acetophenone, 21.8% toluene, and 1.8% benzene. Essentially the same results were obtained when the reaction was performed in the presence of 0.944 mmol of *p*-chlorobenzoyl chloride.

(d) Effect of Oxygen, Triphenylphosphine, *m*-Dinitrobenzene, and $ZnCl_2$. A suspension of 308 mg (0.399 mmol) of chlorobenzoylbis(triphenylphosphine)palladium(II) and 150 μL (1.084 mmol) of tetramethyltin in 4.3 mL of HMPA was stirred at 28 °C for 130 min (1) under argon, (2) under oxygen, (3) in the presence of 205.8 mg (1.225 mmol) of *m*-dinitrobenzene, (4) in the presence of 250.9 mg (0.958 mmol) of triphenylphosphine, and (5) in the presence of 50 mg of $ZnCl_2$. The usual workup and GLC analysis showed that the following yields of acetophenone were obtained, respectively: (1) 74.2, (2) 47.2, (3) 52.7, (4) 21.2, (5) 41.4%.

Reaction of Chloro(4-methylbenzoyl)palladium(II) with Tetramethyltin. A suspension of 272.9 mg (0.350 mmol) of chloro(4-methylbenzoyl)palladium(II) and 0.500 mL (3.61 mmol) of tetramethyltin was stirred at room temperature for 7 h, after which time the mixture blackened. Acetophenone and *sec*-butylbenzene were added as internal standards, and GLC analysis (120–190 °C, 20% Carbowax 20M) after the usual workup showed the formation of the following products: *p*-methylacetophenone (78.3%), *p*-xylene (10.9%), toluene (25.5%), benzene (19.2%).

Kinetic Experiments. The kinetic experiments were conducted in Schlenk tubes equipped with rubber septums and immersed in a constant temperature oil bath. Freshly distilled benzoyl chloride was used, and *p*-methylacetophenone served as an internal standard. At certain intervals small samples of the solutions were withdrawn via a syringe and were quenched by injection into hexane-filled vials. The complex precipitated immediately, and the hexane solution was analyzed by GLC.

Attempted Ketone Synthesis by Carbonylation. To a solution of 1.193 g (7.60 mmol) of bromobenzene and 73.4 mg (0.097 mmol) of I in 4 mL of HMPA in a 90-mL pressure tube was added 2.00 mL (14.44 mmol) of tetramethyltin. The solution was pressurized with 30 atm of CO (in addition to 1 atm of air present) and heated at 65 °C with stirring for 15 h, during which time the Pd metal precipitated and the CO pressure dropped to 2.5 atm (at room temperature). The usual workup of the reaction mixture and GLC analysis showed that only 1.4% of acetophenone was formed (111.7% based on the catalyst), with 95.7% of the bromobenzene remaining unchanged. Similar results were obtained when tetrakis(triphenylphosphine)palladium(0) was used as catalyst. When *m*-nitrobromobenzene was allowed to react with tetramethyltin using this catalyst, 2.4% of *m*-nitroacetophenone was obtained, and 4.1% of this product was formed when the CO pressure was lowered to 1.1 atm.

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Registry No.—1, 22784-59-4; glutaric anhydride, 108-55-4; methyl hydrogen glutarate, 1501-27-5; chloro(4-methylbenzoyl)bis(triphenylphosphine)palladium(II), 69469-77-8; tetrakis(triphenylphosphine)palladium(0), 14221-01-3.

References and Notes

(1) K. Takagi, T. Okamoto, Y. Sakakibara, A. Ohno, S. Oka, and N. Hayama, *Chem. Lett.*, 951 (1975).
(2) M. Kosugi, Y. Shimizu, and T. Migita, *J. Organomet. Chem.*, **129**, C36 (1977).
(3) M. Kosugi, Y. Shimizu, and T. Migita, *Chem. Lett.*, 1423 (1977).
(4) D. Milstein and J. K. Stille, *J. Am. Chem. Soc.*, **100**, 3636 (1978).
(5) G. H. Posner, *Org. React.*, **22**, 253 (1975).
(6) H. B. Haas and M. L. Bender, *J. Am. Chem. Soc.*, **71**, 1767 (1949).
(7) W. K. Detweiler and E. D. Amstutz, *J. Am. Chem. Soc.*, **72**, 2882 (1950).
(8) J. G. A. Luijten and G. J. M. van der Kerk in "The Bond to Carbon", Vol. 1, Part II, A. G. MacDiarmid, Ed., Marcel Dekker, New York, 1968, p 91.
(9) C. J. Cardin, D. J. Cardin, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 767 (1977).
(10) M. Gielen and J. Nasielski, *Organotin Compd. 1972*, **3**, 625 (1972).
(11) L. B. Barkley, W. S. Knowles, H. Raffelson, and Q. E. Thompson, *J. Am. Chem. Soc.*, **78**, 4111 (1956).
(12) P. Fitton, J. E. McKeon, and B. C. Ream, *Chem. Commun.*, 370 (1969).
(13) This mechanism for the generation of the Pd(0) catalyst via the dialkylpalladium(II) species was established in a separate study: D. Milstein and J. K. Stille, submitted for publication.
(14) See, for example, J. Tsuji, "Organic Synthesis by Means of Transition Metal Complexes", Springer-Verlag New York, New York, 1975, and P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, **2**, 271 (1973).
(15) D. R. Fahey and J. E. Mahan, *J. Am. Chem. Soc.*, **98**, 4499 (1976).
(16) C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977), and references therein.
(17) E. Negichi, N. Okukado, A. O. King, D. E. Van Horn, and B. I. Spiegel, *J. Am. Chem. Soc.*, **100**, 2254 (1978).
(18) M. H. Abraham and T. R. Spalding, *Chem. Commun.*, 46 (1968).
(19) M. Gielen and J. Nasielski, *J. Organomet. Chem.*, **1**, 173 (1963).
(20) M. Gielen and J. Nasielski, *J. Organomet. Chem.*, **7**, 273 (1967).
(21) J. K. Stille and K. S. Y. Lau, *Acc. Chem. Res.*, **10**, 434 (1977).
(22) G. Spengler and M. Koll, *Erdoel Kohle, Erdgas, Petrochem.*, **17**, 107 (1964).
(23) D. Seyferth and F. G. A. Stone, *J. Am. Chem. Soc.*, **79**, 515 (1957).
(24) D. R. Coulson, *Inorg. Synth.*, **13**, 121 (1972).
(25) K. Suzuki and M. Nishida, *Bull. Chem. Soc. Jpn.*, **46**, 2887 (1973).
(26) R. F. Naylor, *J. Chem. Soc.*, 1106 (1947).
(27) G. Chiusoli and G. Agnes, *Chim. Ind. (Milan)*, **46**, 548 (1964).
(28) R. C. Weast, "Handbook of Chemistry and Physics", Chemical Rubber Publishing Co., Cleveland, Ohio, 1968.
(29) R. H. Bullard and W. B. Robinson, *J. Am. Chem. Soc.*, **49**, 1368 (1927).
(30) J. B. Pedley and H. A. Skinner, *Trans. Faraday Soc.*, **55**, 544 (1959).

Synthesis of New Branched-Chain Cyclitols Having Epi and Allo Configuration and Myo Configuration Respectively from 3-*O*-Benzyl-5,6-dideoxy-5-[*C*-(1,3-dithian-2-yl)]-6-nitro-D-allofuranose and -L-talofuranose[1a]

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The Michael addition of 2-lithio-1,3-dithiane to 3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-nitro-α-D-*ribo*-hex-5-enofuranose (**3**) gave 3-*O*-benzyl-5,6-dideoxy-5-*C*-(1,3-dithian-2-yl)-1,2-*O*-isopropylidene-6-nitro-β-L-talofuranose (**4**) and -α-D-allofuranose (**5**) in 59% yield (**4**:**5** = 1:1). Intramolecular cyclization of these compounds in weak basic conditions after removal of the isopropylidene group gave branched-chain cyclitols having epi and allo configuration (**11** and **15**) from **5** and myo configuration (**7**) from **4**, respectively, in good yields, and the stereochemistry of cyclization was discussed. The cyclization of 3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-5-*C*-(nitromethyl)-6-nitro-α-D-*ribo*-hexofuranose prepared by the addition of nitromethane to **3** was also described.

In a previous paper,[1b] we reported a simple stereoselective synthesis of branched-chain cyclitols having myo and muco configuration by an intramolecular cyclization of 3-*O*-benzyl-5,6-dideoxy-5-*C*-(1,3-dithian-2-yl)-6-nitro-D-glucofuranose and -L-idofuranose, respectively, in weak basic conditions. In that paper, we disclosed that two bulky groups such as benzyloxy at C-3 and 1,3-dithiane residue at C-5

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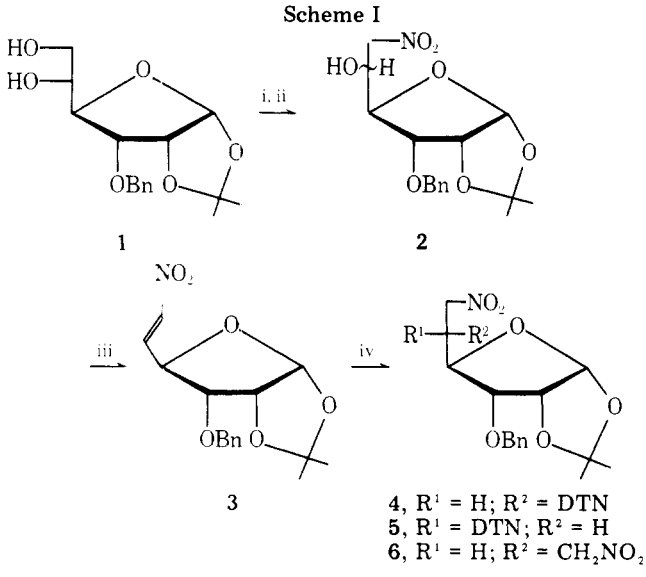
Table I. NMR Parameters (δ) of Branched-Chain *myo-*, *epi-*, and *allo*-Nitroinositol Derivatives (8, 12, and 16)[a]

compd	registry no.	H_1	H_2	H_3	H_4	H_5	H_6	$H_{1'}$	$H_{4'}$	acetyl
myo-8	69177-80-6	5.0 (q, $J_{1,2}$ = 2.8 Hz)	4.06 (t, $J_{2,3}$ = 2.8 Hz)	4.9 (q, $J_{3,4}$ = 12 Hz)	3.42 (s, $J_{4,5}$ = 12 Hz)	4.92 (q, $J_{5,6}$ = 10 Hz)	6.00 (t, $J_{1,6}$ = 10 Hz)		4.06 (d, $J_{4,4'}$ = 2.0 Hz)	1.96 2.00 2.06
epi-12	69224-19-7	2.9 (o, $J_{1,2}$ = 3.0 Hz)	5.92 (q, $J_{2,3}$ = 3.2 Hz)	3.56 (t, $J_{3,4}$ = 3.2 Hz)	5.75 (q, $J_{4,5}$ = 3.0 Hz)	5.28 (q, $J_{5,6}$ = 10 Hz	5.38 (t, $J_{1,6}$ = 10 Hz)	4.10 (d, $J_{1,1'}$ = 4.0 Hz)		1.99 2.13 2.15
allo-16	69224-20-0	3.1 (m, $J_{1,2}$ = 2.4 Hz)	5.94 (q, $J_{2,3}$ = 3.4 Hz)	3.64 (t, $J_{3,4}$ = 3.4 Hz)	5.64 (q, $J_{4,5}$ = 3.6 Hz)	5.4 (q, $J_{5,6}$ = 3.0 Hz)	5.4 (q, $J_{1,6}$ = 11.5 Hz)	4.46 (d, $J_{1,1'}$ = 4.8 Hz)		2.04 2.14 2.14

[a] d = doublet, m = multipet, o = octet, q = quartet, s = sextet, t = triplet.

Scheme I



i, $NaIO_4$; ii, CH_3NO_2/CH_3ONa; iii, MsCl/Et_3N (Ac_2O/AcONa); iv, 2-lithio-1,3-dithiane (nitromethyl anion)

played important roles in determining the stereodirection of cyclization. We thus tried to confirm the validity of the previous results by applying similar intramolecular cyclization to newly prepared 3-*O*-benzyl-5,6-dideoxy-5-*C*-(1,3-dithian-2-yl)-6-nitro-L-talofuranose (**4**) and -D-allofuranose (**5**), C-3 epimers of L-ido- and D-glucofuranose derivatives.

Compounds **4** and **5** were prepared in the same manner as described in the previous paper; 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-allofuranose[2] (**1**) was first of all oxidized in the usual manner with sodium metaperiodate in aqueous methanol, and the resulting aldehyde was then coupled with nitromethane in methanol in the presence of sodium methoxide to give C-5 epimeric nitroalocohols (**2**)[3] in a good yield. Direct dehydration of the compound **2** either by the acetic anhydride/sodium acetate[4] or by the methanesulfonyl chloride/triethylamine system[5] gave 3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hex-5-enofuranose (**3**) in 76–85% yield.

The reaction of nitroolefin **3** with 1.2 equiv of 2-lithio-1,3-dithiane[6] at −45 to −50 °C in dry tetrahydrofuran gave a mixture of 1,4-addition products, 3-*O*-benzyl-5,6-dideoxy-5-*C*-(1,3-dithian-2-yl)-1,2-*O*-isopropylidene-6-nitro-β-L-talofuranose (**4**) and -α-D-allofuranose (**5**) in 59% yield after silica gel column chromatography. The ratio of **4** to **5** was estimated to be 1:1 from NMR analysis (comparison of the intensity of H-1 protons) of the mixture and by a densitometer (comparison of the intensity of two spots on TLC). Fractional crystallization of the crystalline mixture gave pure compounds **4** and **5** respectively in 24 and 22% yields.

Though both NMR spectra gave no diagnostic information on the configuration at C-5, the following intramolecular cyclization between C-1 and C-6 of the free sugars derived from **4** and **5** disclosed that the less polar compound **4** and the more polar compound **5** corresponded to L-talo- and D-allofuranose derivatives, respectively.

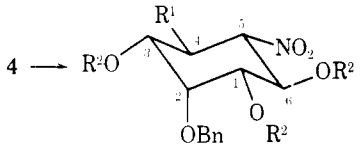
From the theoretical point of view, the L-talo isomer **4** should give branched-chain *epi*- or/and *myo*-inositol derivatives. However, stereodirection of the cyclization is rather limited since it depends on whether or not the benzyloxy group at C-3 can occupy an axial orientation, as we pointed out in the nonbonded interaction of the axial benzyloxy group in the case of the cyclization of D-gluco isomer in the previous paper.[1b]

Therefore, the intramolecular cyclization was conducted first in the case of the compound **4**, in which the benzyloxy group should occupy an axial orientation in a chair conformation, if **4** has L-talo configuration. The 1,2-*O*-isopropylidene group was removed with 90% trifluoroacetic acid for 45 min at room temperature or by refluxing **4** for 2.5 h with 75% acetic acid, and successive treatment of the resulting free sugar with 1.5–2.0 equiv sodium hydrogen carbonate in aqueous methanol for 15–20 h gave stereoselectively an expected *myo*-inositol derivative, 1-D-2-*O*-benzyl-4,5-dideoxy-4-*C*-(1,3-dithian-2-yl)-5-nitro-*myo*-inositol[7] (**7**), in good yield. Acetylation of **7** with acetic anhydride in the presence of *p*-toluenesulfonic acid gave a crystalline triacetate (**8**) in 80% yield. Coupling constants (see Table I) show that the compound **8** possesses the myo configuration, and consequently, compound **4** has the L-talo configuration. The above conclusions are also supported indirectly by the experiment reported by Baer et al.[8] that 6-deoxy-3-*O*-methyl-6-nitro-L-talose cyclized in a weak basic condition to give mainly a *myo*-inositol derivative in addition to three other isomers.

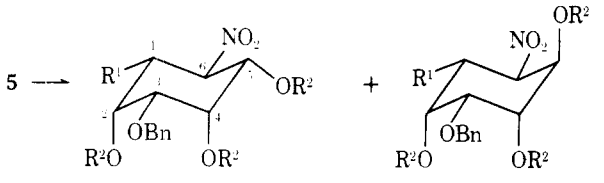
On the other hand, when the free sugar derived from **5** was subjected to the same cyclization in the presence of sodium hydrogen carbonate, almost equal amounts of branched-chain *epi*- and *allo*-inositol derivatives (**11** and **15**) were isolated respectively in 37 and 40% yields. Acetylation of the more polar crystalline *epi*-inositol **11** and the less polar *allo*-inositol **15** gave the corresponding triacetates (**12** and **16**) respectively in good yields. The NMR parameters clearly demonstrate that the compounds **12** and **16** must be *epi*- and *allo*-inositol derivatives having typical rigid chair conformations, respectively (see Table I). The above conclusion, furthermore, was supported also by the chemical evidence that the inositol **15** was not acetonated with acetone/2,2-dimethoxypropane in the presence of *p*-toluenesulfonic acid, but the inositol **11** was easily acetonated in the same conditions to give mono-*O*-isopropylidene derivative (**17**).

Incidently, when the cyclization of both free sugars derived from **4** and **5** was conducted in the presence of sodium car-

Scheme II

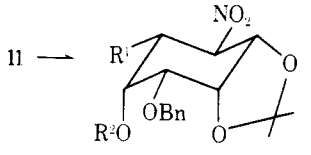


7, R^1 = DTN; R^2 = H
8, R^1 = DTN; R^2 = Ac
9, R^1 = CH_2NO_2; R^2 = H
10, R^1 = CH_2NO_2; R^2 = Ac



11, R^1 = DTN; R^2 = H
12, R^1 = DTN; R^2 = Ac
13, R^1 = CH_2NO_2; R^2 = H
14, R^1 = CH_2NO_2; R^2 = Ac

15, R^1 = DTN; R^2 = H
16, R^1 = DTN; R^2 = Ac



17, R^1 = DTN; R^2 = H
18, R^1 = DTN; R^2 = Ac

Ac = acetyl; DTN = 1,3-dithian-2-yl

bonate in aqueous methanol, nitroolefin formation took place rather preferentially and the yields of the branched-chain cyclitols (**7**, **11**, and **15**) much decreased.

However, when the similar cyclization of a free sugar derived from 5,6-dideoxy-3-*O*-benzyl-1,2-*O*-isopropylidene-5-*C*-(nitromethyl)-6-nitro-α-D-*ribo*-hexofuranose (**6**), easily prepared by addition of nitromethane to the nitroolefin **3**, was conducted in the presence of sodium hydrogen carbonate or sodium carbonate in aqueous methanol, only two inositol derivatives (*myo*-**9** and *epi*-**13**) were isolated in moderate yields in a ratio of 2:1. Interestingly, neither an *allo*-inositol nor a nitrooelfin was detected. The configuration of both inositols was also determined by the NMR parameters of the resulting triacetates (**10** and **14**).

From the experimental facts presented above, it will be naturally understood that the presence of the bulky benzyloxy group as well as the 1,3-dithiane residue (or the nitromethyl group) does influence the stereodirection of the intramolecular cyclization of branched-chain nitro sugars **4**, **5**, and **6**. Precisely speaking, the following thermodynamic criteria must also be involved in this kind of cyclization: (i) the bulky 1,3-dithiane residue or nitromethyl group tends to occupy the equatorial position and (ii) when the benzyloxy group must occupy an axial position, a newly formed hydroxyl group should be equatorial in order to avoid the 1,3-nonbonded interaction to give a single branched-chain cyclitol preferentially.

Experimental Section

Melting points were determined on a Yanagimoto micro-melting-point apparatus and are uncorrected. Solvents were evaporated off in vacuo below 40 °C. NMR spectra (100 MHz) were recorded with a JNM-PS-100 spectrometer in solutions of chloroform-*d* containing tetramethylsilane as the internal reference. IR spectra were recorded with a Hitachi EPI-G2 spectrometer. Optical rotations were measured with a JASCO DIP-4 digital polarimeter. TLC and preparative TLC were effected on plates of silica gel (Merk type 60) with the solvent systems A, 2:1, and B, 10:1 (v/v), of benzene–ethyl acetate.

Periodate Oxidation of 1 and Reaction of the Resulting Aldehyde with Nitromethane. To a cooled (5–10 °C) suspension of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-allofuranose[2] **1** (3.7 g, 12 mmol) in water (10 mL) and methanol (30 mL) was gradually added a solution of sodium metaperiodate (2.7 g, 12.6 mmol) in water (20 mL). The reaction mixture was stirred for 30 min in an ice-water bath and for another 30 min at room temperature. Inorganic materials were filtered off and washed with methanol. The filtrate and washings were evaporated to a residue, which was reextracted several times with methanol. The methanol extracts were concentrated to a clear syrup (3.0 g). To a solution of the syrup in methanol (5 mL) and nitromethane (5 mL) was then added a solution of sodium methoxide prepared from sodium (280 mg) in methanol (10 mL). The solution was stirred for 1.5 h at room temperature, acidified with acetic acid, and concentrated to a crystalline mass, which was dissolved in chloroform, washed with brine, dried ($MgSO_4$), and concentrated to a pale yellow syrup (3.6 g, 88%). This syrup can be used in the next step without further purification. A part of the syrup (500 mg) was placed on a silica gel column and eluted with benzene–acetone (20/1) to give epimeric nitroalcohols (340 mg) having $[\alpha]^{27}_D$ +107° (*c* 1.42, CH_3COCH_3). IR (NaCl) 3450, (OH), 1555, 1380 cm^{-1} (NO_2).

Anal. Calcd for $C_{16}H_{21}NO_7$: C, 56.63; H, 6.24; N, 4.13. Found; C, 56.53; H, 6.34; N, 3.98.

3-*O*-Benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-nitro-α-D-*ribo*-hex-5-enofuranose (3). Method a. A mixture of **2** (1.66 g, 4.9 mmol) and anhydrous sodium acetate (2.8 g) in acetic anhydride (8.5 mL) was stirred overnight at room temperature and poured into aqueous sodium hydrogen carbonate (120 mL). The precipitate was filtered off and the filtrate was extracted with chloroform, washed with aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and concentrated to a syrup (1.36 g), which was placed on a column of silica gel (Wako-gel C-200; 20 g) and eluted with benzene to give a clear syrup (1.2 g, 76%) having $[\alpha]^{28}_D$ +53.4° (*c* 1.05, CH_3COCH_3): IR (NaCl) 1655, 1530, 1360 cm^{-1} (C=CNO_2); NMR δ 1.39, 1.61 (s, 6 H, isopropyl), 3.58 (q, 1 H, $J_{2,3}$ = 4.0 Hz, $J_{3,4}$ = 9.0 Hz, H-3), 4.66 (q, 2 H, J_{gem} = 12.0 Hz, CH_2Ph), ~4.6 (m, 2 H, H-2 and H-4), 5.76 (d, 1 H, $J_{1,2}$ = 4.0 Hz, H-1), 7.1 (m, 2 H, H-5 and H-6), 7.34 (s, 5 H, phenyl).

Method b. To a cooled (0 °C) solution of nitroalcohol **2** (3.4 g, 10 mmol) in dry methylene chloride (10 mL) was added methanesulfonyl chloride (2.5 mL, 32 mmol). Triethylamine (6 mL, 43 mmol) was then gradually added to the above solution and the reaction solution was kept for 30 min at 0 °C. Methylene chloride (10 mL) was then added and the mixture was washed with aqueous sodium hydrogen carbonate, brine, and water, dried ($MgSO_4$), and concentrated in vacuo (1 torr) to a syrup. The syrup was finally purified with a column of silica gel as above to give a pure nitroolefin **3** (2.7 g, 85%).

3-*O*-Benzyl-5,6-dideoxy-5-*C*-(1,3-dithian-2-yl)-1,2-*O*-isopropylidene-6-nitro-α-L-talofuranose (4) and -α-D-allofuranose (5). To a cooled (−50 °C) solution of **3** (4.0 g, 12.5 mmol) in dry tetrahydrofuran (THF) 20 mL) a solution of 2-lithio-1,3-dithiane prepared at −50°C from 1,3-dithiane (1.9 g, 15.8 mmol) and butyllithium (10% hexane solution; 9.2 mL, 14.4 mmol) in dry THF (20 mL) was added at one time. The reaction mixture was kept for 30 min at the same temperature and acidified with acetic acid. The gelatinous mixture was dissolved in methanol, and the resulting solution was concentrated to a residue, which was treated with chloroform and brine. The chloroform layer was washed with water, dried ($MgSO_4$), and evaporated to a syrup (5.2 g), which was placed on a column of silica gel (Wako gel C-200; 50 g), and fractions of solvent B gave a partially crystalline residue (3.2 g, 59%). Fractional crystallization (from ethyl acetate or ethanol) or/and preparative TLC (solvent B) gave the less polar crystal **4** (1.3 g) and the more polar crystal **5** (1.2 g), respectively. **4**: mp 195–196 °C (ethyl acetate) and $[\alpha]^{28}_D$ +53.9° (*c* 0.52, CCl_4). **5**: mp 139–140 °C (ethanol) and $[\alpha]^{28}_D$ 58.7° (*c* 1.08, CCl_4). NMR of **4**: δ 1.33, 1.57 (s, 6 H, isopropyl), 1.8–2.2 and 2.7–3.0 (m, 6 H, trimethylene), 3.08 (m, 1 H, H-5), 3.52 (q, 1 H, $J_{2,3}$ = 4.4 Hz, $J_{3,4}$ = 8.0 Hz, H-3), 4.16–4.76 (m, 7 H, H-2, H-4, H-5′, H-6, and CH_2Ph), 5.73 (d, 1 H, $J_{1,2}$ = 3.6 Hz, H-1), 7.32 (s, 5 H, phenyl). NMR of **5**: δ 1.35, 1.60 (s, 6 H, isopropyl), 1.8–2.2 and 2.7–3.0 (m, 6 H, trimethylene), 3.12 (m, 1 H, H-5), 3.64 (q, 1 H, $J_{2,3}$ = 4.0 Hz, $J_{3,4}$ = 10.0 Hz, H-3), 4.24 (d, 1 H, $J_{5,5'}$ = 6.0 Hz, H-5′), 4.4–4.7 (m, 4 H, H-2, H-4, H-6, and H-6′), 4.70 (9, 2 H, J_{gem} = 12.0 Hz, CH_2Ph), 5.67 (d, 1 H, $J_{1,2}$ = 3.6 Hz, H-1), 7.36 (s, 5 H, phenyl).

Anal. Calcd for $C_{20}H_{27}NO_6S_2$: C, 54.42; H, 6.17; N, 3.17. Found: (**4**) C, 54.20; H, 6.03; N, 3.46; (**5**) C, 54.44; H, 6.06; N, 3.31.

3-*O*-Benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-5-*C*-(nitromethyl)-6-nitro-α-D-*ribo*-hexofuranose (6). A solution of nitroolefin **3** (1.31 g, 4.1 mmol) in absolute methanol (5 mL) was gradually added to a suspension of sodium salt of nitromethane prepared from sodium (0.28 g, 12 mmol) and nitromethane (2 mL) in methanol (10 mL). The reaction mixture was kept for 20 min at 0 °C, acidified with acetic acid, and concentrated to a residue, which was treated with

chloroform and brine. The chloroform layer was then washed with water, dried ($MgSO_4$), and concentrated to a syrup, which gradually crystallized. Recrystallization from ethanol gave pure crystals (1.12 g, 70%): mp 76–77 °C; $[\alpha]^{25}_D$ +22.0° (*c* 1.0, benzene); NMR δ 1.36, 1.57 (s, 6 H, isopropyl), 3.20 (quintet, 1 H, *J* = 6.0 Hz, H-5), 3.65 (q, 1 H, $J_{2,3}$ = 4.0, $J_{3,4}$ = 8.0 Hz, H-3), 4.09 (q, 1 H, $J_{4,5}$ = 8.1 Hz, H-4), 4.60 (q, 2 H, J_{gem} = 12 Hz, CH_2Ph), 4.6 (m, 5 H, H-2 and CH_2NO_2), 5.69 (d, 1 H, $J_{1,2}$ = 4.0 Hz, H-1), 7.35 (s, 5 H, phenyl).

Anal. Calcd for $C_{17}H_{22}O_8N_2$: C, 53.40; H, 5.80; N, 7.33. Found: C, 53.47; H, 5.98; N, 7.26.

1D-2-*O*-benzyl-4,5-dideoxy-4-*C*-(1,3-dithian-2-yl)-5-nitro-*myo*-inositol (7) and Its Triacetate (8). A solution of **4** (400 mg, 0.90 mmol) in 75% acetic acid (35 mL) was refluxed for 2.5 h and evaporated in the presence of ethanol to a pale yellow syrup, which was then dissolved in a mixture of methanol (24 mL) and aqueous sodium hydrogen carbonate (2%, 8 mL). The reaction solution was kept overnight at room temperature, deionized with IR-120 (H^+), and concentrated to an almost pure syrup (360 mg). A part (100 mg) of the syrup was purified with preparative TLC (solvent A) to give pure **7** (60 mg) having $[\alpha]^{28}_D$ −14° (*c* 1.0, CH_3COCH_3).

A solution of the syrup (200 mg) in acetic anhydride (2 mL) containing a catalytic amount of *p*-toluenesulfonic acid was kept overnight at room temperature. Usual work-up gave a crystalline mass, which was recrystallized from ethanol to give needles (**8**, 180 mg, 68%): mp 144–145°c, $[\alpha]^{20}_D$ −28.6° (*c* 1.01, CH_3COCH_3); NMR (see Table I).

Anal. Calcd for $C_{23}H_{29}O_9NS_2$: C, 52.37; H, 5.52; N, 2.66. Found: C, 52.14, H, 5.66; N, 2.88.

1L-3-*O*-Benzyl-1,6-dideoxy-1-*C*-(1,3-dithian-2-yl)-6-nitro-*epi*-inositol (11) and 1L-3-*O*-Benzyl-1,6-dideoxy-1-*C*-(1,3-dithian-2-yl)-6-nitro-*allo*-inositol (15). The compound **5** (710 mg, 1.61 mmol) was dissolved in cooled (5 °C) 90% trifluoroacetic acid (13 mL), and the solution was allowed to stand for 45 min at room temperature. After complete evaporation of the solvent, the resulting syrup was dissolved in a mixture of methanol (40 mL) and aqueous sodium hydrogen carbonate (300 mg, in 10 mL water). The reaction solution was kept overnight at room temperature, deionized with IR-120 (H^+), and concentrated to a syrup, which was placed on a silica gel column (Wako-gel C-200; 20g). From solvent B fractions, less polar syrup **15** (260 mg, 40%), having $[\alpha]^{20}_D$ +33.4° (*c* 1.16, acetone), and more polar crystals **11** (240 mg, 37%), having mp 211–212 °C, $[\alpha]_D^{20}$ +15.0° (*c* 0.85, acetone), were separated from each other, respectively.

Anal. Calcd for $C_{17}H_{23}NO_6S_2$: C, 50.87; H, 5.78; N, 3.49. Found: (**11**) C, 50.77; H, 5.94; N, 3.42; (**15**) C, 50.69; H, 5.87; N, 3.36.

Triacetates (12 and 16). A solution of **11** (100 mg, 0.25 mmol) or **15** (200 mg, 0.5 mmol) in acetic anhydride (**11**; 3 mL, **15**; 5 mL) containing a catalytic amount of *p*-toluenesulfonic acid was kept overnight at room temperature. After usual work-up and purification, a syrupy triacetate **12** (90 mg) having $[\alpha]^{28}_D$ −7.4° (*c* 1.08, CH_3COCH_3) and a crystalline triacetate **16** (190 mg) having mp 187–188 °C and $[\alpha]^{28}_D$ −35.7° (*c* 0.78, $CHCl_3$) were obtained.

NMR spectra of the compounds are listed in Table I.

Anal. Calcd for $C_{23}H_{29}NO_9S_2$: C, 52.37; H, 5.52; N, 2.66. Found: (**12**) C, 52.25; H, 5.67; N, 2.43; (**16**) C, 52.33; H, 5.47; N, 2.72.

1L-3-*O*-Benzyl-1,6-dideoxy-1-*C*-(1,3-dithian-2-yl)-4,5-*O*-isopropylidene-6-nitro-*epi*-inositol (17) and Its Acetate (18). A solution of **11** (120 mg, 0.3 mmol) in acetone (6 mL) and 2,2-dimethoxypropane (3 mL) containing a catalytic amount of *p*-toluenesulfonic acid was kept for 5 h at room temperature and evaporated to a syrup, which was immediately treated with chloroform and aqueous sodium hydrogen carbonate. The chloroform layer was washed with aqueous $NaHCO_3$ and water, dried over $MgSO_4$, and concentrated to a syrup (100 mg). Preparative TLC (solvent B) of the syrup gave pure **17** (70 mg) having $[\alpha]^{28}_D$ −10.5° (*c* 1.3, CH_3COCH_3). Acetylation of **17** in the same way as described above gave syrupy monoacetate **18** having $[\alpha]^{27}_D$ −26.8° (*c* 1.32, CH_3COCH_3). NMR of **18**: δ 1.41, 1.67 (s, 6 H, isopropyl), 2.20 (s, 3 H, OAc), 1.8–2.3 and 2.6–3.1 (m, 6 H, trimethylene), 3.1 (m, 1 H, H-1), 3.65 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 3.6 Hz H-3), 4.10 (d, 1 H, $J_{1,1'}$ = 3.6 Hz, H-1), 4.37–4.64 (m, 2 H, H-6 and H-4), 4.78 (dd, 2 H, J_{gem} = 13.5 Hz, CH_2Ph), 5.18 (q, 1 H, $J_{1,6}$ = 12.0 Hg $J_{5,6}$ = 7.8 Hz, H-6), 6.02 (1 H, $J_{1,2}$ = 2.0 Hz, H-2), 7.42 (s, 5 H, phenyl).

1D-2-*O*-Benzyl-4,5-dideoxy-4-*C*-(nitromethyl)-5-nitro-*myo*-inositol (9) and 1L-3-*O*-benzyl-1,6-dideoxy-1-*C*-(nitromethyl)-6-nitro-*epi*-inositol (13). A solution of **6** (240 mg, 0.63 mmol) in 80% acetic acid (5 mL) was refluxed for 2 h, and the solvent was completely removed to a syrup, which was dissolved in methanol (10 mL) and water (6 mL) containing sodium carbonate (94 mg, 0.88 mmol). The mixture was stirred overnight at room temperature, deionized with IR-120 (H^+), and concentrated to a syrup (210 mg) involving two components. A more polar *myo*-inositol derivative **9** (50 mg) and a less polar *epi*-inositol derivative **13** (40 mg) were separated respectively from each other by preparative TLC (solvent B).

9: mp 130–132 °C (benzene); $[\alpha]^{28}_D$ +7.0° (*c* 0.40, CH_3OH). Anal. Calcd for $C_{14}H_{18}N_2O_8$; C, 49.12; H, 5.30; N, 8.18. Found: C, 49.34; H, 5.25; N, 7.93.

13: mp 171–172 °C (ethanol); $[\alpha]^{28}_D$ +4.1° (*c* 0.58, CH_3OH). Found: C, 49.32; H, 5.25; N, 8.05.

Acetylation of the compounds **9** and **13** was done in the same way described above to give a crystalline triacetate **10** having mp 126–128 °C (ethanol) and $[\alpha]^{28}_D$ +14.2° (*c* 0.32, CH_3COCH_3) and a syrupy triacetate **14**. NMR of *myo*-**10**: δ 1.88, 1.92, 1.95 (s, OAc × 3), 3.5 (m, 1 H, H-4), 4.12 (t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 3.0 Hz, H-2), 4.2–4.8 (not assigned), 4.92 (q, 1 H, H-1), 5.90 (t, 1 H, $J_{5,6}$ = $J_{1,6}$ = 10 Hz, H-6), 7.24 (s, 5 H, phenyl). NMR of *epi*-**14**: 1.99, 2.11 × 2 (s, 9 H, acetyl), 3.17 (m, 1 H, H-1), 3.70 (t, 1 H, H-3), 4.2–4.7 (not assigned), 5.00 (t, 1 H, $J_{1,6}$ = $J_{5,6}$ = 11.0 Hz, H-6), 5.40 (q, 1 H, $J_{4,5}$ = 3.2 Hz, H-5), 5.67 (t, 1 H H-4), 5.79 (q, 1 H, $J_{1,2}$ = 2.8, $J_{2,3}$ = 3.2 Hz, H-2), 7.34 (s, 5 H, phenyl).

Registry No.—**1**, 57099-04-4; **2** isomer 1, 69177-81-7; **2** isomer 2, 69177-82-8; **3**, 69177-83-9; **4**, 69203-99-2; **5**, 69190-63-2; **6**, 69177-84-0; **7**, 69256-31-1; **9**, 69177-85-1; **10**, 69177-86-2; **11**, 69177-87-3; **13**, 69224-21-1; **14**, 69224-22-2; **15**, 69224-23-3; **17**, 69177-88-4; **18**, 69177-89-5; 3-*O*-benzyl-5,6-dideoxy-5-*C*-(1,3-dithian-2-yl)-6-nitro-β-L-talofuranose, 69177-90-8; 3-*o*-benzyl-5,6-dideoxy-5-*C*-(1,3-dithian-2-yl)-6-nitro-α-D-allofuranose; 2-lithio-1,3-dithiane, 36049-90-8; nitromethane sodium salt, 25854-38-0; nitromethane, 75-52-5.

References and Notes

(1) (a) Branched-Chain Sugars. Part 16 (Part 15: ref 1c); (b) M. Funabashi and J. Yoshimura, *J. Chem. Soc., Perkin Trans. 1*, in press; (c) M. Funabashi, H. Wakai, K. Sato, and J. Yoshimura, *ibid.*, in press.
(2) J. S. Brimacombe and O. A. Ching, *Carbohydr. Res.*, **8**, 82 (1968).
(3) NMR spectrum of **2** showed the presence of almost equal amounts of C-5 epimers.
(4) R. L. Whistler and P. E. Pyler, *Carbohydr. Res.*, **12**, 201 (1970).
(5) (a) J. Melton and J. E. McMurry, *J. Org. Chem.*, **40**, 2138 (1975); (b) H. H. Baer and F. F. Z. Georges, *ibid.*, **41**, 3474 (1976).
(6) (a) D. Seebach and H. F. Leitz, *Angew. Chem.*, **81**, 1047 (1969); (b) D. Seebach, H. F. Leitz, and V. Ehrig, *Chem. Ber.*, **108**, 1924 (1975).
(7) Nomenclature follows the IUPAC-IUB 1973 Recommendations for Cyclitols: *Pure Appl. Chem.*, **37**, 285 (1974).
(8) J. Kovar and H. H. Baer, *Carbohydr. Res.*, **45**, 161 (1975).