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Note

The synthesis of some substituted D-glucose 1-phosphate derivatives and their reactivity towards nucleophilic substitution

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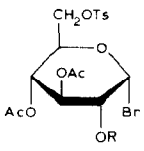
The synthesis of D-glucose 1-phosphates *via* the condensation of D-glucosyl halides with such reagents as silver[1–3] and triethylammonium[4,5] salts of diphenyl phosphate or dibenzyl phosphate is a well-established synthetic route. The concept of using D-glucose 1-(diphenyl or dibenzyl phosphate) as protected intermediates in the synthesis of amino, deoxy, and ulose derivatives of glucosyl phosphates is an attractive one, limited by the chemical reactivity of the protected phosphate function[6]. We now describe the synthesis of some derivatives of D-glucose 1-(dibenzyl phosphate) and report on their reactivity in nucleophilic substitution reactions.

The 6-*O*-tosyl (**3**) and 2,6-di-*O*-tosyl (**4**) derivatives of β-D-glucopyranose 1-(dibenzyl phosphate) were prepared by condensation of the corresponding glucosyl bromides[7,8] **1** and **2** with silver dibenzyl phosphate in benzene. The β anomer was isolated after each reaction, as expected, since the 1,2-*trans* isomer is normally formed in reactions of this type involving hexoses[9], though not necessarily with pentoses[10]. The n.m.r. data ($J_{1,2}$ 7.6 and 7.5 Hz, respectively) of **3** and **4** confirmed the β configuration; $^{1}H,^{32}P$ couplings of 7.6 and 7.5 Hz, respectively, were also observed, the signal for H-1 appearing as a triplet.



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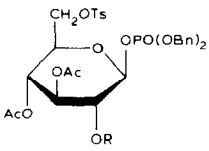

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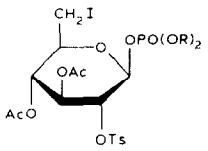
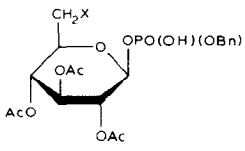


5 R = Ph
6 R = Bn



7 X = N_3
8 X = I

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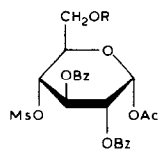
The corresponding diphenyl phosphate derivatives, obtained using silver diphenyl phosphate, were syrupy and highly susceptible to decomposition, confirming the observations of others[11,12]. Substituted derivatives of α-D-glucopyranose 1-(diphenyl phosphate) have been isolated crystalline[13]; during attempts to prepare such a derivative, the 6-iodo compound **5** was isolated following the reaction of 3,4-di-*O*-acetyl-6-deoxy-6-iodo-2-*O*-tosyl-α-D-glucopyranosyl bromide[6] with silver diphenyl phosphate. This reaction is unusual since the β anomer was formed, whereas the α anomer (1,2-*cis* or 1,2-*trans*) is generally formed using this reagent. The result may be attributable to steric interference by TsO-2 with nucleophilic attack at C-1. The β configuration was again confirmed by the n.m.r. spectrum, which was remarkably similar to that of the β-(dibenzyl phosphate) **6**, synthesised using the silver dibenzyl phosphate route. Thus $^{1}H,^{32}P$ couplings of 7.5 Hz were recorded for each compound, and the signals for H-1 appeared as triplets at δ 6.18 and 6.28, respectively.

Treatment of **3** with sodium azide in *N,N*-dimethylformamide and with sodium iodide in butanone gave the 6-azido **7** and 6-iodo **8** derivatives, respectively, of D-glucopyranose 1-(benzyl hydrogen phosphate) in moderate yields following deionisation of the monosodium salts, demonstrating that nucleophilic substitution on protected glucose 1-phosphates may represent a practical synthetic route. The selective debenzylation of dibenzyl phosphate derivatives in the presence of strong nucleophiles has been noted[14,15] and refined for use in synthesis[16,17].

A similar approach was used to investigate the feasibility of nucleophilic substitution reactions at secondary positions on protected glucose 1-phosphates. The 4,6-di-*O*-mesyl derivative **9** was obtained *via* acetolysis of the corresponding methyl glycoside[18]. Subsequent conversion into the 1-bromide **11** using hydrogen bromide in glacial acetic acid proceeded smoothly, and condensation of **11** with silver dibenzyl phosphate gave the crystalline β-(dibenzyl phosphate) **13** in good yield. The corresponding tri-*O*-benzoyl-4-*O*-mesyl derivatives **12** and **14** were likewise prepared from methyl 2,3,6-tri-*O*-benzoyl-4-*O*-mesyl-α-D-glucopyranoside[19], as possible intermediates in the synthesis of 4-amino-4-deoxy-galactose 1-phosphates.

Treatment of **13** with azide in *N,N*-dimethylformamide at 80° did not give a 4-azido derivative, although the 6-azido-4-*O*-mesyl derivative **15** was obtained in moderate yield after 6 h. Prolonged reaction times resulted in decomposition and



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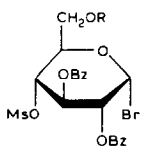

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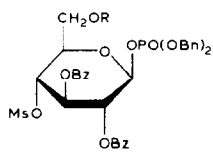

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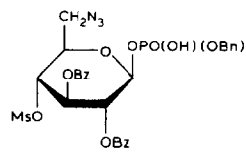

15

the formation (t.l.c.) of numerous products, possibly as a result of the loss of $^{-}$OPO(ONa)(OBn) from C-1. The use of elevated temperatures and hexamethylphosphoric triamide as solvent served only to accelerate this decomposition. Attempts to effect nucleophilic substitution at C-4, using the tri-*O*-benzoyl-4-*O*-mesyl derivative **14**, were unsuccessful.

Thus, nucleophilic substitution of suitable derivatives of D-glucose 1-(dibenzyl phosphate) at C-6 is a feasible route to substituted D-glucose 1-phosphates, but similar reactions at C-4 are unlikely to constitute a viable synthetic pathway.

EXPERIMENTAL

Solutions were concentrated under reduced pressure below 40°. Melting points were measured on a Kofler hot-stage and are uncorrected. ^{1}H-N.m.r. spectra were recorded with a Varian HA-100 spectrometer, using $CDCl_3$ as solvent unless otherwise stated. First-order coupling constants were measured to ±0.2 Hz. Optical rotations were measured on 1% solutions in chloroform, using a Perkin–Elmer 141 polarimeter at 20 ±2°. T.l.c. was performed on Kieselgel G (Merck), with detection by charring with sulphuric acid. Light petroleum having b.p. 40–60° was used throughout.

2,3,4-Tri-O-acetyl-6-O-tosyl-β-D-glucopyranose 1-(dibenzyl phosphate) (**3**). — 2,3,4-Tri-*O*-acetyl-6-*O*-tosyl-α-D-glucopyranosyl bromide[7] (5 g) was dissolved in dry benzene, and powdered silver dibenzyl phosphate (7.5 g) and Drierite (5 g) were added. The suspension was stirred in the dark and the temperature slowly raised to boiling during 0.5 h. The mixture was then boiled gently under reflux for 1.5 h and filtered, and the insoluble material was thoroughly washed with dichloromethane. The combined filtrate and washings were concentrated to a clear syrup which was dissolved in dichloromethane, filtered, and concentrated. Treatment of the syrupy residue with ether gave a white precipitate which was crystallised from chloroform–light petroleum to give **3** (6.3 g, 92%), m.p. 115–117°, $[\alpha]_D$ +6° (Found: C, 55.4; H, 5.1. $C_{33}H_{37}O_{14}PS$ calc.: C, 55.0; H, 5.15%). ^{1}H-N.m.r. data (C_5D_5N): δ 6.08 (t, 1 H, $J_{1,2} = J_{1,P} = 7.6$ Hz, H-1), 5.83 (t, 1 H, $J_{2,3} = J_{3,4} = 9.3$ Hz, H-3), 5.5 (dd, 1 H, $J_{1,2}$ 7.6, $J_{2,3}$ 9.3 Hz, H-2), 5.5 (t, 1 H, $J_{3,4} = J_{4,5} = 9.3$ Hz, H-4), 4.5 (m, 3 H, H-5,6,6′).

3,4-Di-O-acetyl-2,6-di-O-tosyl-β-D-glucopyranose 1-(dibenzyl phosphate) (**4**). — 3,4-Di-*O*-acetyl-2,6-di-*O*-tosyl-α-D-glucopyranosyl bromide[8] (5 g) was treated with silver dibenzyl phosphate (7.5 g), as described above. The resulting syrup was crystallised from chloroform–ethanol to give **4** (6.1 g, 79%), m.p. 162–163°, $[\alpha]_D$ +19° (Found: C, 55.0; H, 5.1. $C_{38}H_{41}O_{15}PS_2$ calc.: C, 54.8; H, 4.95%). ^{1}H-N.m.r. data (C_5D_5N): δ 6.2 (t, 1 H, $J_{1,2} = J_{1,P} = 7.5$ Hz, H-1), 6.0 (t, 1 H, $J_{2,3} = J_{3,4} = 9.6$ Hz, H-3), 5.58 (t, 1 H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4), 5.4 (dd, 1 H, $J_{1,2}$ 7.5, $J_{2,3}$ 9.6 Hz, H-2), 4.5 (m, 3 H, H-5,6,6′).

3,4-Di-O-acetyl-6-deoxy-6-iodo-2-O-tosyl-β-D-glucopyranose 1-(diphenyl phosphate) (**5**). — 3,4-Di-*O*-acetyl-6-deoxy-6-iodo-2-*O*-tosyl-α-D-glucopyranosyl

bromide[6] (1 g) was treated with silver diphenyl phosphate (1.5 g), as described above. The combined filtrate and washings were concentrated to a grey syrup from which residual silver salts were removed by dissolution in ether followed by filtration. The filtrate was concentrated and the procedure repeated until a clear syrup was obtained. The syrup crystallised from 2-propanol to afford **5** (0.82 g, 64%), m.p. 108–109°, $[\alpha]_D$ +9° (Found: C, 45.8; H, 4.0. $C_{29}H_{30}IO_{12}PS$ calc.: C, 45.8; H, 3.95%). ^{1}H-N.m.r. data (C_5D_5N): δ 6.28 (t, 1 H, $J_{1,2} = J_{1,P} = 7.5$ Hz, H-1), 5.96 (t, 1 H, $J_{2,3} = J_{3,4} = 9.5$ Hz, H-3), 5.38 (t, 1 H, $J_{3,4} = J_{4,5} = 9.5$ Hz, H-4), 5.32 (dd, 1 H, $J_{1,2}$ 7.5, $J_{2,3}$ 9.5 Hz, H-2), 4.10 (m, 1 H, H-5), 3.5 (dd, 1 H, $J_{5,6}$ 3.1, $J_{6,6'}$ 11.7 Hz, H-6), 3.32 (dd, 1 H, $J_{5,6'}$ 6.0, $J_{6,6'}$ 11.7 Hz, H-6′).

*3,4-Di-*O*-acetyl-6-deoxy-6-iodo-2-*O*-tosyl-β-*D*-glucopyranose 1-(dibenzyl phosphate)* (**6**). — 3,4-Di-*O*-acetyl-6-deoxy-6-iodo-2-*O*-tosyl-α-D-glucopyranosyl bromide (1 g) was treated with silver dibenzyl phosphate as described above. The resulting syrup crystallised on treatment with ether, and recrystallisation from 2-propanol yielded **6** (1.2 g, 92%), m.p. 132–134°, $[\alpha]_D$ +11.5° (Found: C, 47.2; H, 4.2. $C_{31}H_{34}IO_{12}PS$ calc.: C, 47.2; H, 4.3%). ^{1}H-N.m.r. data (C_5D_5N): δ 6.18 (t, 1 H, $J_{1,2} = J_{1,P} = 7.5$ Hz, H-1), 5.95 (t, 1 H, $J_{2,3} = J_{3,4} = 9.6$ Hz, H-3), 5.40 (dd, 1 H, $J_{1,2}$ 7.5, $J_{2,3}$ 9.5 Hz, H-2), 5.40 (t, 1 H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4), 4.10 (m, 1 H, H-5), 3.56 (dd, 1 H, $J_{5,6}$ 3.1, $J_{6,6'}$ 11.7 Hz, H-6), 3.34 (dd, 1 H, $J_{5,6'}$ 6.0, $J_{6,6'}$ 11.7 Hz, H-6′).

*1-*O*-Acetyl-2,3-di-*O*-benzoyl-4,6-di-*O*-mesyl-α-*D*-glucopyranose* (**9**). — A solution of methyl 2,3-di-*O*-benzoyl-4,6-di-*O*-mesyl-α-D-glucopyranoside[18] (20 g) in conc. sulphuric acid (4 mL) and acetic anhydride (96 mL) was left at 20° for 24 h, and then poured into ice–water (100 mL) with stirring. After 1 h, the resulting white precipitate was collected, washed with water, and recrystallised from methanol. Recrystallisation of the crude product (17.2 g; 83%) gave **9**, m.p. 179–182°, $[\alpha]_D$ +128° (Found: C, 49.1; H, 4.5. $C_{24}H_{26}O_{13}S_2$ calc.: C, 49.0; H, 4.4%). ^{1}H-N.m.r. data: δ 6.54 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 6.05 (t, 1 H, $J_{2,3} = J_{3,4} = 3.8$ Hz, H-3), 5.39 (dd, 1 H, $J_{1,2}$ 3.8, $J_{2,3}$ 9.2 Hz, H-2), 5.07 (t, 1 H, $J_{3,4} = J_{4,5} = 9.2$ Hz, H-4), 4.40 (m, 3 H, H-5,6,6′).

*2,3-Di-*O*-benzoyl-4,6-di-*O*-mesyl-α-*D*-glucopyranosyl bromide* (**11**). — To a solution of crude **9** (11.6 g) in the minimum volume of dichloromethane was added a 45% solution of hydrogen bromide in glacial acetic acid (35 mL). After storage for 2 h at 20°, the mixture was diluted with cold dichloromethane (80 mL) and washed successively with ice–water, saturated, aqueous sodium hydrogen carbonate (2 × 80 mL) and ice–water, dried ($MgSO_4$), filtered, and concentrated at 10°. The syrupy residue crystallised on the addition of ether, and recrystallisation from chloroform–ether gave **11** (11 g, 89%), m.p. 96–98°, $[\alpha]_D$ +178° (Found: C, 42.9; H, 3.9. $C_{22}H_{23}BrO_{11}S_2$ calc.: C, 43.5; H, 3.8%). ^{1}H-N.m.r. data: δ 6.73 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1). 6.12 (t, 1 H, $J_{2,3}$ 9.8, $J_{3,4}$ 9.2 Hz, H-3), 5.20 (dd, 1 H, $J_{1,2}$ 4.0, $J_{2,3}$ 9.8 Hz, H-2), 5.14 (t, 1 H, $J_{3,4} = J_{4,5} = 9.2$ Hz, H-4), 4.5 (m, 3 H, H-5,6,6′).

*2,3-Di-*O*-benzoyl-4,6-di-*O*-mesyl-β-*D*-glucopyranose 1-(dibenzyl phosphate)* (**13**). — Compound **11** (5 g) was treated with silver dibenzyl phosphate (7.5 g) as

described above. The resulting syrup crystallised from ethanol to give **13** (4.7 g; 71%), m.p. 131–136°, $[\alpha]_D$ +32° (Found: C, 53.1; H, 4.6. $C_{36}H_{37}O_{15}PS_2$ calc.: C, 53.7; H, 4.6%). ^{1}H-N.m.r. data: δ 6.48 (t, 1 H, $J_{1,2} = J_{1,P} = 7.6$ Hz, H-1), 6.56 (t, 1 H, $J_{2,3} = J_{3,4} = 9.6$ Hz, H-3), 6.08 (dd, 1 H, $J_{1,2}$ 7.6, $J_{2,3}$ 9.5 Hz, H-2), 5.67 (t, 1 H, $J_{3,4} = J_{4,5} = 9.5$ Hz, H-4), 4.9 (m, 1 H, H-5), 4.7 (m, 2 H, H-6,6′).

1-O-Acetyl-2,3,6-tri-O-benzoyl-4-O-mesyl-α-D-glucopyranose (**10**). — Methyl 2,3,6-tri-*O*-benzoyl-4-*O*-mesyl-α-D-glucopyranoside[19] (1.4 g) was acetolysed as described above. Recrystallisation of the product from ethanol gave **10** (1.1 g, 73%), which was contaminated by ~5% of the β anomer that was difficult to remove (Found: C, 59.2; H, 4.5. $C_{30}H_{28}O_{12}S$ calc.: C, 58.8; H, 4.6%). ^{1}H-N.m.r. data: δ 6.78 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 6.12 (t, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.55 (q, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 9.7 Hz, H-2), 5.22 (t, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 4.55 (m, 2 H, H-6,6′), 4.42 (m, 1 H, H-5). The mixture was used directly for the next stage.

2,3,6-Tri-O-benzoyl-4-O-mesyl-α-D-glucopyranosyl bromide (**12**). — Crude **10** (1 g) was treated with 45% hydrogen bromide in glacial acetic acid (3 mL) as described above. Crystallisation of the product (0.8 g, 77%) from ethanol gave **12**, m.p. 138–142°, $[\alpha]_D$ +162.5° (Found: C, 53.8; H, 4.0. $C_{28}H_{25}BrO_{10}S$ calc.: C, 53.1; H, 4.0%). ^{1}H-N.m.r. data: δ 6.80 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 6.19 (t, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.26 (t, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.25 (dd, 1 H, $J_{1,2}$ 4.0, $J_{2,3}$ 9.7 Hz, H-2), 4.7 (m, 3 H, H-5,6,6′).

2,3,6-Tri-O-benzoyl-4-O-mesyl-β-D-glucopyranose 1-(dibenzyl phosphate) (**14**). — The bromide **12** (0.4 g) and silver dibenzyl phosphate (0.6 g) were treated as described above. Recrystallisation of the product from ethanol afforded **14** (0.4 g, 76%), m.p. 141–144°, $[\alpha]_D$ +35° (Found: C, 60.8; H, 4.8. $C_{42}H_{39}O_{14}PS$ calc.: C, 60.7; H, 4.7%). ^{1}H-N.m.r. data (C_5D_5N): δ 6.63 (t, 1 H, $J_{2,3} = J_{3,4} = 9.4$ Hz, H-3), 6.54 (t, 1 H, $J_{1,2} = J_{1,P} = 7.6$ Hz, H-1), 6.22 (dd, 1 H, $J_{1,2}$ 7.6, $J_{2,3}$ 9.4 Hz, H-2), 5.87 (t, 1 H, $J_{3,4} = J_{4,5} = 9.4$ Hz, H-4), 5.0 (m, 3 H, H-5,6,6′).

Reaction of **3** *with sodium iodide*. — A mixture of **3** (0.5 g), sodium iodide (1 g), and butanone (10 mL) was heated for 6 h under reflux with stirring. A white flocculent precipitate appeared after 5 min. The mixture was then concentrated to dryness, the residue was extracted with dichloromethane (20 mL), the extract was filtered, and the insoluble material was washed well with dichloromethane (20 mL). Concentration of the combined filtrate and washings gave a red syrup, treatment of which with propanone (5 mL) yielded a white solid which was collected and washed with propanone, and a solution in water was passed through a column of Dowex-50 (H^+) resin. Concentration of the colourless eluate and crystallisation of the residue from chloroform–light petroleum gave 2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-β-D-glucopyranose 1-(benzyl hydrogen phosphate) (**8**; 0.22 g, 51%), m.p. 106–109°, $[\alpha]_D$ +15° (Found: C, 46.5; H, 4.8. $C_{19}H_{24}IO_5P$ calc.: C, 46.5; H, 4.9%). ^{1}H-N.m.r. data (C_5D_5N): δ 6.21 (t, 1 H, $J_{1,2}$ 7.6, $J_{1,P}$ 8.5 Hz, H-1), 5.84 (t, 1 H, $J_{2,3} = J_{3,4} = 9.2$ Hz, H-3), 5.57 (dd, 1 H, $J_{1,2}$ 7.6, $J_{2,3}$ 9.2 Hz, H-2), 5.43 (d, 2 H, J 7.0 Hz, ArCH_2), 5.38 (t, 1 H, $J_{3,4} = J_{4,5} = 9.2$ Hz, H-4), 3.91 (ddd, 1 H, H-5), 3.56 (dd, 1 H, $J_{5,6}$ 3.1, $J_{6,6'}$ 11.3 Hz, H-6), 3.38 (dd, 1 H, $J_{5,6}$ 5.5, $J_{6,6'}$ 11.3 Hz, H-6′).

Reaction of **3** *with sodium azide.* — To a solution of **3** (1.5 g) in the minimum volume of *N,N*-dimethylformamide (2 mL) was added sodium azide (1.2 g). The mixture was heated at 80° for 4 h, chloroform (10 mL) was then added to the cooled mixture, and the resulting suspension was filtered. The precipitate was washed well with chloroform, and the combined filtrate and washings were concentrated to a syrup which gave a white precipitate of the monosodium salt on addition of propanone (5 mL). A methanolic solution of the salt was deionised by using a column of Dowex 50-X2 (H^+) resin and then concentrated. The syrupy residue crystallised on the addition of ether (5 mL). Recrystallisation from chloroform–ether gave 2,3,4-tri-*O*-acetyl-6-azido-6-deoxy-β-D-glucopyranose 1-(benzyl hydrogen phosphate) (**7**; 0.7 g, 67%), m.p. 112–116°, $[\alpha]_D$ +18° (Found: C, 45.0; H, 4.8; N, 8.4. $C_{19}H_{24}N_3O_{11}P$ calc.: C, 45.4; H, 4.8; N, 8.4%). ^{1}H-N.m.r. data (C_5D_5N): δ 6.13 (t, 1 H, $J_{1,2}$ 7.4, $J_{1,P}$ 8.5 Hz, H-1), 5.80 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.2 Hz, H-3), 5.54 (dd, 1 H, $J_{1,2}$ 7.4, $J_{2,3}$ 9.2 Hz, H-2), 5.45 (m, 3 H, H-4 and PhCH_2), 4.16 (m, 1 H, H-5), 3.52 (m, 2 H, H-6,6′).

Reaction of **13** *with sodium azide.* — To a solution of **13** (2 g) in the minimum volume of *N,N*-dimethylformamide (2 mL) was added sodium azide (1.5 g). The mixture was heated at 80° for 6 h and then concentrated to dryness, and the resulting solid was extracted with chloroform (15 mL). The suspension was filtered and concentrated to a red syrup which gave a buff-coloured precipitate on treatment with propanone at 0°. The solid was collected and a solution in methanol was eluted from a column of Dowex 50-X2 (H^+) resin (10 g) with methanol. Crystallisation occurred during concentration of the combined eluants. Recrystallisation from methanol gave 6-azido-2,3-di-*O*-benzoyl-6-deoxy-4-*O*-mesyl-β-D-glucopyranose 1-(benzyl hydrogen phosphate) (**15**; 0.9 g, 54%), m.p. 164–166°, $[\alpha]_D$ +22° (Found: C, 50.8; H, 4.5; N, 5.9. $C_{28}H_{28}N_3O_{12}PS$ calc.: C, 50.8; H, 4.3; N, 6.3%). ^{1}H-N.m.r. data (C_5D_5N): δ 6.24 (t, 1 H, $J_{1,2}$ 8.0, $J_{1,P}$ 8.4 Hz, H-1), 6.19 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.1 Hz, H-3), 5.84 (dd, 1 H, $J_{1,2}$ 8.0, $J_{2,3}$ 9.1 Hz, H-2), 5.32 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.1 Hz, H-4), 4.21 (ddd, 1 H, $J_{4,5}$ 9.1, $J_{5,6}$ 3.0, $J_{5,6'}$ 4.6 Hz, H-5), 3.87 (dd, 1 H, $J_{5,6}$ 3.0, $J_{6,6'}$ 13.5 Hz, H-6), 3.62 (dd, 1 H, $J_{5,6'}$ 4.6, $J_{6,6'}$ 13.5 Hz, H-6′).

When the reactants were left for 30 h at 80°, 30% of **15** was obtained. No products were isolated after longer reaction times.

ACKNOWLEDGMENT

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