5), 68.0 (C-6), 72.6 (C-2), 73.9 (C-4), 100.6 (C-1), 101.5 (PhCH), 124.8 126.9, 127.6, 136.2 (Ph). Mass spectrum: m/z 422 $[M + H]^+$. Anal. Calcd for $C_{18}H_{26}O_5$ (322.4): C, 67.06; H, 8.17. Found: C, 66.98; H, 8.11.

*Methyl 4,6-*O*-benzylidene-2-[(1*E*,2*Z*)-3-chloro-3-phenylprop-2-enylidene]-2-deoxy-α-*D*-*erythro*-hexopyranosid-3-ulose* (**8**) *and methyl 4,6-*O*-benzylidene-2-[(1*Z*,2*Z*)-3-chloro-3-phenylprop-2-enylidene]-2-deoxy-α-*D*-*erythro*-hexopyranosid-3-ulose* (**9**).—Methyl 4,6-*O*-benzylidene-2-deoxy-α-*D*-*erythro*-hexopyranosid-3-ulose[23] (**7**; 350 mg, 1.32 mmol) was treated with **1** (427 mg, 1.45 mmol) and DBU (221 mg, 1.45 mmol) as described above for **3**. After column chromatography (benzene – EtOAc, 80:1), three main products were obtained with R_f 0.35, 0.24, and 0.10 (starting material **7**, 72 mg, 20.5%). The product with R_f 0.24 was identified as **8** (121 mg, 22.1%): yellow needles, mp 185°C (dec), $[\alpha]_D^{20}$ +139° (c, 1.0, $CHCl_3$). NMR data: ^1H, δ 3.52 (s, 3 H, OCH_3), 3.85 (dd, 1 H, $J_{5,6a}$ 9.8, $J_{6a,6e}$ 10.1 Hz, H-6a), 4.20 (d, 1 H, $J_{4,5}$ 10.2 Hz, H-4), 4.30 (ddd, 1 H, H-5), 4.42 (dd, 1 H, $J_{5,6e}$ 5.0 Hz, H-6e), 5.58 (s, 1 H, PhC*H*), 5.62 (d, 1 H, $J_{1,1'}$ 1.2 Hz, H-1), 6.85 (d, 1 H, $J_{1',2'}$ 11.6 Hz, H-2'), 7.32–7.72 (m, 10 H, 2 Ph), 7.89 (dd, 1 H, H-1'); NOE: enhancement of the intensity during irradiation at δ 6.85, δ 5.62 and δ 7.67; ^{13}C, δ 55.1 (OCH_3), 62.0 (C-5), 69.2 (C-6), 81.3 (C-4), 98.3 (C-1), 102.3 (PhCH), 119.0 (C-2'), 133.0 (C-3'), 135.8 (C-1'), 126.5, 127.0, 128.3, 128.7, 129.3, 130.6, 136.7, 137.0 (2 Ph), 145.5 (C-2), 189.5 (C-3). Mass spectrum: m/z 413 $[M + H]^+$. Anal. Calcd for $C_{23}H_{21}ClO_5$ (412.9): C, 66.91; H, 513. Found: C, 66.68; H, 4.93.

The component with R_f 0.35 was **9** (109 mg, 19.9%): yellow needles, mp 189°C (dec), $[\alpha]_D^{20}$ −67° (c, 1.0, $CHCl_3$). NMR data: ^1H, δ 3.49 (s, 3 H, OCH_3), 3.89 (dd, 1 H, $J_{5,6a}$ 9.7, $J_{6a,6e}$ 9.9 Hz, H-6a), 4.26 (d, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.36 (ddd, 1 H, H-5), 4.43 (dd, 1 H, $J_{5,6e}$ 4.8 Hz, H-6e), 5.37 (s, 1 H, H-1), 5.60 (s, 1 H, PhC*H*), 7.06 (dd, 1 H, $J_{1',1}$ 0.6, $J_{1',2'}$ 11.0 Hz, H-1'), 7.36–7.74 (m, 10 H, 2 Ph), 7.99 (d, 1 H, H-2'); NOE: enhancement of the intensity during irradiation at δ 7.06, δ 5.37; enhancement of the intensity during irradiation at δ 7.99, δ 7.71; ^{13}C, δ 55.1 (OCH_3), 62.7 (C-5), 69.4 (C-6), 82.9 (C-4), 102.2 (PhCH), 103.0 (C-1), 120.6 (C-2'), 132.7 (C-3'), 136.5 (C-1'), 126.4, 127.1, 128.3, 128.5, 129.3, 130.3, 136.6, 137.7 (2 Ph), 143.7 (C-2), 191.9 (C-3). Mass spectrum: m/z 413 $[M + H]^+$. Anal. Calcd for $C_{23}H_{21}ClO_5$ (412.9): C, 66.91; H, 5.13. Found: C, 66.84; H, 4.86.

*Methyl 4,6-*O*-benzylidene-3-*C*-butyl-2-deoxy-α-*D*-ribo-hexopyranoside* (**10**).—The

reaction of **7** (350 mg, 1.32 mmol) and butyllithium (1.3 mL of a 1.6 M solution in hexane, 2.08 mmol) was carried out as described above for **5**. Besides some starting material (R_f 0.44, 87.0 mg, 24.9%), compound **10** (R_f 0.55) could be separated after column chromatography (benzene–EtOAc, 4:1) as a white solid (222 mg, 52.0%), mp 104–107°C, $[\alpha]_D^{20}$ +87° (*c*, 1.05, $CHCl_3$). NMR data: ^1H (Me_2SO-d_6), δ 0.87 (t, 3 H, $J_{3',4'}$, 6.7 Hz, H-4'), 1.19–1.63 (m, 6 H, H-1',2',3'), 1.76 (dd, 1 H, $J_{1,2a}$ 4.1, $J_{2a,2e}$ 14.6 Hz, H-2a), 1.85 (d, 1 H, H-2e), 3.72 (s, 3 H, OCH_3), 3.46 (d, 1 H, $J_{4,5}$ 9.4 Hz, H-4), 3.69 (dd, 1 H, $J_{5,6a} = J_{6a,6e} = 10.0$ Hz, H-6a), 3.89 (s, 1 H, OH), 4.00 (ddd, 1 H, H-5), 4.21 (dd, 1 H, $J_{5,6e}$ 5.1 Hz, H-6e), 4.75 (d, 1 H, H-1), 5.63 (s, 1 H, PhC*H*), 7.35–7.48 (m, 5 H, Ph); ^{13}C, δ 14.0 (C-4'), 23.0 (C-3'), 25.1 (C-2'), 37.4, 38.6 (C-2, C-1'), 55.2 (OCH_3), 59.3 (C-5), 69.3 (C-6), 70.2 (C-3), 82.2 (C-4), 98.9 (C-1), 101.8 (Ph*C*H), 126.1, 128.0, 128.8, 137.6 (Ph). Mass spectrum: *m/z* 323 $[M + H]^+$. Anal. Calcd for $C_{18}H_{26}O_5$ (322.4): C, 67.06; H, 8.17. Found: C, 66.97; H, 817.

*(1Z,3E/Z)-6,7,8,10-Tetra-*O*-acetyl-5,9-anhydro-1-chloro-1,2,3,4-tetradeoxy-4-nitro-1-phenyl-*D-glycero-L-manno-*deca-1,3-dienitol* (**12**) *and* (**13**).—3,4,5,7-Tetra-*O*-acetyl-2,6-anhydro-1-deoxy-1-nitro-D-*glycero*-L-*manno*-heptitol[24] (**11**; 350 mg, 0.89 mmol) was treated with **1** (289 mg, 0.98 mmol) and DBU (150 mg, 0.98 mmol) as described above. Column chromatography ($CHCl_3$–EtOAc, 5:1) provided a syrupy mixture of **12** and **13** (189 mg, 39.1%). NMR data: ^1H, δ 1.91, 1.91, 1.93, 1.93, 1.98, 1.98, 2.00, 2.00 (m, 12 H, 4 CH_3), 4.06–4.19 (m, 3 H, H-9,10a,10b), 5.14–5.53 (m, 2 H, H-6,7), 5.49–5.57 (m, 2 H, H-5,8), 7.40–7.75 (m, 5 H, Ph), 7.56 (d, 1 H, $J_{2,3}$ 11.8 Hz, H-2 or H-3), 8.33 (d, 1 H, H-2 or H-3); ^{13}C, δ 20.2, 20.3 20.4 (4 CH_3), 61.3 61.6 (C-10), 67.3, 67.5, 68.3 68.6 71.5, 71.7, 73.1, 73.5, 74.8, 74.9, 75.5, 75.6 (C-4–C-9), 117.1, 120.7 (C-2), 129.5 (C-1), 133.7, 134.5 (C-3), 127.3, 128.3, 128.6, 130.8, 130.9, 136.8 (Ph), 146.5, 147.3 (C-4), 169.2, 169.4, 169.6, 169.7, 170.1 (C = O). Mass spectrum: *m/z* 539 $[M + H]^+$.

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