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SYNTHESIS OF A 6-*C*-NITRO-D-GLUCOPYRANOSE DERIVATIVE HAVING PHOSPHORUS IN THE HEMIACETAL RING

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ABSTRACT

5,6-Dideoxy-6-*C*-nitro-5-(phenylphosphino)-D-glucopyranose was prepared by addition of phenylphosphine to 3-*O*-acetyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-α-D-*xylo*-hex-5-enofuranose, followed by hydrolysis of the resulting 3-*O*-acetyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-5-(phenylphosphino)-D-glucofuranose (**10**). Acetylation of **10** gave the crystalline 1,2,3,4-tetraacetate (**16**). 5,6-Dideoxy-6-*C*-nitro-5-(phenylphosphinyl)-D-glucopyranose (**15**) was obtained by oxidation of **10**, and hydrolysis of the resulting 5-phenylphosphinyl compound. Acetylation of **15** gave the 1,2,3,4-tetraacetate (**17**). Although the n.m.r. spectrum of **17** was complex, the n.m.r. spectrum of **16** was rather simple. The n.m.r. data showed that **16** is the α anomer in the $^4C_1$(D) conformation.

INTRODUCTION

Sugar analogs having phosphorus in the hemiacetal ring are interesting, not only from the point of view of their chemistry, but also from that of the possible utility of their biological activities. However, only a few reports[1] thereon have been published; moreover, all of them discussed compounds of the pentopyranose type, prepared from 5-deoxy-5-halo derivatives *via* a Michaelis–Arbuzov reaction, reduction, and hydrolysis. As revealed in a preliminary communication[2], we have now succeeded in the synthesis of a hexopyranose having phosphorus in the hemiacetal ring by using the addition reaction of a phosphine to an active olefinic sugar, namely, 3-*O*-acetyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-α-D-*xylo*-hex-5-enofuranose[3] (**1**). We now report the synthesis in detail.

RESULTS

Addition of methyl ethylphosphonite to **1** gave a mixture* of the D-*gluco* (**2**)

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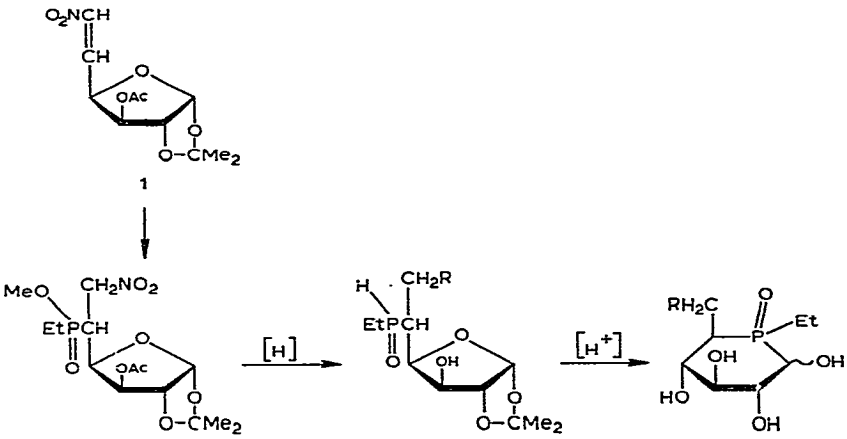
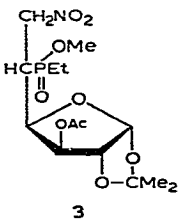
*The p.m.r. spectrum showed that the mixture consisted of **2** and **3** in the ratio of ~1:1.

and L-*ido* (**3**) compounds in 90% yield. From the mixture, crystalline 3-*O*-acetyl-5,6-dideoxy-5-*C*-[ethyl(methoxy)phosphinyl]-1,2-*O*-isopropylidene-6-*C*-nitro-α-D-glucofuranose (**2**) was separated in 20% yield. We attempted to obtain the target compound **5** from **2** *via* reduction and hydrolysis in the usual way, as described before. Reduction

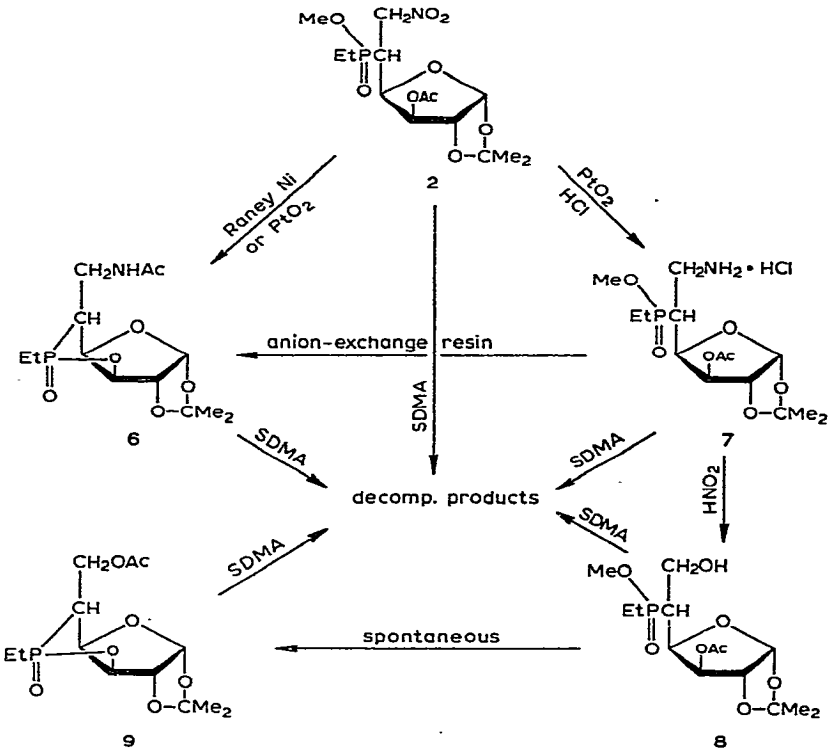




of **2** with lithium aluminum hydride (LAH) or sodium dihydrobis(2-methoxyethoxy)-aluminate (SDMA) led to decomposition products, instead of formation of the 5-*C*-(ethylphosphinyl) compound (**4**). Reduction of **2** with hydrogen in the presence of Raney nickel gave, in 69% yield, crystalline 6-acetamido-5-(3-*O*-cyclo-ethylphosphinate)-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (**6**) (m.p. 243°) with cyclization of the phosphinate group and transfer of the acetyl group. The p.m.r. spectrum of **6** in chloroform-*d* showed that the acetyl signal had shifted from δ 2.10 to 1.96 and the POMe signal had disappeared. The i.r. spectrum of **6** showed that the C=O absorption had changed from 1735 cm^{-1} (acetyl carbonyl) to 1650 cm^{-1} (amide carbonyl).

Reduction of **6** with SDMA gave decomposition products. To protect the phosphinate group from cyclization, and prevent transfer of the acetyl group, reduction of **2** was conducted in the presence of hydrochloric acid in methanol, with platinum oxide as the catalyst, to afford, in 80% yield, unstable compound **7**, namely, 3-*O*-acetyl-6-amino-5,6-dideoxy-5-*C*-[ethyl(methoxy)phosphinyl]-1,2-*O*-isopropylidene-α-D-glucofuranose hydrochloride. By treatment of **7** with an anion-exchange

resin in methanol, **7** was converted into **6**. Treatment of **7** with SDMA led to decomposition products. Deamination of **7** with nitrous acid gave compound **8**, namely, 3-*O*-acetyl-5-deoxy-5-*C*-[ethyl(methoxy)phosphinyl]-1,2-*O*-isopropylidene-α-D-glucofuranose, which was spontaneously converted into compound **9**, m.p. 228°. Compound **9** was also obtained by treatment of **8** with SDMA. By study of its p.m.r. spectrum and by elemental analysis, the structure of **9** was determined to be 3-*O*-acetyl-5-(3-*O*-cyclo-ethylphosphinate)-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose. Treatment of **8** or **9** with an excess of SDMA led to decomposition products.



All of these attempts to convert the phosphinate group into a phosphine oxide group failed, so we considered the use of another method, namely, addition of phenylphosphine to **2** (instead of addition of phosphonites and reduction). Addition of phenylphosphine to **2** for 1 h at 40–50° afforded a mixture of the D-*gluco* compound **10** and the L-*ido* compound **11**, and 1:2 adducts. From the mixture, a syrup containing **10** and **11** (3:1 from the p.m.r. spectrum) was separated in 63% yield from the 1:2 adducts (34%) by column chromatography on silica gel. The addition of a small amount of methanol or ethanol to the syrupy **10** plus **11** afforded crystalline **10**, 3-*O*-acetyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-5-(phenylphosphino)-α-D-glucofuranose (44% yield); m.p. 105.5–106°, $[\alpha]_D^{29}$ −15.8° (*c* 1.14, methanol), optical circular dichroism $[\theta]_{299nm}$ −12,460 (trough) (*c* 0.2, methanol). The negative Cotton-effect shows that **10** has the D-*gluco* configuration[4]. In the p.m.r. spectrum

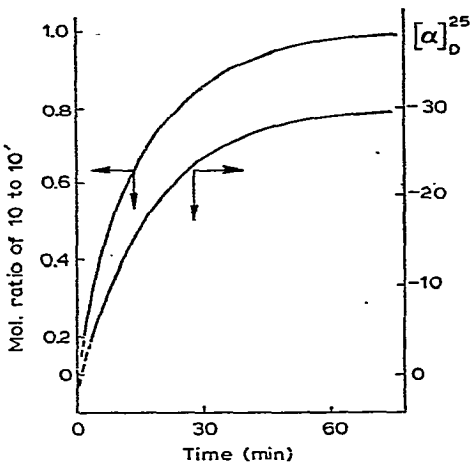


Fig. 1. Variation of **10**/**10'** and $[\alpha]_D^{25}$ (*c* 8.0, $CDCl_3$) as a function of time.

(chloroform-*d*), a characteristic P-H signal was observed (J_{PH} 218 Hz), and the i.r. spectrum (KBr) showed P-H absorption at 2280 cm^{-1}, but no P=O group absorption was found.

When **10** was dissolved in chloroform-*d*, the optical rotation and the intensity ratio of the signals of the acetyl groups in the p.m.r. spectrum changed as shown in Fig. 1, and reached equilibrium after 60 min, indicating that, in the solution, there exist two rotatory isomers **10** and **10'** in the ratio of ~1 : 1. Evaporation of the solution gave **10** in the pure state again; thus, **10** is the stable form in the crystal. The p.m.r. data for the two isomers are given in Table I.

Treatment of **10** in methanol with an equivalent of hydrogen peroxide gave,

TABLE I

PROPERTIES OF THE TWO ISOMERS **10** AND **10'**

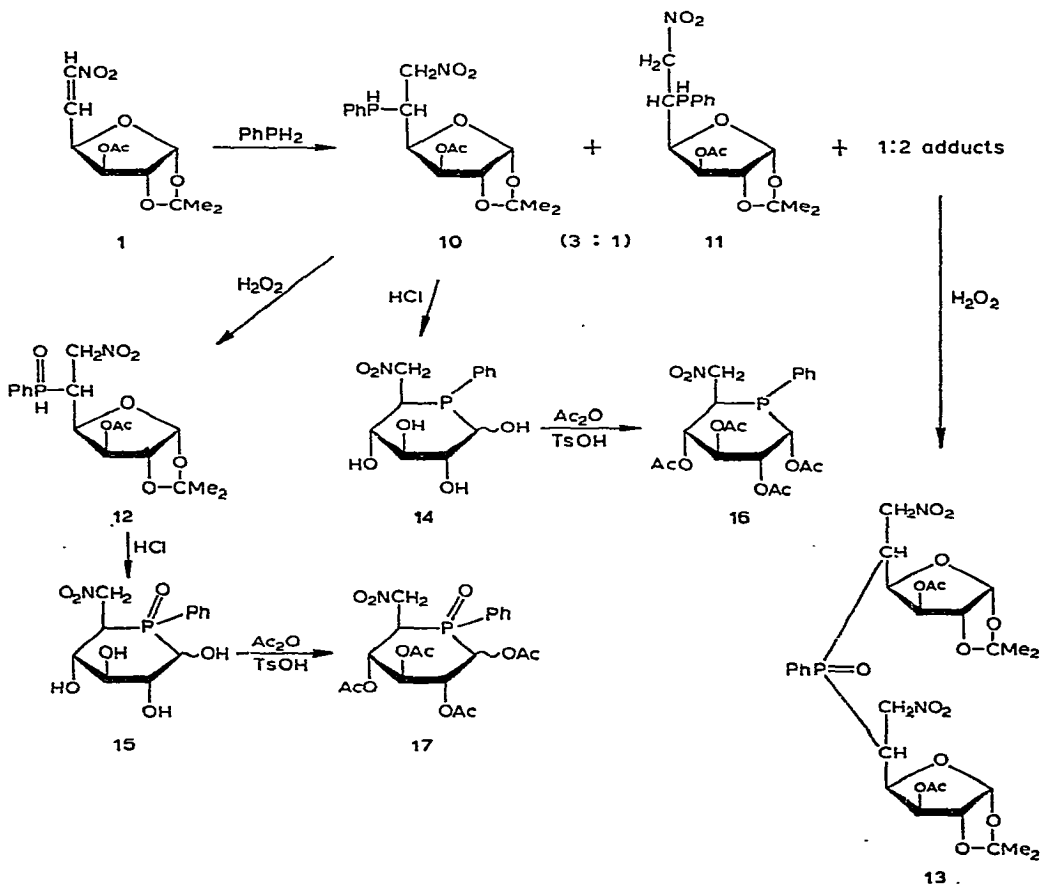
Compound	$[\alpha]_D^{25}$ *(degrees)*[a]	*P.m.r. data* δ	*Assignment*
10	+1.5	2.12	OAc
		5.87 ($J_{1,2}$ 4.0 Hz)	H-1
		5.13 ($J_{3,4}$ 2.5 Hz)	H-5
		4.33 ($J_{P,H}$ 219 Hz)	
		($J_{P,5}$ 6.1 Hz)	P–H
10'	−62	2.04	OAc
		5.89 ($J_{1,2}$ 4.0 Hz)	H-1
		5.13 ($J_{3,4}$ 2.5 Hz)	H-5
		4.30 ($J_{P,H}$ 211 Hz)	
		($J_{P,5}$ 3.5 Hz)	P–H

[a]In $CDCl_3$ (*c* 8.0).

almost quantitatively, crystalline compound **12**; m.p. 169–171°, $[\alpha]_D^{24}$ −35.6° (*c* 1.35, methanol). The p.m.r. spectrum (chloroform-*d*) of **12** showed a characteristic J_{P-H} value of 520 Hz, and the i.r. spectrum (KBr) showed absorption, due to a P-H group, at 2376 cm^{-1} and that due to a P=O group at 1210 cm^{-1}. These results indicated that compound **12** is 3-*O*-acetyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-5-(phenylphosphinyl)-α-D-glucofuranose.

Treatment of the syrupy 1:2 adducts in methanol with one equivalent of H_2O_2 gave, in 34% yield, crystalline **13**; m.p. 209–210.5°, $[\alpha]_D^{24}$ −23.8° (*c* 0.52, methanol). Compound **13** was determined to be bis(3-*O*-acetyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-α-D-glucofuranose-5-yl)phenylphosphine oxide from the preponderant formation of the D-*gluco* compound **10** in the 1:1 adduct mixture (**10** + **11**); therefore, the original 1:2 adducts seemed to consist mainly of the corresponding phosphine compound.

Hydrolysis of **10** and **12** with 3M HCl for 3 h at 80–100° afforded syrupy **14** and crystalline **15** in 81 and 67% yields, respectively. Study of the p.m.r. spectra (dimethyl sulfoxide-d_6) and i.r. spectra of **14** and **15** showed that these compounds did not possess acetyl, isopropylidene, and P-H groups. Acetylation of **14** and **15**



in acetic anhydride with *p*-toluenesulfonic acid as the catalyst gave crystalline compounds **16** (m.p. 150–152°) and **17** [m.p. 269° (dec.)], respectively; the p.m.r. spectra (chloroform-*d*) thereof showed that **16** and **17** had four acetyl groups. The p.m.r. spectroscopy indicated that the structures of **16** and **17** were 1,2,3,4-tetra-*O*-acetyl-5,6-dideoxy-6-*C*-nitro-5-(phenylphosphino)-D-glucopyranose and 1,2,3,4-tetra-*O*-acetyl-5,6-dideoxy-6-*C*-nitro-5-(phenylphosphinyl)-D-glucopyranose, respectively.

The p.m.r. spectrum of **17** was not well resolved, even at 100 MHz, but that of **16** was well resolved at 100 MHz, and the spectrum was amenable to first-order analysis. The ordering of the signals of the different protons was provided by application of the double-resonance technique ($J_{1,2}$ 2.5, $J_{2,3}$ 9.6, $J_{3,4}$ 9.6, $J_{1,P}$ 8.5, $J_{2,P}$ 2.5, and $J_{1,5}$ 1.2 Hz). Large diaxial, space couplings of 9.6 Hz appear between H-2 and H-3, and H-3 and H-4; these data show that **16** has the $^4C_1$(D) conformation. The small value of the coupling constant $J_{1,2}$ (2.5 Hz) indicates that **16** is the α-D anomer. Long-range coupling of 1.2 Hz was observed between H-5 and H-1.

EXPERIMENTAL

General. — Melting points are uncorrected. The i.r. spectra were recorded with a Hitachi–Perkin–Elmer 337 spectrophotometer, and the p.m.r. spectra with Hitachi–Perkin–Elmer R-20 (at 60 MHz) and Varian HA-100 (at 100 MHz) spectrophotometers, with tetramethylsilane as the internal reference-standard. Optical rotations (sodium D line) were measured with a Hitachi PO-B polarimeter by use of a 0.5-dm cell. Thin-layer chromatography (t.l.c.) was conducted on layers of silica G-10 (Nakarai Chemicals, Ltd., Japan): the compounds were detected by spraying the plates with 1 : 9 (v/v) sulfuric acid–ethanol and then heating them. Periodic monitoring by t.l.c. permitted determination of reaction conditions suitable for the preparative reactions.

Materials. — 3-*O*-Acetyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-α-D-*xylo*-hex-5-enofuranose (**1**) (m.p. 112°) was prepared by the method of Whistler and Pyler[3]. Methyl ethylphosphonite (b_{19} 75–76.5°) was prepared by the method of Arbuzov *et al.*[5], and phenylphosphine (b_{760} 159°) by the method of Mann and Millar[6].

Reaction of 3-O-acetyl-5,6-dideoxy-1,2-O-isopropylidene-6-C-nitro-α-D-xylo-hex-5-enofuranose (**1**) *with methyl ethylphosphonite.* — A solution of **1** (0.5 g) in methyl ethylphosphonite (2 mL) was heated for 7–10 h at 70–80°, and the excess of methyl ethylphosphonite was evaporated off *in vacuo*. A solution of the residual syrup in hot ether was kept in a refrigerator, to afford crystalline 3-*O*-acetyl-5,6-dideoxy-5-*C*-[ethyl(methoxy)phosphinyl]-1,2-*O*-isopropylidene-6-*C*-nitro-α-D-glucofuranose (**2**), m.p. 138.5–140°, $[\alpha]_D^{16}$ −15.4° (*c* 1.94, $CHCl_3$); ν_{max}^{KBr} 1735 (OAc) and 1200 cm^{-1} (P=O); p.m.r. data ($CDCl_3$): δ 5.85 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.21 (d, 1 H, $J_{3,4}$ 2.8 Hz, H-3), 4.45 (d, 1 H, H-2), 4.9–4.4 (m, 3 H, H-4,6,6'), 3.24 (m, 1 H, $J_{5,P}$ 16.5 Hz, $J_{5,4}$ 10.0 Hz, $J_{5,6}$ 5.5 Hz, $J_{5,6'}$ 3.0 Hz, H-5), 3.68 (d, 3 H, J_{POMe} 10.0 Hz, POMe),

2.09 (s, 3 H, OAc), 1.49, 1.29 (s, 6 H, CMe_2), 1.96 (o, 2 H, PCH_2), and 1.23 (hex, 3 H, PCMe).

Reduction of **2**. — (*A*) A solution of **2** (0.38 g) in methanol (20 mL) was stirred for 12 h in the presence of Raney nickel (W-4; from 1 g of alloy) under a hydrogen atmosphere (80–130 atm.). The nickel was filtered off, and the filtrate was evaporated *in vacuo*, to give crystalline **6** (0.22 g, 69%), m.p. 240–243° (from ethanol); ν_{max}^{KBr} 3300 (Amide I) and 1655 cm^{-1} (Amide II); p.m.r. data ($CDCl_3$): δ 6.00 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 5.0–4.4 (m, 5 H, H-2,3,4,6,6'), 3.8–2.8 (m, 1 H, H-5), 1.96 (s, 3 H, OAc), 1.46, 1.31 (s, 6 H, CMe_2), 2.2–0.9 (m, 5 H, PCH_2CH_3); Calc. for $C_{13}H_{22}NO_6P$: *m/e* 319.3. Found *m/e* 319.

(*B*) A solution of **2** (1.0 g) in methanol (100 mL) containing an equivalent of hydrochloric acid was stirred for 10 h under a hydrogen atmosphere in the presence of platinum (from 0.3 g of platinum oxide) as the catalyst. The catalyst was filtered off, and the filtrate evaporated *in vacuo*, to give unstable, crystalline **7** (0.82 g, 80%), m.p. 162–167° (dec.) (from ethanol–ethyl ether); p.m.r. data ($CDCl_3$): δ 5.8 (d, 1 H, H-1), 3.7 (d, 3 H, POMe), 2.1 (s, 3 H, OAc), and 1.5, 1.3 (s, 6 H, CMe_2).

Deamination of **7**. — To a solution of **7** (0.28 g) in water (5 mL) were added sodium nitrite (0.28 g) and acetic acid (0.16 mL) at 0°. Nitrogen gas was passed into the solution for 1 h at a room temperature, and the solution was extracted with chloroform; the extract was washed with aqueous sodium hydrogencarbonate, dried (sodium sulfate), and evaporated *in vacuo*. The residual oil was separated by preparative t.l.c. (ethyl acetate), to give syrupy **8** (0.15 g, 59%); ν_{max}^{film} 1735 cm^{-1} (OAc); p.m.r. data ($CDCl_3$); δ 5.74 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.17 (d, 1 H, $J_{2,3}$ 2.0 Hz, H-3), 4.7–3.3 (m, 6 H, H-2,4,5,6,6', OH), 3.66 (d, 3 H, J_{POMe} 10.0 Hz, POMe), 2.06 (s, 3 H, OAc), and 1.48, 1.29 (s, 6 H, CMe_2).

Treatment of **8** *with SDMA*. — To a solution of **8** (0.153 g) in tetrahydrofuran (THF; 20 mL) was added, at 0°, SDMA (3 equiv.) in THF (10 mL). The excess of SDMA was decomposed by addition of water, the resulting precipitate was filtered off, and the filtrate was evaporated *in vacuo*, to give crystalline **9** (0.109 g, 78%), m.p. 228° (from ethyl acetate); ν_{max}^{KBr} 1725 cm^{-1} (OAc); p.m.r. data ($CDCl_3$); δ 5.90 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 5.1–4.2 (m, 5 H, H-2,3,4,6,6'), 2.6–2.1 (m, 1 H, H-5), 2.02 (s, 3 H, OAc), 1.47, 1.30 (s, 6 H, CMe_2), and 2.0–0.8 (m, 5 H, PCH_2CH_3).

Anal. Calc. for $C_{13}H_{21}O_7P$: C, 48.75; H, 6.61. Found: C, 48.46; H, 6.74.

Reaction of **1** *with phenylphosphine*. — To a solution of **1** (2.73 g) in benzene (30 mL) was added phenylphosphine (16.5 g, 15 mol.equiv.) in benzene (10 mL) at 40–50° under a nitrogen atmosphere; the whole was kept for 1 h at 40–50°, and the excess of phenylphosphine was evaporated off *in vacuo*, to give a mixture of **10**, **11**, and the 1:2 adducts. The mixture was separated by column chromatography on silica gel with 1:4 (v/v) ethyl acetate–hexane into a mixture of **10** plus **11** (2.41 g, 63%), and the 1:2 adducts (1.54 g, 34%) with 1:1 (v/v) ethyl acetate–hexane. The syrup consisting of **10** and **11** was crystallized by addition of a small amount of methanol, or ethanol, giving colorless needles of **10** (1.67 g, 44%), m.p. 105.5–106° (from ethanol), $[\alpha]_D^{29}$ −15.8° (*c* 1.14, methanol); optical circular dichroism $[\theta]_{296nm}$ −12,640

(trough) (*c* 0.2, methanol); ν_{max}^{KBr} 2280 (PH) and 1730 cm^{-1} (OAc); p.m.r. data ($CDCl_3$): δ 7.9–7.2 (m, 5 H, Ph), 5.87, 5.89 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 5.13 (d, 1 H, $J_{3,4}$ 2.5 Hz, H-3), 4.7–3.9 (m, 4 H, H-2,4,6,6'), 3.5–2.8 (m, 1 H, H-5), 4.33, 4.30 (q, 1 H, $J_{P,H}$ 218 Hz, $J_{PH,5}$ 6.1 Hz, $J_{P,H'}$ 211 Hz, $J_{PH',5}$ 3.5 Hz, PH), 2.12, 2.04 (s, 3 H, OAc), and 1.28, 1.40 (s, 6 H, CMe_2); Calc. for $C_{17}H_{22}NO_7P$: *m/e* 383.3. Found: *m/e* 383.

Oxidation of **10**. — To a solution of **10** (0.383 g) in methanol (20 mL) was added a methanol solution (20 mL) containing one equivalent of aqueous, 35% hydrogen peroxide at 0°. After 5 h, the solution was evaporated *in vacuo* to yield, almost quantitatively, crystalline **12**, m.p. 169–170° (from ethanol), $[\alpha]_D^{24}$ −35.6° (*c* 1.35, methanol); ν_{max}^{KBr} 2350 (PH), 1730 (OAc), and 1210 cm^{-1} (P=O); p.m.r. data ($CDCl_3$): δ 8.0–7.2 (m, 5 H, Ph), 5.90 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.50 (d, 1 H, H-2), 5.00 (d, 1 H, $J_{3,4}$ 2.4 Hz, H-3), 4.00 (o, 1 H, $J_{4,5}$ 9.8 Hz, $J_{P,4}$ 5.8 Hz, H-4), 3.9–3.0 (m, 1 H, H-5), 7.85 (d, 1 H, $J_{P,H}$ 520 Hz, $J_{PH,5}$ 0.0 Hz, PH), 2.12 (s, 3 H, OAc), and 1.31, 1.28 (s, 6 H, CMe_2).

Oxidation of the 1:2 adducts. — The 1:2 adducts were treated as just described, and the syrup obtained was crystallized by addition of ethanol, to give, in 34% yield, **13**, m.p. 209–210.5° (from benzene–ethanol), $[\alpha]_D^{24}$ −23.8° (*c* 0.52, methanol); p.m.r. data ($CDCl_3$): δ 8.2–7.2 (m, 5 H, Ph), 6.18 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 6.07 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 5.48 (d, 1 H, H-3), 5.3–4.0 [m, 9 H, H-3',4,4',5,5',6,6', (6,6')'], 1.16, 1.09 (s, 6 H, OAc, OAc'), and 1.56, 1.37, 1.34 (s, 12 H, CMe_2, CMe_2').

*1,2,3,4-Tetra-*O*-acetyl-5,6-dideoxy-6-*C*-nitro-5-(phenylphosphino)-α-*D*-glucopyranose* (**16**). — To a solution of **10** (0.383 g) in THF (5 mL) were added concentrated hydrochloric acid (0.8 mL) and water (20 mL) under a nitrogen atmosphere, and the whole was heated for 4 h at 90–100°; the solution was evaporated *in vacuo*, the residual syrup was dissolved in water, and the solution was made neutral with an anion-exchange resin (IR-410), and evaporated *in vacuo* to a syrup **14** (0.235 g, 87%). To the syrup (0.386 g) were added acetic anhydride (8 mL) and *p*-toluenesulfonic acid (0.05 g), and the mixture was kept for 3 days at 40°, and evaporated *in vacuo*; a solution of the residual syrup in chloroform (30 mL) was washed with water, dried (sodium sulfate), and evaporated *in vacuo*. The resulting syrup was dissolved in ethyl acetate, and the solution was separated by column chromatography on silica gel with ethyl acetate, to give crystalline **16** (by addition of methanol) (0.115 g, 26%), m.p. 150–152° (from methanol), $[\alpha]_D^{15}$ −9.3° (*c* 0.43, chloroform); p.m.r. data ($CDCl_3$): δ 8.2–7.5 (m, 5 H, Ph), 6.25 (o, 1 H, $J_{1,P}$ 8.5 Hz, $J_{1,5}$ 1.2 Hz, H-1), 5.75 (dd, 1 H, $J_{2,3} = J_{3,4}$ = 9.6 Hz, H-3), 5.4–5.0 (m, 3 H, H-4,6,6'), 4.90 (ddd, 1 H, $J_{2,P}$ 2.5 Hz, H-2), 4.5–4.0 (m, 1 H, H-5), and 2.25, 2.00, 1.98, 1.96 (s, 12 H, OAc).

Anal. Calc. for $C_{20}H_{24}NO_{10}P$: C, 51.18; H, 5.36; N, 2.98. Found: C, 50.83; H, 5.36; N, 2.86.

*1,2,3,4-Tetra-*O*-acetyl-5,6-dideoxy-6-*C*-nitro-5-(phenylphosphinyl)-*D*-glucopyranose* (**17**). — Compound **12** was treated as just described, to give crystalline **17** (29% yield from **12**), m.p. 269° (dec.).

Anal. Calc. for $C_{20}H_{24}NO_{11}P$: C, 49.49; H, 4.98; N, 2.90. Found: C, 49.41; H, 4.94; N, 3.08.

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