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Stereochemistry of Nucleophilic Addition Reactions. VIII.[1] Preparation of 1,5-Anhydro-4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-D-*erythro*-hex-2-enitol and Its Reactions with Some Nucleophiles

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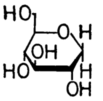
The title compound was synthesized from 1,5-anhydro-D-glucitol *via* nitromethane cyclization. The reduction of the compound with sodium borodeuteride afforded a mixture of saturated nitro compounds having an axial and equatorial deuterium atom at C-2 in an approximate ratio of 2: 1. On the other hand, the reaction with hydrogen cyanide gave predominantly the adduct with the *manno* configuration, together with small amounts of a cyano olefin. The reaction with hydrazoic acid yielded addition products with the *gluco* and *manno* configurations; the ratio was strongly affected by the solvent used.

Our own studies of nucleophilic addition reactions to methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-*erythro*-hex-2-enopyranoside (**1**)[2] and its α-anomer **2**,[3] 1-*O*-acetyl-4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-*erythro*-hex-2-enopyranose (**3**), and its α-anomer **4**,[4] and methyl 6-*O*-benzoyl-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranosid-4-ulose,[5] as well as other reports,[6] strongly suggest that these reactions are controlled by steric hindrance, stereoelectronic control, and electrostatic interaction. In the reactions of **1** with nucleophiles, we have proposed an important role of electrostatic interaction between the incoming nucleophile and both C_1–O_1 and C_1–O_5 bonds.[2a] If a nucleophile is an anion or has nonbonded electron pairs, electrostatic repulsion becomes the decisive factor, but if a nucleophile is electronically neutral, it becomes less important and the reaction is probably controlled by other factors. Furthermore, if a nucleophile has a cationic part, attractive forces such as hydrogen bonding may be operative. On the basis of this surmise, we can explain the results of many reactions.

In order to confirm this surmise and to elucidate whether or not both C_1–O_1 and C_1–O_5 bonds are required to control the approach of a nucleophile at C-2, we have synthesized the title compound **8** and performed some nucleophilic addition reactions.

Results and Discussion

Oxidation of 1,5-anhydro-D-glucitol (**5**)[7] with sodium metaperiodate, followed by nitromethane cyclization in the presence of catalytic amounts of sodium methoxide, afforded a syrup, the subsequent benzylidenation of which gave 1,5-anhydro-4,6-*O*-benzylidene-3-deoxy-3-nitro-D-glucitol (**6**) in 40% yield from **5**. Acetylation of **6** with pyridine–acetic anhydride or sodium acetate–acetic anhydride afforded the acetate **7** in good yield. In contrast to the corresponding methyl α-[8] and β-pyranoside,[9] treatment of **7** with sodium hydrogencarbonate in refluxing benzene caused a partial double-bond migration from C-2 to C-1, giving the glucal **9** besides the desired nitro olefin **8**, before the completion of the elimination of acetic acid. The double-bond migration was observed even when **8** was warmed in a methanol–DMSO solution at 50 °C. The reaction, therefore, was stopped at the stage where the intensities of the absorption bands of the unsaturated and saturated nitro groups were nearly equal in the IR spectrum. After the separation of most **7** by crystallization from carbon tetrachloride, these compounds were separated by column chromatography. The nitro olefin structure for **8** was deduced from elemental analysis, IR (1525 cm^{-1} conjugated nitro olefin), and the NMR spectrum (olefinic proton at δ 7.00 in chloroform-*d*). The glucal structure for **9** was determined from the IR (1640 and 1560 cm^{-1} nonconjugated carbon–carbon double bond and saturated nitro group respectively) and the NMR spectrum (olefinic proton at δ 6.48 and 4.37 in chloroform-*d*), together with elemental analysis.



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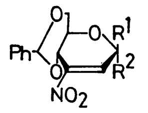
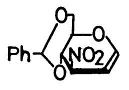


1; R^1 = OMe, R^2 = H
2; R^1 = H , R^2 = OMe
3; R^1 = OAc, R^2 = H
4; R^1 = H , R^2 = OAc
8; R^1 = R^2 = H



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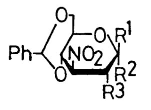
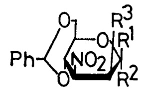
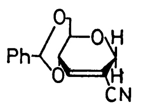


6: R^1 = R^2 = H , R^3 = OH
7: R^1 = R^2 = H , R^3 = OAc
10: R^1 = OMe, R^2 = H, R^3 = D
12: R^1 = H, R^2 = OMe, R^3 = D
14: R^1 = R^2 = H, R^3 = D
19: R^1 = R^2 = H, R^3 = N_3



11: R^1 = H, R^2 = OMe, R^3 = D
13: R^1 = R^2 = H, R^3 = D
15: R^1 = R^2 = R^3 = H
16: R^1 = R^2 = H, R^3 = CN
18: R^1 = R^2 = H, R^3 = N_3



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Selective reduction of the double-bond moiety of **1** and **2** was achieved by Baer and Rank; however, its stereochemistry was not investigated.[10] Reduction of **1** and **2** with sodium borodeuteride in methanol-d_4 exclusively afforded the saturated nitro compounds, **10** and **11**, respectively. The signals for the H-1 of **10** and **11** appeared as doublets with splitting of 9.8 and <1.0 Hz respectively. A similar reduction of the 2-deuterated derivative of **2** with sodium borohydride afforded the compound **12** ($J_{1,2}$=3.5 Hz).[11] These results showed that the deuteride ion exclusively entered from the opposite side of the glycosidic group. An

TABLE 1. CHEMICAL SHIFT (δ)[a)] AND FIRST-ORDER COUPLING CONSTANTS (Hz) AT 100 MHz ($CDCl_3$)

Compd	H-1a	H-1e	H-2	H-3	H-4	H-5	H-6a	H-6e	PhCH
7	3.28(q)	4.22(q)	5.40(se)	4.77(t)	4.09(t)	3.40(m)	3.73(t)	4.33(q)	5.50(s)
	$J_{1a,1e}=11.3$, $J_{1a,2}=10$, $J_{1e,2}=6.0$, $J_{2,3}=J_{3,4}=J_{4,5}=J_{5,6a}=J_{6a,6e}=10$, $J_{5,6e}=5.0$								
8	←4.40—4.46→		7.00(m)	—	4.65(m)	3.57(m)	3.85(t)	4.34(q)	5.68(s)
	$J_{1a,1e}$, $J_{1a,2}$, $J_{1e,2}$, $J_{1a,4}$, $J_{1e,4}$, $J_{2,4}<3.0$, $J_{4,5}=7.5$, $J_{5,6a}=J_{6a,6e}=10$, $J_{5,6e}=4.4$								
9	6.48(q)		4.87(q)	5.23(se)	4.43(t)	←3.8—4.5→			5.58(s)
	$J_{1,2}=6.3$, $J_{1,3}=1.9$, $J_{2,3}=2.2$, $J_{3,4}=8.2$, $J_{4,5}=8.9$								
15[b)]	2.62(se)	3.38(o)	c	4.26(o)	3.84(t)	2.89(se)	3.35(t)	4.02(q)	5.17(s)
	$J_{1a,2a}=11.9$, $J_{2a,3}=11.9$, $J_{2e,3}=5.2$, $J_{3,4}=J_{4,5}=9.7$, $J_{5,6a}=8.9$, $J_{5,6e}=5.2$, $J_{6a,6e}=10.8$								
16[d)]	3.61(q)	4.22(q)	3.55(m)	4.75(q)	4.44(q)	3.44(se)	3.87(t)	4.35(q)	5.67(s)
	$J_{1a,1e}=12.7$, $J_{1a,2}=2.2$, $J_{1e,2}=1.9$, $J_{2,3}=5.2$, $J_{3,4}=10$, $J_{4,5}=J_{5,6a}=J_{6a,6e}=10.5$, $J_{5,6e}=4.9$								
17	←4.3—4.4→		—	3.76(q)	4.24(m)	3.50(o)	3.76(t)	4.35(q)	5.58(s)
	$J_{1a,3}$, $J_{1e,3}$, $J_{1a,4}$, $J_{1e,4}$, $J_{3,4}<2.0$, $J_{4,5}=8.2$, $J_{5,6a}=J_{6a,6e}=9.7$, $J_{5,6e}=4.1$								
18[d)]	3.69(q)	4.21(q)	4.29(q)	4.67(q)	4.47(t)	3.41(se)	3.84(t)	4.39(q)	5.69(s)
	$J_{1a,1e}=12.7$, $J_{1a,2}=1.5$, $J_{1e,2}=2.0$, $J_{2,3}=3.7$, $J_{3,4}=J_{4,5}=J_{5,6a}=J_{6a,6e}=9.7$, $J_{5,6}=4.5$								
19	3.35(t)	4.19(q)	4.24(m)	4.57(t)	4.03(t)	3.37(m)	3.72(t)	4.34(q)	5.50(s)
	$J_{1a,1e}=12.5$, $J_{1a,2}=12.5$, $J_{1e,2}=5.0$, $J_{2,3}=J_{3,4}=J_{4,5}=J_{5,6a}=J_{6a,6e}=10$, $J_{5,6e}=5.0$								

a) Me_4Si as the internal standard; (se) and (o) indicate sextet and octet respectively. b) This compound was recorded in benzene-d_6. c) $\delta=1.78$ (o, 1, H-2a) and 1.34 (m, 1, H-2e); $J_{1a,2e}=2.5$, $J_{1e,2a}=5.2$, $J_{1e,2e}=1.5$, and $J_{2a,2e}=12.7$ Hz. d) The assignments of H-1a and H-1e were tentative.

important role of the anomeric methoxyl group in such a highly stereoselective reduction was proved by a similar reduction of **8**, in which a mixture of saturated nitro compounds with axial and equatorial deuterio groups was formed in an approximate ratio of 2: 1, as judged from the NMR spectrum. It is noteworthy that the C-3 position of the crude product, produced by sodium borodeuteride reduction of **1** in methanol-d_4, was also deuterated; however, this deuterium atom was exchanged for a hydrogen atom after purification by column chromatography on silica gel.

On the other hand, a selective axial approach, as in the cases of **2**[3a)] and **4**,[4)] was observed in the reaction of **8** with hydrogen cyanide. When the nitro olefin **8** was treated with hydrogen cyanide in acetonitrile in the presence of small amounts of aqueous potassium cyanide, three products were formed which were detectable by TLC and NMR spectroscopy. Separation by column chromatography afforded the *manno* isomer **16** as the major product, together with trace amounts of an unidentified product and a cyano olefin **17**. The *manno* configuration for **16** was deduced from the NMR data, analyzed by the help of the decoupling technique; $J_{1a,2}=2.2$, $J_{1e,2}=1.9$, $J_{2,3}=5.2$, and $J_{3,4}=10$ Hz. The structure of the cyano olefin **17**, which was obtained in good yield by treatment of **16** with triethylamine, was determined from the IR (2210 cm^{-1}; CN) and NMR data (olefinic proton at δ 3.76). This reaction was proved to be insensitive to the solvents used (THF, dioxane, acetonitrile, and DMF), giving the *manno* isomer **16** as the major product. When trace amounts of triethylamine were used as a catalyst, double-bond migration predominantly occurred to give the glucal **9**, together with small amounts of the addition products, as judged from the NMR spectrum.

More complicated results were obtained in the reaction of **8** with hydrazoic acid. Treatment of **8** with hydrazoic acid in THF afforded a mixture of the *manno* **18** and the *gluco* isomer **19** in an approximate ratio of 1.2: 1, as judged by NMR spectroscopy. Under the

TABLE 2. SOLVENT EFFECTS ON THE REACTION OF **8** WITH HYDRAZOIC ACID[a)]

Entry	Solvent (ml)		Product ratios			
			0.5 h	1.5 h	5 h	20.5 h[b)]
1	Benzene	(0.15)	r	r	r	r
2	$CDCl_3$	(0.15)	r	r	r	r
3	$CDCl_3$	(0)[c)]	r	r	r (t of **19**)	8 : 1 (t of **8**)
4	THF	(0.15)	r	1 : 1.2 (70% r)	1 : 1.2 (55% r)	1 : 1.2
5	Acetone-d_6	(0.15)	1 : 1.2 (70% r)	1 : 1.2 (35% r)	1 : 1.2	1 : 1.2
6	DMSO-d_6	(0.15)	1 : 5	1 : 5	1 : 5	1 : 5

a) The nitro olefin **8** (13 mg, 0.05 mmol) was treated with hydrazoic acid (*ca.* 0.08 mmol) in $CDCl_3$ (0.05 ml) in a NMR sample-tube at room temperature, and the ratio was determined by NMR spectroscopy. b) Reaction time. c) Without dilution, 0.2 ml of a $CDCl_3$ solution containing hydrazoic acid was used. d) r and t indicate recovery and trace amounts respectively.

same conditions, the reaction of **1**[12] and **3**[4] with hydrazoic acid exclusively affordcd the *gluco* isomer (90 and 84% yields respectively), whereas the same reaction of **2**[3a] and **4**[4] predominantly afforded the *manno* isomer (76 and 82% respectively). The present finding, therefore, indicated the important role of the substituent at the anomeric carbon for the approach of the azide ion to C-2.

Compounds **18** and **19** were separated by column chromatography on silica gel. The IR spectra of both compounds showed the presence of an azide (2110 cm^{-1}) and a nitro group (1560 cm^{-1}). The *manno* and *gluco* structures for **18** and **19** were assigned from the coupling constants; $J_{1a,2}=1.5$, $J_{1e,2}=2.0$, $J_{2,3}=3.7$, and $J_{3,4}=9.7$ Hz for **18** and $J_{1a,2}=12.5$, $J_{1e,2}=5.0$, $J_{2,3}=10$, and $J_{3,4}=10$ Hz for **19**.

As shown in Table 2, the product ratios and the rates were strongly affected by the solvents. In such a relatively nonpolar solvent as chloroform, the reaction did not occur even after 20.5 h (Entries 1 and 3); however, in the presence of excess hydrazoic acid (*ca.* 6 equiv.), it slowly proceeded to give the *gluco* isomer **19**, as the major product (Entry 3). On the other hand, in DMSO the reaction occurred readily to afford the *manno* isomer **18**, as the major product (Entry 6). Furthermore, in THF and acetone it was somewhat retarded, affording nearly equal amounts of **18** and **19** (Entries 4 and 5). Similar solvent effects had previously been observed in the case of **2**[3a] and **4**;[4] the exceptional, predominant formation of the *gluco* isomer in a chloroform solution was attributed to hydrogen bonding between hydrazoic acid and the oxygen atom (O-1) at the anomeric carbon atom. However, this explanation is not applicable to the present reaction, because compound **8** has no such oxygen atom. Presently we can not give any reasonable explanation of these solvent effects.

Because the reactions of the 1,5-anhydro sugar **8** as well as the α-anomers (**2** and **4**) with hydrazoic acid were affected by the solvents, the similar reaction of the β-anomer **1** was performed in several solvents (DMSO, THF, and chloroform). It was found to be insensitive to these solvents, affording exclusively the *gluco* isomer.

As had previously been described, nucleophiles predominantly entered from the axial side of **8**, except in one case, to give the *manno* isomer. Therefore, the stereoselective approach of nucleophile from the equatorial side of the β-anomers (**1** and **3**) requires, at least, an equatorially orientated anomeric methoxyl or acetoxyl group.

Experimental

The melting points were determined in capillaries and are uncorrected. The IR spectra were recorded on KBr discs with a Hitachi 215 IR spectrometer. The NMR spectra were determined for solutions in chloroform-*d* (tetramethylsilane as internal standard), unless otherwise noted, with a JNM-PS-100 (JEOL) spectrometer. The solutions were evaporated under reduced pressure. Column chromatography was carried out on silica gel (C-300, Wakogel, Japan). Silica gel CF-254 was used for the TLC.

*1,5-Anhydro-4,6-*O*-benzylidene-3-deoxy-3-nitro-*D*-glucitol (6).* A solution of sodium metaperiodate (47 g, 0.22 mol) in 300 ml of water was cooled in an ice–water bath, and then a mixture of 1,5-anhydro-D-glucitol (**5**) (16.4 g, 0.1 mol)[7] and sodium hydrogencarbonate (8.4 g, 0.1 mol) was added in portions over 20 min with stirring. The mixture was allowed to warm to 21 °C and was stirred for additional 3 h, and then the precipitated sodium iodate was removed by filtration. The filtrate was concentrated to a partly crystalline mass, to which 100 ml of ethanol was added. After the removal of the insoluble material, the solution was evaporated to a syrup, which was subsequently dissolved in ethanol; the solution was then filtered from the remnant salt and evaporated. This procedure was repeated if the dissolution of the resulting syrup in ethanol caused an appreciable quantity of salt to separate. The syrupy dialdehyde was dissolved in 200 ml of methanol, and 6 ml (0.11 mol) of nitromethane was added. This solution was cooled in an ice–water bath, and 1 mol dm^{-3} sodium methoxide was added until the solution showed pH 9. The solution was brought to 21 °C, kept at that temperature for overnight, and then deionized by Amberlite IR-120 (H$^+$) cation-exchange resin. After the removal of the resin, the solution was evaporated completely to a syrup, the IR spectrum of which showed the presence of a nitro group (1560 cm^{-1}). Without further purification, the syrup was benzylidenated. Powdered anhydrous zinc chloride (26 g) was added to a flask containing the syrup and benzaldehyde (60 ml). The mixture was stirred at 21 °C for 20 h and then poured into a solution of water (100 ml) and hexane (250 ml) with stirring, whereby the crude acetal was precipitated. The precipitate was washed well with water and hexane. Recrystallization from ethanol afforded 11.8 g of **6** (40.4% from **5**); mp 154—155.5 °C; $[\alpha]_D^{21}$ −36.2 (*c* 1, CHCl$_3$); IR 3545, 3450, 3210 (OH), and 1555 cm^{-1} (NO$_2$).

Found: C, 55.57; H, 5.43; N, 5.13%. Calcd for C$_{13}$H$_{15}$NO$_6$: C, 55.51; H, 5.38; N, 4.98%.

*2-i-*O*-Acetyl-1,5-anhydro-·4,6-*O*-benzylidene-3-deoxy-nitro-*D*-glucitol (7).* *a*): A solution of **6** (9 g, 0.032 mol) in 90 ml of anhydrous pyridine was cooled in an ice–water bath, and to this solution was added slowly 26 ml of acetic anhydride. The mixture was brought to 21 °C, kept at that temperature for 3 h, and then poured into 300 ml of ice–water. The precipitate was filtered and washed with water. Recrystallization from ethanol gave 7.6 g (73.8%) of **7**; mp 199—199.5 °C; $[\alpha]_D^{21}$ −31.7° (*c* 1, CHCl$_3$); IR 1760 (CO) and 1560 cm^{-1} (NO$_2$).

Found: C, 56.04; H, 5.36; N, 4.37%. Calcd for C$_{15}$H$_{17}$NO$_7$: C, 55.72; H, 5.30; N, 4.33%.

b): The nitro alcohol **6** (100 mg, 0.36 mmol) and sodium acetate (200 mg) in acetic anhydride (2 ml) were heated at *ca.* 100 °C for 5 min, until the solution turned orange. The mixture was then poured into ice–water, and the precipitate that separated was collected and washed with water. Recrystallization from ethanol gave 64 mg (55.6%) of **7**.

Elimination of Acetic Acid from the Acetate **7**. The acetate **7** (646 mg, 2 mmol, desiccator-dried) and sodium hydrogencarbonate (1.5 g, desiccator-dried) were added to distilled benzene (10 ml). The mixture was heated under reflux with stirring. From time to time, a small test sample was withdrawn from the supernant solution and allowed to evaporate on a sodium chloride plate for inspection by means of IR spectroscopy. A gradual decrease in the relative intensity of the carbonyl band at 1760 cm^{-1} and a gradual increase in the nitro olefin band at 1530 cm^{-1} and in the carbon–carbon double bond at 1635 cm^{-1} indicated that the isomerization of **8** to **9** occurred before the completion of the elimination of acetic acid. When the intensities of the bands of the unsaturated and saturated nitro group were almost the same (*ca.* 7 d), the reaction was stopped. After cooling, the inorganic material was filtered off and washed with acetone. The filtrate was evaporated to give a solid residue (610 mg). Most of the starting material, **7** (270 mg), was removed by the addition of carbon tetrachloride (10 ml), followed by filtration. The filtrate was evaporated and chromatographed on silica gel, eluting with benzene. Each fraction was inspected by IR spectroscopy. The first fraction consisted of 90 mg of crystalline **9**, which was recrystallized from diisopropyl ether; 79 mg (15%); mp 90.0—91.0 °C; $[\alpha]^{21}_{D}$ −158° (*c* 1, $CHCl_3$); IR 1635 (C=C) and 1550 cm^{-1} (NO_2); R_f 0.61 (benzene)

Found: C, 59.09; H, 4.98; N, 5.21%. Calcd for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98; N, 5.32%.

The second fraction was a mixture of **8** and **9** (52 mg) (1.5: 1 from NMR spectroscopy).

The third fraction consisted of 145 mg of **8**, which was recrystallized from diisopropyl ether; 128 mg (24.3%); mp 87.5—88.0 °C; $[\alpha]^{21}_{D}$ −238° (*c* 1, $CHCl_3$); IR 1530 cm^{-1} (NO_2); R_f 0.36 (benzene).

Found: C, 59.57; H, 5.03; N, 5.26%. Calcd for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98; N, 5.32%.

The fourth fraction consisted of 35 mg of **7** (total 305 mg, 47.2%); R_f 0.28 (benzene).

*Reduction of the Nitro Olefins **1**, **2**, and **8** with Sodium Borodeuteride.* To a solution of **1** (20 mg, 0.07 mmol) in methanol-d_4 (0.4 ml) was added sodium borodeuteride (5 mg, 0.12 mmol) at 21 °C. The mixture was allowed to stand for 20 min and then concentrated. The NMR spectrum of the crude product showed that it was deuterated both at C-2 (equatorial position) and C-3; NMR δ=4.55 (d, 1, $J_{1,2}$=9.8 Hz, H-1), 2.18 (d, 1, H-2a) and 4.17 (d, 1, $J_{4,5}$=9.7 Hz, H-4). The crude product was chromatographed on silica gel, eluting with benzene–ethyl acetate (10: 1, v/v), to give 17 mg (84%) of **10**; NMR δ=4.55 (d, 1, $J_{1,2}$=9.8 Hz, H-1), 2.18 (q, 1, $J_{2,3}$=11.9 Hz, H-2a), 4.78 (q, 1, $J_{3,4}$=9.7 Hz, H-3), 4.17 (t, 1, $J_{4,5}$=9.7 Hz, H-4), 3.46 (m, 1, H-5), 3.86 (t, 1, $J_{5,6a}$=$J_{6a,6e}$=10.4 Hz, H-6a), and 4.38 (q, 1, $J_{5,6e}$=4.5 Hz, H-6e).

A similar reduction of **2** (20 mg) afforded **11** in 91% yield (after purification with column chromatography); NMR δ= 4.87 (broad s, 1, $J_{1,2}$ <1.0 Hz, H-1), 2.46 (broad d, 1, $J_{2,3}$= 5.2 Hz, H-2e), and 5.06 (q, 1, $J_{3,4}$= 10 Hz, H-3).

A similar reduction of methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-deuterio-3-nitro-α-D-*erythro*-hex-2-enopyranoside (20 mg)[13] with sodium borohydride (5 mg) yielded **12** (89%, after column chromatography); NMR (60 MHz) δ=4.85 (d, 1, $J_{1,2}$=3.5 Hz, H-1), 2.34 (q, 1, $J_{2,3}$=11.2 Hz, H-2a), and 5.04 (q, 1, $J_{3,4}$=9.7 Hz, H-3).

A similar reduction of **8** (56.3 mg. 0.21 mmol) with sodium borohydride (15.6 mg, 0.41 mmol) in methanol (1.2 ml) afforded 45 mg (79%) of a syrup (after column chromato, graphy). Crystallization from diisopropyl ether–hexane afforded 30 mg (52.6%) of **15**; mp 71—71.5 °C; $[\alpha]^{24}_{D}$ −26° (*c* 0.5, $CHCl_3$); IR 1545 cm^{-1} (NO_2); R_f 0.41 (benzene).

Found: C, 58.84; H, 5.70; N, 5.14%. Calcd for $C_{13}H_{15}NO_5$: C, 58.86; H, 5.70; N, 5.28%.

A similar reaction of **8** (18 mg, 0.07 mmol) with sodium borodeuteride (5 mg) afforded a mixture (14 mg) of **13** and **14** as a syrup. Although the H-2a and H-2e signals overlap in chloroform-*d*, they separate in benzene-d_6; the ratio of **13**: **14**=2: 1 was determined. The assignment of the signals of these compounds was performed by comparison with the deuterated and the corresponding undeuterated products.

*1,5-Anhydro-4,6-*O*-benzylidene-2-cyano-2,3-dideoxy-3-nitro-*D-*mannitol (**16**).* To an acetonitrile solution (3.3 ml) containing hydrogen cyanide (*ca.* 6 equiv.) was added **8** (78.9 mg, 0.3 mmol) and an aqueous solution of potassium cyanide (0.06 ml, 1.9 mg) at 28 °C. The mixture was stirred at the ambient temperature for 2.5 h and then evaporated to give a residue. The residue was dissolved in chloroform and washed with water. The organic layer was evaporated to give a residue, which was subsequently crystallized from ethanol to give 74 mg of **16**. Recrystallization from isopropyl alcohol afforded 65 mg (74.7%) of **16**; mp 124—125 °C; $[\alpha]^{30}_{D}$ −154° (*c* 1, $CHCl_3$); IR 2230 (CN) and 1565 cm^{-1} (NO_2); R_f 0.41 (benzene–ethyl acetate, 10: 1, v/v).

Found: C, 57.75; H, 4.93; N, 9.63%. Calcd for $C_{14}H_{14}N_2O_5$: C, 57.93; H, 4.86; N, 9.65%.

The mother liquor was concentrated and chromatographed on silica gel, eluting with benzene–ethyl acetate (30: 1, v/v); the first fraction consisted of 6 mg of **17**, which was found to be identical with an authentic sample by a comparison with the IR and NMR spectral data. The second fraction consisted of 5 mg of an undetermined product, although it seems to be the *gluco* isomer, as judged from IR and NMR spectroscopy. The third fraction was composed of 5 mg of **16** (total yield of **16**: 80.4%).

*1,5-Anhydro-4,6-*O*-benzylidene-2-cyano-2,3-dideoxy-*D-*erythro-hex-2-enitol (**17**).* To a solution of **16** (22 mg, 0.067 mmol) in acetone (1.5 ml) was added triethylamine (0.2 ml). The mixture was stirred at 30 °C for 6 h and then evaporated to give a solid residue (18.4 mg). Recrystallization from isopropyl alcohol gave 13 mg (70.6%) of **17**; mp 170.5—171.5 °C; $[\alpha]^{30}_{D}$ +36.9° (*c* 1, $CHCl_3$); IR 2210 cm^{-1} (CN); R_f 0.69 (benzene–ethyl acetate, 10: 1, v/v).

Found: C, 69.15; H, 5.37; N, 5.96%. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76%.

*Attempt at the Direct Preparation of **17** from **8**.* To an ice-water-cooled chloroform solution (2.1 ml) of **8** (13 mg, 0.05 mmol) containing hydrogen cyanide (5 equiv.) was added 0.02 ml of triethylamine. The mixture was kept for 23 h in a refrigerator and then washed with *ca.* 1 mol dm^{-3} HCl solution and water. The NMR spectrum of the crude product showed that it consisted of **9** (>60%) and small amounts of **16** and **17**.

*1,5-Anhydro-2-azido-4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-*D-*mannitol (**18**) and glucitol (**19**).* *a) From the Nitro Olefin **8**:* To a solution of **8** (26.3 mg, 0.1 mmol) in acetone (0.5 ml) was added a chloroform solution containing hydrazoic acid (0.3 mmol) at 21 °C. The mixture was allowed to stand at that temperature for 21 h and then evaporated to give a syrup (30 mg), the NMR spectrum of which showed the presence of only **18** and **19** in a ratio of 1.2 : 1. The syrup (30 mg+28 mg) was chromatographed on silica gel, eluting with benzene; the first fraction consisted of 20 mg of NMR spectroscopically pure **19**. Recrystallization from ethanol gave 16 mg (26%) of **19**; mp 126.5—127.5 °C; $[\alpha]^{20}_{D}$ —66.9° (*c* 0.5, $CHCl_3$); IR 2110 (N_3) and 1560 cm^{-1} (NO_2); R_f 0.59 (benzene).

Found: C, 51.14; H, 4.48; N, 18.18%. Calcd for $C_{13}H_{14}N_4O_5$: C, 50.98; H, 4.61; N, 18.29%.

The second fraction was a mixture of **18** and **19** (8 mg).

The third fraction was composed of 28 mg of pure **18**, which crystallized from diisopropyl ether to afford 20 mg (32.7%) of **18**; mp 127.5—128.5 °C; $[\alpha]^{20}_{D}$ −170° (*c* 0.5, $CHCl_3$); IR 2100 (N_3) and 1560 cm^{-1} (NO_2); R_f 0.47 (benzene).

Found: C, 51.15; H, 4.50; N, 18.03%. Calcd for $C_{13}H_{14}N_4O_5$: C, 50.98; H, 4.61; N, 18.29%.

*b) From the Acetate **7**:* To a solution of **7** (83 mg, 0.26 mmol) in acetonitrile (4 ml)–water (0.5 ml) was added sodium azide (19 mg, 0.29 mmol). The mixture was stirred at 28 °C for 24 h and then evaporated to give a residue. The residue was dissolved in dichloromethane and washed with water.

The organic layer was dried over $MgSO_4$ and evaporated to give a solid residue, which was similarly chromatographed on silica gel to give a mixture (52 mg) of **18** and **19** (3.1: 1, as judged from NMR spectroscopy), besides the starting material (14 mg).

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