Radical Rearrangement of 2-O-(Diphenylphosphoryl)glycosyl Bromides. A New Synthesis for 2-Deoxy Disaccharides and 2-Deoxy Ribonucleosides

Andreas Koch, Clemens Lamberth,‡ Frank Wetterich, and Bernd Giese*

Department of Chemistry, University of Basel, St. Johanns-Ring 19, CH-4056 Basel, Switzerland, and Institute of Organic Chemistry, TH Darmstadt, Petersenstrasse 22, D-6100 Darmstadt, Germany

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2-Deoxy-1-O-diphenylphosphoryl glycosides react with nucleophiles under mild conditions giving access to 2-deoxy disaccharides and nucleosides. The intermediate 2-deoxy-1-O-diphenylphosphoryl compounds were generated in situ by a radical 2 → 1 migration of the phosphate ester group. This is the first observation of a rearrangement of a phosphate ester in radicals. ESR experiments and quenching of the radical at C2 by tin hydride or tin deuteride were used to detect the intermediates and to prove their structure.

Introduction

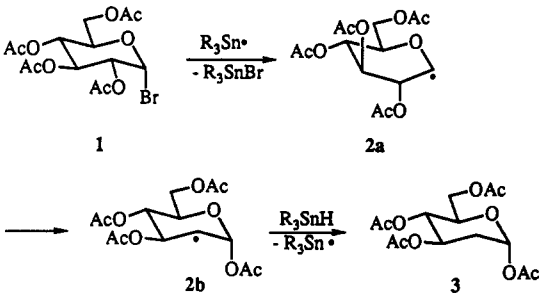
The 2 → 1 migration of the acyloxy group in acetylated and benzoylated glycosyl radicals is of particular interest as a new route to 2-deoxy sugars.[1] Thus, a solution of the radical precursor **1**, treated with tri-*n*-butyltin hydride either under irradiation (20 °C) or in the presence of a catalytic amount of AIBN (80 °C), gives 2-deoxy sugar **3** via radicals **2a** and **2b**. To avoid direct reduction of the precursor the tin hydride concentration was maintained at a very low level by syringe pump addition of a tin hydride solution over a period of 8–30 h.[2] Alternatively, tris(trimethylsilyl)silane could be used[3a] as a less reactive hydrogen atom donor.[3b]

Mechanistic and ESR studies by Giese and Sustmann et al.[4] unequivocally showed the radical pathway of this 2 → 1 migration for acetylated and benzoylated galacto- and glucopyranoses. Ingold et al.[5] observed an acceleration of a related migration where an electron-attracting substituent is present in the migrating group. Due to the wide variety of biological processes involving phosphate groups, we were interested in studying the scope of phosphate as a migrating group. If the rearrangement were to occur in these phosphorylated substrates then the resulting compounds, with the phosphoric ester group at the anomeric carbon, might be reactive enough to undergo nucleophilic substitution, thus giving access to a variety of 2-deoxy glycosides.

Results and Discussion

Characterization of the Rearrangement Products. Starting from partially acyl-protected carbohydrate derivatives **4**[6] and **7**,[7] the radical precursors 3,4,6-tri-O-acetyl-2-O-(diphenylphosphoryl)-α-D-glucopyranosyl bromide (**6**)

Scheme I



and 3,5-di-O-benzoyl-2-O-(diphenylphosphoryl)-α-D-ribofuranosyl bromide (**9**) could be obtained in two steps in 90 and 85% yield, respectively. When the glycosyl bromides **6** and **9** were irradiated in the presence of 1.2 equiv of tri-*n*-butyltin hydride hydrogen atoms were transferred to the rearranged radicals generating the 2-deoxy compounds. In the glucose series 3,4,6-tri-O-acetyl-2-deoxy-1-O-(diphenylphosphoryl)-α-D-*arabino*-hexopyranose (**15a**) was formed quantitatively by a photolytically initiated radical reaction.

Neither the unrearranged reduction product **13** nor any other compound could be detected in the ^{1}H-NMR spectrum of the crude reaction mixture. Thus, we concluded that the rearranged product was formed (see Experimental Section) in a ratio of greater than 95:5 (detection limits in ^{1}H-NMR). With a large excess (10 equiv) of tri-*n*-butyltin hydride a small amount of the direct reduction product **13** was formed. Under pseudo-first-order conditions (10-fold excess of tin hydride) the ratio of rearranged to unrearranged products [**15a**]/[**13**] is described by eq 1.

$$\frac{[\mathbf{15a}]}{[\mathbf{13}]} = \frac{k_R}{k_H[Bu_3SnH]} \qquad (1)$$

The rate constant for hydrogen transfer from tin hydride to secondary alkyl radicals was determined by Ingold et al.[8,9] For cyclohexyl radicals k_H is 2.2×10^6 M^{-1} s^{-1} at 27 °C. By variation of the tin hydride concentration (0.27–

‡ Institute of Organic Chemistry, TH Darmstadt.

(1) Giese, B.; Gröninger, K. S. *Org. Synth.* **1990**, *69*, 66–71.
(2) Giese, B.; Gilges, S.; Gröninger, K. S.; Lamberth, C.; Witzel, T. *Liebigs Ann. Chem.* **1988**, 615–617.
(3) (a) Giese, B.; Kopping, B.; Chatgilialoglu, C. *Tetrahedron Lett.* **1989**, *30*, 681–684. (b) Chatgilialoglu, C.; Dickhaut, J.; Giese, B. *J. Org. Chem.* **1991**, *56*, 6399–6403.
(4) Korth, H.-G.; Sustmann, R.; Gröninger, K. S.; Leising, M.; Giese, B. *J. Org. Chem.* **1988**, *53*, 4364–4369.
(5) Barclay, L. R. C.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 1793–1796.
(6) Helferich, B.; Zirner, J. *Chem. Ber.* **1962**, *95*, 2604–2611.
(7) (a) Brodfuehrer, P. R.; Sapino, C.; Howell, H. G. *J. Org. Chem.* **1985**, *50*, 2597–2598. (b) Ness, R. K.; Diehl, H. W.; Fletcher, H. G. *J. Am. Chem. Soc.* **1954**, *76*, 763–767.
(8) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739–7742.
(9) Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickreyma, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4594–4596.

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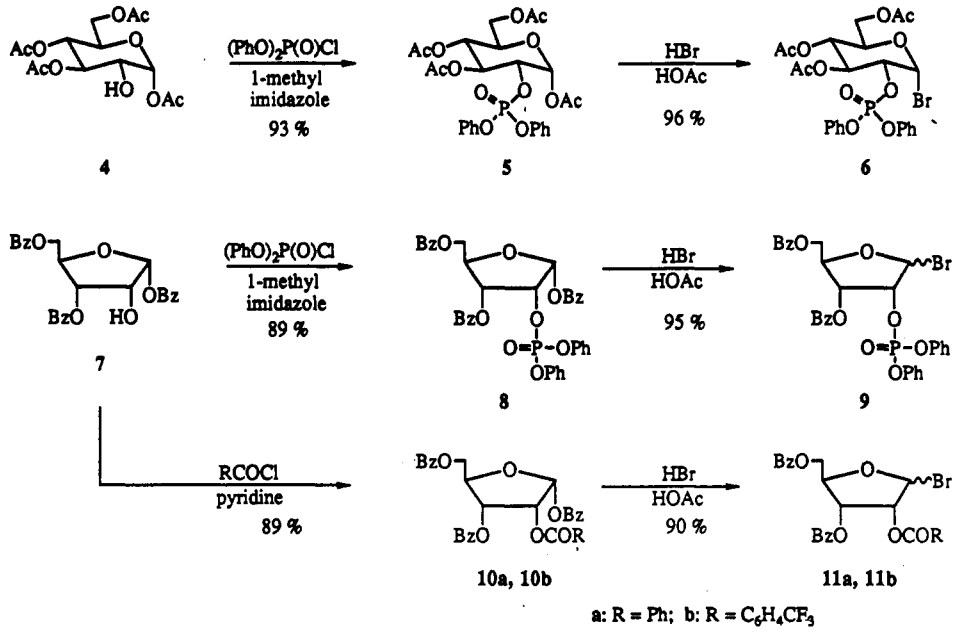
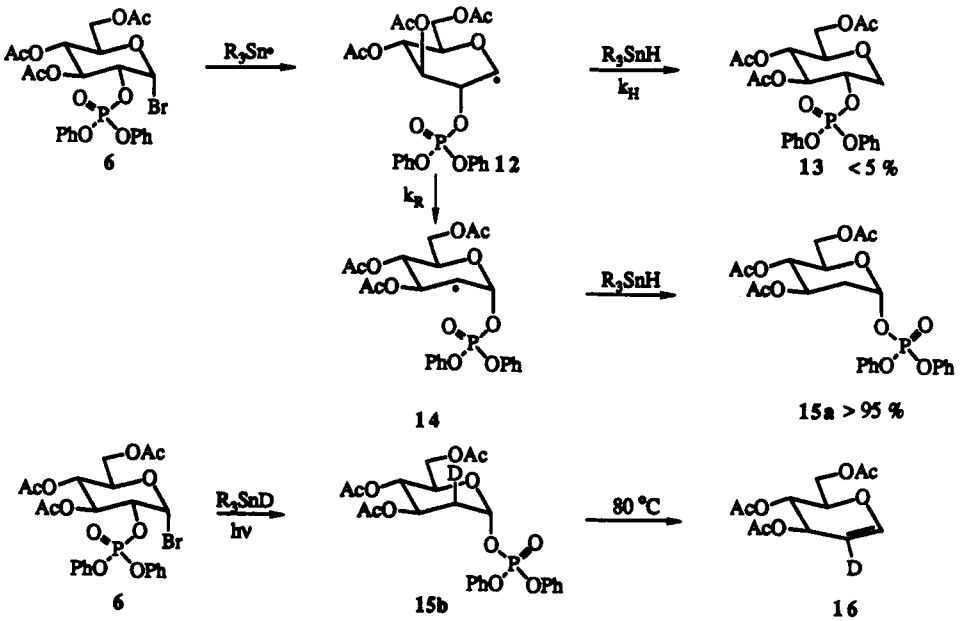
Scheme II



Scheme III



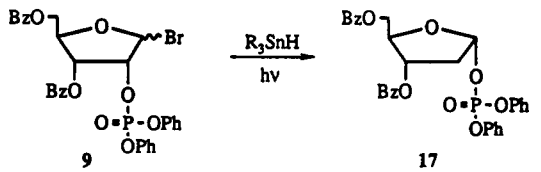
0.96 M) for the reaction of **6** the ratio of k_R to k_H was determined to be 4.0 mol. Thus, the rate of rearrangement k_R for the diphenylphosphoryl group is at least 8×10^6 s^{-1} at 27 °C. The rate constant for the rearrangement of an acetyl group (**2a** → **2b**) had been determined to be 5.3×10^1 s^{-1} at 27 °C.[4] Therefore, on swapping the migrating group from acetyl to diphenylphosphoryl a dramatic acceleration is observed for the unimolecular 2 → 1 rearrangement reaction.

3,4,6-Tri-*O*-acetyl-2-deoxy-1-*O*-(diphenylphosphoryl)-α-D-*arabino*-hexopyranose (**15a**) is an unstable intermediate that can be kept at room temperature for only a few hours. It was possible to characterize this compound by ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy. In the ^{1}H-NMR spectrum we found couplings between the phosphorus, the hydrogen at C1, and the axial hydrogen at C2, respectively. This ^4J-coupling indicates a W-configuration of hydrogen and phosphorus.[10,11] In the ^{13}C-NMR spectra of the phosphorylated compounds it is possible to detect $^2J_{C,P}$ and $^3J_{C,P}$ couplings.[12] For compound **15a** the coupling constants were $^2J_{C1,P}$ = 5.8 Hz and $^3J_{C2,P}$ = 8.6 Hz.

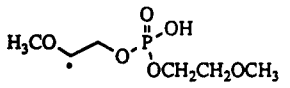
When the irradiation of 3,4,6-tri-*O*-acetyl-2-*O*-(diphenylphosphoryl)-α-D-glucopyranosyl bromide (**6**) was carried out in the presence of tri-*n*-butyltin deuteride more than 95% deuterium incorporation occurred at C2. The ratio of axial vs equatorial deuterium was determined to be 90:10 by ^{2}H-NMR indicating an effective shielding of the bottom face of the pyranose ring.[13] On prolonged standing or on exposure to temperatures of up to 80 °C **15a** decomposed, eliminating diphenylphosphoric acid to yield 3,4,6-tri-*O*-acetyl-D-glucal (3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitol). This elimination process

(10) (a) Thiem, J.; Franzkowiak, M. *J. Carbohydr. Chem.* **1989**, *8*, 1–28. (b) Sabesan, S.; Neira, S. *Carbohydr. Res.* **1992**, *223*, 169–185.
(11) *Phosphorus-31 NMR-Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Weinheim, 1987; p 383.
(12) Franzkowiak, M.; Thiem, J.; Demoulin, C. *Carbohydr. Res.* **1986**, *158*, 13–35.
(13) Giese, B. *Angew. Chem., Int. Ed. Engl* **1989**, *28*, 969.

Scheme IV



9 17



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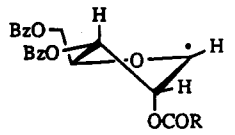

19 a: R = Ph; b: R = $C_6H_4CF_3$

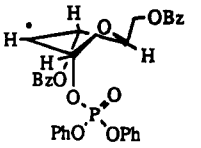

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Table I. ESR Coupling Constants (G) and *g* Values for Carbohydrate Radicals at 7 °C

radical	*g*	a_α(H)	a_β(H)	a_β(H)	a_γ(H)	a_γ(H)	a_γ(P)
2a[a]	2.0030	18.3	12.2		1.5	3.4	
2b[a]	2.0026	21.9	12.0	36.9	0.88		
14	2.0026	21.8	9.3	38.0	0.90		4.5
19a	2.0031	18.0	9.9		0.84	2.9	
19b	2.0031	18.3	10.0		0.84	2.9	
20	2.0023	23.0	12.7	28.0			5.4
18	2.0030	17.5	6.2	6.2			5.1

[a] Reference 4.

was shown to proceed in a cis-dominant manner because thermal decomposition (80 °C) of the deuterated substance **15b** gave 3,4,6-tri-*O*-acetyl-2-deuterio-D-glucal **16** deuterated to an extent of at least 70%. Attempts to isolate **15a** by chromatography led to elimination and hydrolysis.

In the ribose series irradiation of **9** in the presence of tri-*n*-butyltin hydride led to formation of 3,5-di-*O*-benzoyl-2-deoxy-1-*O*-(diphenylphosphoryl)-α-D-*erythro*-pentofuranose (**17**). Complete decomposition of **17** occurred within 5–10 min; however, characterization of this compound by NMR spectroscopy was possible. In the ^{1}H-NMR spectrum the proton at C1 appears as a triplet. In the case of the α-configurated deoxy sugars, one of the $^3J_{H1,H2}$ couplings is small and sometimes not discernible. The observed triplet results from the other $^3J_{H1,H2}$ coupling and the $^3J_{H1,P}$ coupling with the diphenylphosphoryl group. Additional proof for the presence of the phosphate at C1 are the signals in the ^{13}C-NMR spectrum. Both the $^2J_{C1,P}$ and the $^3J_{C2,P}$ couplings are in the range of 9 Hz. No coupling is observed for C3, again indicating that the phosphorus is located at C1.

ESR Investigations. The mechanism of the reaction was studied by ESR. A solution of the radical precursor and hexabutylditin in benzene was irradiated in the cavity of the ESR spectrometer at 7 °C. In the acetyl case radical **2a** was observed predominantly in the ESR spectrum.[2] In contrast, the diphenylphosphoryl-substituted precursor **6** gave rise to ESR spectra (Figure 1) showing exclusively the rearranged radical **14**. The α-hyperfine splitting constant of 22 G is a common value for α-hydrogen atoms in unperturbed π-type alkyl radicals.[14] The *g* value of 2.0026 is in the range generally found for alkyl radicals and indicates the absence of an α-bonded oxygen.[14]

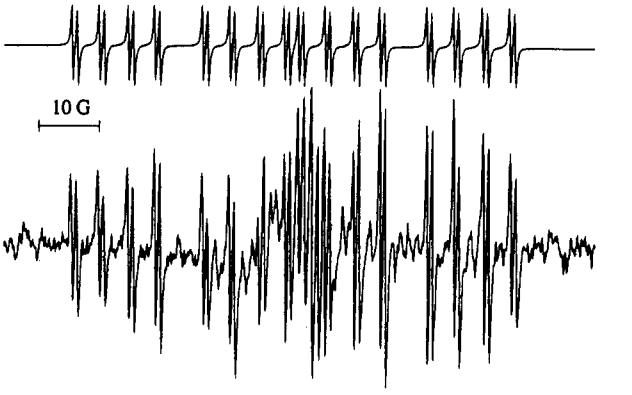


Figure 1. ESR spectrum obtained by photolyzing **6** with hexabutylditin at 7 °C. The upper spectrum is the simulation of the rearranged radical **14**.

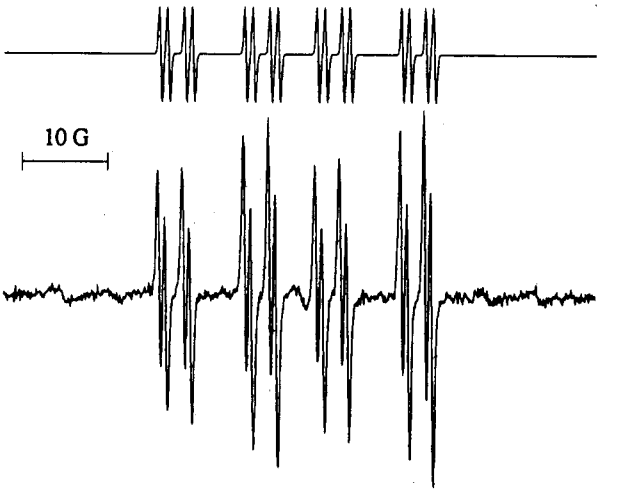


Figure 2. ESR spectrum obtained by photolyzing **11b** with hexabutylditin at 7 °C. The upper spectrum is the simulation of the nonrearranged radical **19b**.

The phosphorus atom gives rise to an additional splitting of the ESR signals clearly indicating the presence of the phosphoric ester in the radical. The other hydrogen-hyperfine coupling constants of radical **14** closely resemble the values reported for **2b** in the acetyl system;[2] thus, we have to conclude that radical **14** exists in the $^4C_1$ conformation, as it is described for deoxypyranosan-2-yl radicals.[15] In this conformation the C,O-bond of the sugar phosphate is nearly eclipsed to the singly occupied orbital of the radical. A similar conformation was reported for the open-chain phosphoryl-substituted radical **18**.[16] The phosphorus coupling of 4.5 G for **14** is very close to the phosphorus coupling for radical **18** (5.1 G).

In the ribose series the results are in principle the same. For the benzoyl- and 3-(trifluoromethyl)benzoyl-substituted ribosyl bromides **11a** and **11b** the spectra (Figure 2) only show signals for the nonrearranged radicals even at higher temperatures (up to 70 °C). This is indicated by a *g* value of 2.0031 and an α-coupling of 18.3 G. From the β-coupling of 10 G a dihedral angle between the proton at C2 and the half-filled p-orbital of about 60° is inferred.[17]

(14) *Landolt-Börnstein. New Series*; Fischer, H., Hellwege, K. H., Eds.; Springer-Verlag: Berlin, 1977; Vol. II/9b.
(15) Korth, H. G.; Sustmann, R.; Gröninger, K. S.; Witzel, T.; Giese, B. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1461–1464.
(16) (a) Behrens, G.; Koltzenburg, G.; Schulte-Frohlinde, D. *Z. Naturforsch.* **1982**, *37c*, 1205–1227. (b) Behrens, G.; Koltzenburg, G.; Ritter, A.; Schulte-Frohlinde, D. *Int. J. Radiat. Biol.* **1978**, *33*, 163.

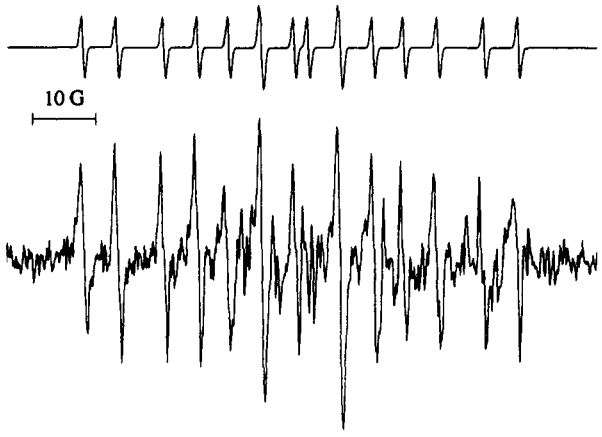


Figure 3. ESR spectrum obtained by photolyzing **9** with hexabutylditin at 7 °C. The upper spectrum is the simulation of the rearranged radical **20**.

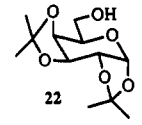
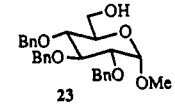
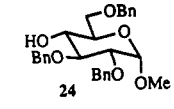
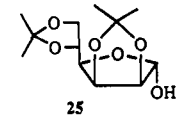
This leads to the conclusion that the radical exists in a $_2$E conformation **19**.[18] The ESR spectrum of the rearranged radical **20** was obtained in the ribose series by photolyzing the diphenylphosphoryl substituted bromide **9** (Figure 3). It is characterized by its smaller g value (2.0023) and larger α-coupling (23 G). The two different β-couplings of 13 and 28 G imply the two dihedral angles of about 60° and 40° between the half-filled p-orbital and the protons at C1 and C3. The smaller coupling could be the coupling with the proton at C1 because due to its strong anomeric effect the phosphate group should be quasi axial. The dominance of the rearranged radicals in the ESR spectra of the precursors with the diphenylphophoryl group confirms the high rate constant for the rearrangement process as depicted before.

Synthetic Applications. The 2-deoxy sugar **15a** with a phosphate group at the anomeric center is reactive toward nucleophiles like alcohols and yields 2-deoxy glycosides **21**α and **21**β. If the alcohol is a suitably protected carbohydrate we could obtain 2-deoxydisaccharides by a simple reaction sequence. The disaccharides presented in Table II were synthesized in accordance with Scheme V. Coupling with a primary hydroxy group in the glycosyl acceptor yielded the disaccharides in up to 79%; in the case of secondary hydroxy groups the yields were up to 72%.

In general, the glycosyl bromide and tri-*n*-butyltin hydride were irradiated in diethyl ether or THF for 15 min. This solution was added to the appropriate hydroxy compound and 0.1 equiv of anhydrous magnesium perchlorate. After being stirred at room temperature for 15 min, the reaction was quenched by the addition of 5 equiv of triethylamine, and the disaccharide was isolated and purified by chromatography on silica gel.

Addition of magnesium perchlorate greatly accelerates the substitution process of the diphenylphosphoryl group by the alcohol. Without this salt primary alcohols require 24 h to reach the same yields that occur within 15 min in the presence of magnesium perchlorate. Secondary alcohols react only if the diphenylphosphoryl group is activated. Numerous compounds were tested as potential activating agents. These can be divided in three groups: acceleration of disaccharide formation ($SnCl_4$, Bu_4NBr, $ZnCl_2$, LiBr, $FeCl_3$, $Mg(ClO_4)_2$, $Fe(ClO_4)_3$), no effect on the rate ($Ti(^iOPr)_4$, $TiCl(^iOPr)_3$, $Al(OEt)_3$, CuBr, $CuBr_2$, $LiClO_4$, $(C_4H_9)_3SnCH_2CH{=}CH_2$, $MgBr_2$), and decomposition of carbohydrate compounds in presence of the additive ($AlCl_3$, $Cu(ClO_4)_2$, $Cu(BF_4)_2$, $BF_3{\cdot}OEt_2$, TMSOTf, $HClO_4$).

Table II. 2-Deoxy Discaccharides Prepared in Accordance with Scheme V

hydroxy compd	disaccharide	yield of α/β mixture	α/β ratio
 22	26	79 %	2.5 / 1
 23	27	72 %	2.3 / 1
 24	28	72 %	4.5 / 1
 25	29	49 %	3.3 / 1

The radical reaction for the generation of the glycosyl donor **15a** could be carried out in benzene as well as in ether or THF. But solvents other than ether or THF for the coupling step (e.g., benzene, dichloromethane, 1,4-dioxane, acetonitrile) reduced the yield of the disaccharide. The α/β ratio was only moderately affected by the solvent variation, leading to a slightly more pronounced preference for the formation of the α-isomer in benzene solution. Salts or Lewis acids have only a very small effect on the α/β ratio. The stereochemistry of the resulting disaccharides was unequivocally assigned from the ^{1}H-NMR coupling constants of H1′ and the chemical shifts of H5′.[19]

No activation of the phosphoryl group was required for the synthesis of the 2-deoxynucleosides **30**. Furthermore it was also not necessary to activate the heterocyclic bases, by addition of an inorganic base like NaH[20] or a phase-transfer catalyst,[21] the way it is described for the synthesis of deoxy nucleosides using 1-chloro-3,5-di-*O*-(*p*-toluoyl)-α-D-*erythro*-pentofuranose[22] as the sugar moiety. The bromide **9** and tributyltin hydride were just mixed together with the N-heterocycle, and then the mixture was irradiated for a few minutes (using a 1-kW Hg–Xe-lamp, 2.5–4 min were sufficient). In this manner we synthesized the following new 2-deoxynucleosides **31–35**.

A variety of readily available N-heterocycles were chosen for testing as suitable bases. All gave similar α/β ratios, which are between 2.4:1 and 1:1. This low selectivity with free heterocycles is similar to that of 1-chloro-3,5-di-*O*-(*p*-toluoyl)-α-D-*erythro*-pentofuranose, which gives β-products only if sodium salts are used.[20] The ratio of the

(17) Fischer, H. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, p 435.
(18) Altona, C.; Sundaralingam, M. *J. Am. Chem. Soc.* **1973**, *95*, 2333.
(19) Sabesan, S.; Neira, S. *J. Am. Chem. Soc.* **1991**, *56*, 5468–5472.
(20) Kazimierczuk, Z.; Cottom, H. B.; Revankar, G. R.; Robins, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 6379–6382.
(21) Seela, F.; Bourgeois, W. *Synthesis* **1989**, 912–918.
(22) Hoffer, M. *Chem. Ber.* **1960**, *93*, 2777–2781.

Scheme V

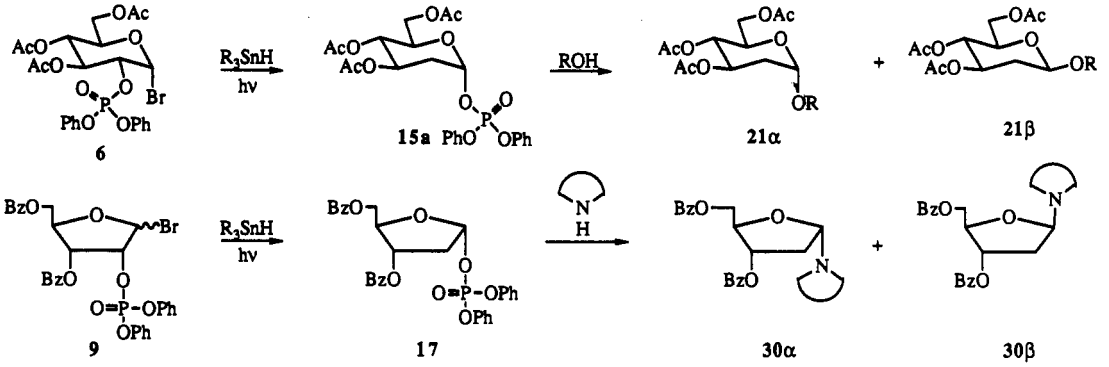
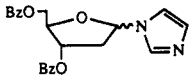
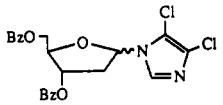
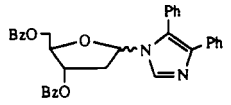
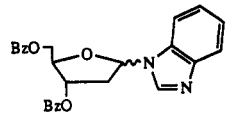
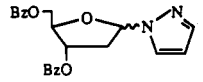
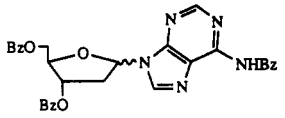


Table III. 2-Deoxy Nucleosides Prepared in Accordance with Scheme V

2-deoxynucleoside	compd	yield of α/β mixture	α/β ratio
	31	60 %	1 / 1
	32	66 %	2.4 / 1
	33	54 %	1.8 / 1
	34	47 %	1.5 / 1
	35	82 %	1.4 / 1
	36	42 %	1 / 1

anomers was determined by NMR-spectroscopy of the crude reaction mixtures looking at the integrals of the protons at C1 and C2. For determination of the anomeric conformation the rules of Robins and Robins were used confirming the pattern of the proton at C1[23] and the chemical shift difference between the protons at C4.[24] The anomeric mixtures could be easily separated by chromatography on silica gel. All yields are those of isolated products after chromatography.

Experimental Section

ESR Measurements. Radicals were generated by UV irradiation of solutions in Suprasil quartz tubes (outer diameter 5.0 mm) with the filtered light (water-cooled Schott Filter UG-5) of a Hanovia 977-B1 1-kW Hg–Xe high-pressure lamp. The lamp housing and the optical equipment were identical to those described by Fischer.[25] The ESR solutions were composed of the sugar derivative (ca. 80 mg), dry benzene (0.4 mL), and hexabutylditin (0.1 mL). Oxygen was removed from the solutions by purging with dry argon for 30 min. ESR hyperfine coupling constants were refined by simulation of the manually evaluated ESR spectra with the simulation program integrated in the Bruker software. *g* values were determined with the help of a microwave frequency counter and a NMR field measuring unit.

1,3,4,6-Tetra-*O*-acetyl-2-*O*-(diphenylphosphoryl)-α-D-glucopyranose (5). 1,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranose (4; 9.0 g, 25.9 mmol) was placed in a two-necked flask with septum, gas inlet, and magnetic stirring bar. After being purged with nitrogen the compound was dissolved in dry dichloromethane (100 mL) and the flask was cooled in an ice–water bath. Diphenylphosphoryl chloride (8.33 g, 31.0 mmol, 1.2 equiv) and 1-methylimidazole (2.54 g, 31.0 mmol, 1.2 equiv) were added over a period of 15 min. Stirring was continued for 16 h with gradual warming to room temperature. The dichloromethane was then evaporated and the oily residue redissolved in dichloromethane and evaporated a second time to remove traces of 1-methylimidazole. A solution of the residue in dichloromethane (200 mL) was washed successively with ice–water (100 mL), saturated aqueous sodium hydrogen carbonate solution (2 × 100 mL), and water (100 mL). The organic layer was dried with magnesium sulfate and the solvent removed in vacuo. The oily residue was crystallized from diethyl ether and then recrystallized from dichloromethane/ether to yield 1,3,4,6-tetra-*O*-acetyl-2-*O*-(diphenylphosphoryl)-α-D-glucopyranose (5) as a white solid in 93% yield: mp 101–103 °C; ^{1}H NMR ($CDCl_3$) δ 7.39–7.16 (m, 10 H, Ph), 6.38 (d, *J* = 3.8 Hz, 1 H, H1), 5.57 (t, *J* = 9.8 Hz, 1 H, H3), 5.14 (t, *J* = 9.8 Hz, 1 H, H4), 4.81 (ddd, *J* = 3.8, 8.8, 9.8 Hz, 1 H, H2), 4.28 (dd, *J* = 4.4, 12.8 Hz, 1 H, H6a), 4.11–4.04 (m, 2 H, H5, H6b), 2.08 (s, 6 H, Ac), 2.04, 1.86 (2s, 6 H, Ac); ^{13}C NMR ($CDCl_3$) δ 170.4, 170.1, 169.2, 168.2 (4 C, CH_3COO), 150.2, 150.1 (2d, *J* = 7.2 Hz, 2 C, ipso-C_6H_5OP), 129.8 (4 C, *m*-C_6H_5OP), 125.6 (2 C, *p*-C_6H_5OP), 119.8, 119.7 (2d, *J* = 4.7 Hz, 4 C, *o*-C_6H_5OP), 88.8 (d, *J* = 3.4 Hz, 1 C, C1), 73.8, 70.3 (2d, *J* = 5.7 Hz, 2 C, C2, C3), 69.3 (1 C, C5), 67.7 (1 C, C4), 61.2 (1 C, C6), 20.5, 20.4 (4 C, CH_3COO); ^{31}P NMR ($CDCl_3$) δ −12.2 (d, *J* = 8.6 Hz); MS (FAB, KCl) 581 ($M^+ + 1$), 521 ($M^+ - OAc$). Anal. Calcd for $C_{26}H_{29}O_{13}P$ (580.48): C, 53.81; H, 5.04. Found: C, 53.84; H, 4.75.

3,4,6-Tri-*O*-acetyl-2-*O*-(diphenylphosphoryl)-α-D-glucopyranosyl Bromide (6). 1,3,4,6-Tetra-*O*-acetyl-2-*O*-(diphenylphosphoryl)-α-D-glucopyranose (5; 6.0 g, 10.3 mmol) was placed in a flask equipped with a magnetic stirring bar and dissolved in the minimum amount of dry dichloromethane (20 mL). After the solution was cooled in an ice–water bath 10 mL of a cold solution of hydrogen bromide in acetic acid (4 °C, 33% by weight) was added. Stirring was continued for 16 h with gradual warming to room temperature. During this time the flask was placed under a nitrogen atmosphere, allowing for expansion on warming of the reaction mixture. The reaction mixture was diluted with dichloromethane (100 mL) and transferred to a separating funnel containing ice. After mixing and separating the organic layer

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(24) Nuhn, P.; Zschunke, A.; Heller, D.; Wagner, G. *Tetrahedron* **1969**, *25*, 2139–2144.
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was washed successively with water (50 mL), saturated aqueous sodium hydrogen carbonate solution (2 × 50 mL), and water (50 mL). After the organic layer was dried over magnesium sulfate the solvent was removed in vacuo. The glycosyl bromide 6 was obtained as an oil in 96% yield and could be used in synthesis without further purification, although flash chromatography (silica gel) was possible. The compound was stored at −20 °C for several weeks without decomposition: ^{1}H NMR ($CDCl_3$) δ 7.41–7.22 (m, 10 H, Ph), 6.40 (d, J = 4.0 Hz, 1 H, H1), 5.63 (t, J = 9.7 Hz, 1 H, H3), 5.17 (t, J = 9.7 Hz, 1 H, H4), 4.68 (ddd, J = 4.0, 9.0, 9.7 Hz, 1 H, H2), 4.34–4.28 (m, 2 H, H5, H6a), 4.17–4.12 (m, 1 H, H6b), 2.11, 2.06, 1.86 (3s, 9 H, Ac); ^{13}C NMR ($CDCl_3$) δ 170.7, 170.1, 169.5 (3 C, CH_3COO), 150.5, 150.2 (2d, J = 7.6 Hz, 2 C, *ipso*-C_6H_5OP), 130.1, 130.0 (4 C, *m*-C_6H_5OP), 126.0, 125.8 (2d, J ≈ 1.0 Hz, 2 C, *p*-C_6H_5OP), 120.4, 119.9 (2d, J = 5.0 Hz, 4 C, *o*-C_6H_5OP), 86.7 (d, J = 3.6 Hz, 1 C, C1), 74.4 (d, J = 5.2 Hz, 1 C, C2), 72.1 (1 C, C5), 70.8 (d, J = 5.7 Hz, 1 C, C3), 66.8 (d, J = 1.0 Hz, 1 C, C4), 60.6 (1 C, C6), 20.3, 20.2, 20.1 (3 C, CH_3COO); ^{31}P NMR ($CDCl_3$) δ −12.0 (d, J = 8.6 Hz); MS (FAB, KCl) 603, 601 (M^+ + 1), 521 (M^+ − Br). Anal. Calcd for $C_{24}H_{26}O_{11}PBr$ (601.34): C, 47.94; H, 4.36. Found: C, 48.10; H, 4.22.

1,3,5-Tri-*O*-benzoyl-2-*O*-(3-(trifluoromethyl)benzoyl)-α-D-ribofuranose (10b). 1,3,5-Tri-*O*-benzoyl-α-D-ribofuranose (7; 1.7 g, 3.6 mmol) was dissolved in 20 mL of absolute dichloromethane under nitrogen. At 0 °C 3-(trifluoromethyl)benzoyl chloride (0.60 mL, 0.84 g, 4.1 mmol) and absolute pyridine (1.0 mL) were added over a period of 10 min. Stirring was continued for 15 h with gradual warming to room temperature. Ice–water was added, and the organic layer was separated and washed successively with 2 N hydrochloric acid (25 mL), saturated aqueous sodium hydrogen carbonate solution (25 mL), and ice–water (50 mL). After the solution was dried over magnesium sulfate the solvent was removed in vacuo and the product was purified by flash chromatography eluting with diethyl ether/pentane = 2/1. After the solvents were removed 2.0 g (3.2 mmol, 89%) of the crystalline product **10b** was obtained: mp 102 °C; ^{1}H NMR ($CDCl_3$) δ 8.14–7.34 (m, 19 H, Ar), 6.94 (d, J = 4.4 Hz, 1 H, H1), 5.92 (dd, J = 2.2, 6.5 Hz, 1 H, H3), 5.83 (dd, J = 4.4, 6.5 Hz, 1 H, H2), 4.96 (m, 1 H, H4), 4.78 (dd, J = 3.2, 12.2 Hz, 1 H, H5a), 4.67 (dd, J = 3.2, 12.2 Hz, 1 H, H5b); ^{13}C NMR ($CDCl_3$) δ 166.0, 165.7, 165.1 (3 C, C_6H_5COO), 163.6 (1 C, 3-$F_3CC_6H_4COO$), 133.7–126.4 (Ar, CF_3), 94.9 (1 C, C1), 82.6 (1 C, C4), 71.5, 70.7 (2 C, C2, C3), 64.0 (1 C, C5); MS (FAB, KCl) 673 (M^+ + K), 513 (M^+ − OBz). Anal. Calcd for $C_{34}H_{25}O_9F_3$ (634.56): C, 66.80; H, 4.12. Found: C, 66.70; H, 4.21.

3,5-Di-*O*-benzoyl-2-*O*-(3-(trifluoromethyl)benzoyl)-α-D-ribofuranosyl Bromide (11b). Prepared by the same procedure as described for **6**. To suppress the ionic benzoyl rearrangement described by Brodfuehrer,[7] the reaction time was shortened to 1 h and the extraction process was performed quickly with cold solvents. The bromide was obtained as the α-anomer with only small traces of the β-anomer in a yield of 90%: ^{1}H NMR ($CDCl_3$) δ 8.36–7.34 (m, 19 H, Ar), 6.97 (d, J = 4.4 Hz, 1 H, H1), 5.85 (dd, J = 3.2, 7.1 Hz, 1 H, H3), 5.47 (dd, J = 4.4, 7.1 Hz, 1 H, H2), 4.93 (q, J = 3.2 Hz, 1 H, H4), 4.82 (dd, J = 3.2, 12.4 Hz, 1 H, H5a), 4.72 (dd, J = 3.2, 12.4 Hz, 1 H, H5b); ^{13}C NMR ($CDCl_3$) δ 165.9, 165.8 (2 C, C_6H_5COO), 163.7 (1 C, 3-$F_3CC_6H_4COO$), 133.7–126.4 (Ar, CF_3), 88.7 (1 C, C1), 83.4 (1 C, C4), 72.9, 69.6 (2 C, C2, C3), 63.0 (1 C, C5).

1,3,5-Tri-*O*-benzoyl-2-*O*-(diphenylphosphoryl)-α-D-ribofuranose (8). Reaction of 1,3,5-tri-*O*-benzoyl-α-D-ribofuranose (7; 5.0 g, 11 mmol) with 1.2 equiv of diphenylphosphoryl chloride and 1.2 equiv of 1-methylimidazole following the procedure for phosphorylation of 4 yielded 1,3,5-tri-*O*-benzoyl-2-*O*-(diphenylphosphoryl)-α-D-ribofuranose (8) as an oily residue. The crude product was purified by flash chromatography eluting with ether/pentane = 3/2 or by crystallization from diethyl ether/pentane to give 6.7 g (9.6 mmol, 89%) of 8: mp 82 °C; ^{1}H NMR ($CDCl_3$) δ 8.12–7.08 (m, 25 H, Ph), 6.75 (d, J = 4.2 Hz, 1 H, H1), 5.66 (dd, J = 2.0, 6.2 Hz, 1 H, H3), 5.36 (ddd, J = 4.2, 6.2, 8.6 Hz, 1 H, H2), 4.75 (dt, J = 2.0, 3.0 Hz, 1 H, H4), 4.67 (dd, J = 3.0, 12.5 Hz, 1 H, H5a), 4.58 (dd, J = 3.0, 12.5 Hz, 1 H, H5b); ^{13}C NMR ($CDCl_3$) δ 165.9, 165.6, 164.9 (3 C, C_6H_5COO), 150.1, 150.0 (2 C, ipso-C_6H_5OP), 133.6–119.6 (Ph), 93.9 (d, J = 5.4 Hz, 1 C, C1), 83.0 (1 C, C4), 74.2, 70.5 (2d, J = 5.2, 4.6 Hz, 2 C, C2, C3), 62.9 (1 C, C5); ^{31}P NMR ($CDCl_3$) δ −12.4 (d, J = 9.0 Hz); MS (FAB, KCl) 694 (M^+), 693 (M^+ − 1). Anal. Calcd for $C_{38}H_{31}O_{11}P$ (694.46): C, 65.72; H, 4.49. Found: C, 65.87; H, 4.47.

3,5-Di-*O*-benzoyl-2-*O*-(diphenylphosphoryl)-D-ribofuranosyl Bromide (9). Prepared according to the procedure for bromination of **6**. The bromide (oil, 95% yield) was obtained as an anomeric mixture, β/α = 2.5/1: MS (FAB, KCl) 694, 692 (M^+ + K). **3,5-Di-*O*-benzoyl-2-*O*-(diphenylphosphoryl)-α-D-ribofuranosyl bromide (9α)**: ^{1}H NMR ($CDCl_3$) δ 8.10–7.12 (m, 20 H, Ph), 6.65 (d, J = 4.5 Hz, 1 H, H1), 5.56 (dd, J = 2.5, 7.0 Hz, 1 H, H3), 5.22 (ddd, J = 4.5, 7.0, 9.0 Hz, 1 H, H2), 4.88–4.59 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 165.5, 165.3 (2 C, C_6H_5COO), 149.8, 149.7 (2 C, ipso-C_6H_5OP), 133.5–119.4 (Ph), 87.9 (d, J = 6.1 Hz, 1 C, C1), 83.9 (1 C, C4), 75.2, 69.1 (2d, J = 4.5, 5.2 Hz, 2 C, C2, C3), 62.8 (1 C, C5); ^{31}P NMR ($CDCl_3$) δ −12.6 (d, J = 8.6 Hz). **3,5-Di-*O*-benzoyl-2-*O*-(diphenylphosphoryl)-β-D-ribofuranosyl bromide (9β)**: ^{1}H NMR ($CDCl_3$) δ 8.12–7.08 (m, 20 H, Ph), 6.44 (s, 1 H, H1), 6.10 (m, 1 H, H3), 5.68 (dd, J = 4.0, 7.1 Hz, 1 H, H2), 4.88–4.59 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 165.8, 165.1 (2 C, C_6H_5COO), 149.9, 149.8 (2 C, ipso-C_6H_5OP), 133.5–119.4 (Ph), 86.6 (d, J = 2.9 Hz, 1 C, C1), 82.4, 70.8 (2d, J = 5.5, 5.7 Hz, 2 C, C2, C3), 80.5 (1 C, C4), 62.9 (1 C, C5); ^{31}P NMR ($CDCl_3$) δ −13.0 (d, J = 6.4 Hz); MS (FAB, KCl) 694, 692 (M^+ + K).

3,4,6-Tri-*O*-acetyl-2-deoxy-1-*O*-(diphenylphosphoryl)-α-D-*arabino*-hexopyranose (15a) (Glycosyl Donor). 3,4,6-Tri-*O*-acetyl-2-*O*-(diphenylphosphoryl)-α-D-glucopyranosyl bromide (6; 0.6 g, 1.0 mmol) was placed in a water-cooled jacket flask equipped with magnetic stirring bar, gas inlet, septum, and a Heraeus TQ-150 mercury high-pressure lamp (water-cooled, Pyrex tube). After being purged with nitrogen the glycosyl bromide was dissolved in 20 mL of dry diethyl ether or THF and 0.35 g (1.2 mmol) tri-*n*-butyltin hydride was added. On cooling with water (20 °C) the mixture was irradiated for 15 minutes and the reaction was monitored by TLC. The polar compounds detectable by TLC were the result of hydrolysis of the glycosyl donor at the anomeric center to yield 3,4,6-tri-*O*-acetyl-2-deoxy-D-*arabino*-hexopyranose. The resulting solution was used for glycosylation reactions. To characterize the rearrangement product 0.5–1 mL of the reaction mixture was removed by syringe and the solvent evaporated at room temperature. The residue was dissolved in deuterated solvent, and the ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded.

Alternatively, 60 mg (0.1 mmol) of 3,4,6-tri-*O*-acetyl-2-*O*-(diphenylphosphoryl)-α-D-glucopyranosyl bromide (**6**) and 33 mg (0.1 mmol) triphenyltin hydride were dissolved in 0.7 mL of hexadeuteriobenzene, and the solution was transferred to an NMR tube. The sample was irradiated for 30 s with the filtered light of a Hanovia 977-B1 1-kW Hg–Xe high-pressure lamp, and then the NMR spectra were recorded: ^{1}H NMR ($CDCl_3$) δ 7.40–7.18 (m, 10 H, Ph), 6.10–6.05 (m, 1 H, H1), 5.34 (ddd, J = 5.2, 9.7, 11.4 Hz, 1 H, H3), 5.07 (t, J = 9.9 Hz, 1 H, H4), 4.22 (dd, J = 3.9, 12.5 Hz, 1 H, H6a), 4.06 (ddd, J = 2.2, 3.9, 10.1 Hz, 1 H, H5), 3.84 (dd, J = 2.2, 12.5 Hz, 1 H, H6b), 2.35 (ddd, J = 1.1, 5.2, 13.5 Hz, 1 H, H2e), 2.04, 2.03, 1.99 (3s, 9 H, Ac), 1.99–1.88 (m, 1 H, H2a); ^{1}H NMR (C_6D_6) δ 7.35–6.77 (m, 10 H, Ph), 5.98–5.94 (m, 1 H, H1, irrad. at 1.99 → dd, J = 3.1, 5.6 Hz), 5.44 (ddd, J = 5.1, 9.7, 11.4 Hz, 1 H, H3), 5.21 (t, J = 9.9 Hz, 1 H, H4), 4.27 (dd, J = 3.9, 12.5 Hz, 1 H, H6a), 4.03 (ddd, J = 2.0, 3.9, 10.2 Hz, 1 H, H5), 3.85 (dd, J = 2.0, 12.5 Hz, 1 H, H6b), 1.99 (ddd, J = 1.3, 5.1, 13.7 Hz, 1 H, H2e), 1.68, 1.65, 1.58 (3s, 9 H, Ac), 1.32 (ddt, J = 3.3, 11.4, 13.7 Hz, 1 H, H2a, irrad. at 5.96 → ddd, J = 3.6, 11.5, 13.7 Hz); ^{13}C NMR ($CDCl_3$) δ 170.5, 170.0, 169.6 (3 C, CH_3COO), 150.3, 150.1 (2d, J = 7.0 Hz, 2 C, ipso-C_6H_5OP), 129.8, 129.77 (4 C, *m*-C_6H_5OP), 125.6, 125.5 (2 C, *p*-C_6H_5OP), 120.0, 119.9 (2d, J = 4.8 Hz, 4 C, *o*-C_6H_5OP), 96.8 (d, J = 5.8 Hz, 1 C, C1), 69.9, 67.8, 67.4 (3 C, C3, C4, C5), 61.1 (1 C, C6), 34.7 (d, J = 8.6 Hz, 1 C, C2), 20.3, 20.1, 20.0 (3 C, CH_3COO); ^{31}P NMR ($CDCl_3$) δ −13.2. The ^{1}H–^{31}P couplings were not discernible in the ^{31}P NMR.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-deuterio-1-*O*-(diphenylphosphoryl)-α-D-*arabino*-hexopyranose (15b). For the preparation of the deuterated compound **15b** 60 mg (0.1 mmol) of 3,4,6-tri-*O*-acetyl-2-*O*-(diphenylphosphoryl)-α-D-glucopyranosyl bromide (**6**) and 33 mg (0.11 mmol) tri-*n*-butyltin deuteride were dissolved in 0.7 mL of hexadeuteriobenzene, and the solution was transferred to an NMR tube. The sample was irradiated for 30 s with the filtered light of a Hanovia 977-B1 1-kW Hg–Xe high-pressure

lamp, and then the NMR spectra were recorded, showing complete conversion: ^{1}H NMR (C_6D_6) δ 7.35–6.77 (m, 10 H, Ph), 5.95 (bd, J = 6.8 Hz, 1 H, H1), 5.44 (dd, J = 5.1, 9.6 Hz, 1 H, H3), 5.21 (t, J = 9.9 Hz, 1 H, H4), 4.27 (dd, J = 3.9, 12.5 Hz, 1 H, H6a), 4.03 (ddd, J = 2.0, 3.9, 10.2 Hz, 1 H, H5), 3.85 (dd, J = 2.0, 12.5 Hz, 1 H, H6b), 1.99 (bd, J = 5.0 Hz, 0.9 H, H2e), 1.68, 1.65, 1.58 (3s, 9 H, Ac), 1.32 (H2a, obscured by alkyl groups of tri-n-butyltin deuteride); ^{31}P NMR (C_6D_6) δ −12.5 (d, J = 6.8 Hz).

This sample was transferred to a flask, 5 mL of benzene was added, and the solution was heated to reflux for 10 h. The solvent was then evaporated under reduced pressure and the residue dissolved in acetonitrile. After extraction with pentane and removal of the acetonitrile in vacuo the deuterated 3,4,6-tri-O-acetyl-D-glucal was isolated by flash chromatography (ether/pentane/dichloromethane = 1/1/1). By comparison, with a sample of the nondeuterated 3,4,6-tri-O-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol, MS indicated the presence of at least 70% deuterium in **16**.

In another experiment for the preparation of the deuterated compound **15b** 60 mg (0.1 mmol) of 3,4,6-tri-O-acetyl-2-O-(diphenylphosphoryl)-α-D-glucopyranosyl bromide (**6**) and 33 mg (0.11 mmol) of tri-n-butyltin deuteride were dissolved in 0.7 mL of nondeuterated benzene, and the solution was transferred to an NMR tube. The sample was irradiated for 30 s with the filtered light of a Hanovia 977-B1 1-kW Hg–Xe high-pressure lamp and used afterwards for recording the ^{2}H NMR: ^{2}H NMR (C_6H_6) δ 2.15–1.71 (bs, 0.1 D, equatorial), 1.70–0.80 (bs, 0.9 D, axial).

3,4,6-Tri-O-acetyl-1,5-anhydro-2-O-(diphenylphosphoryl)-D-glucitol (13). Following the preparation of **15a** 3,4,6-tri-O-acetyl-2-O-(diphenylphosphoryl)-α-D-glucopyranosyl bromide (**6**; 0.5 g, 0.83 mmol) was placed in a water-cooled jacket flask equipped with magnetic stirring bar, gas inlet, septum, and a Heraeus TQ-150 mercury high-pressure lamp (water-cooled, Pyrex tube). After being purged with nitrogen the glycosyl bromide was dissolved in 35 mL of dry diethyl ether and 2.47 g (8.5 mmol, 10 equiv) of tri-n-butyltin hydride was added. On being cooled with water (20 °C) the mixture was irradiated for 15 min. After purification three times by flash chromatography (ether/pentane/dichloromethane = 1/1/1, ether/pentane/acetonitrile = 10/1/1, and then dichloromethane/acetonitrile = 5/1) **13** (10 mg, 0.02 mmol) was obtained pure: ^{1}H NMR ($CDCl_3$) δ 7.38–7.17 (m, 10 H, Ph), 5.27 (t, J = 9.3 Hz, 1 H, H3), 5.00 (t, J = 9.8 Hz, 1 H, H4), 4.71 (dddd, J = 5.8, 8.2, 9.3, 10.6 Hz, 1 H, H2), 4.23–4.16 (m, 2 H, H1e, H6a), 4.10 (dd, J = 2.3, 12.5 Hz, 1 H, H6b), 3.61 (ddd, J = 2.3, 4.8, 10.0 Hz, 1 H, H5), 3.39 (t, J = 11.0 Hz, 1 H, H-1a), 2.09, 2.02, 1.84 (3s, 9 H, Ac); ^{13}C NMR ($CDCl_3$) δ 170.6, 170.3, 169.5 (3 C, CH_3COO), 150.3, 150.2 (2d, J = 7.3 Hz, 2 C, ipso-C_6H_5OP), 129.9 (4 C, m-C_6H_5OP), 125.7, 125.6 (2d, J = 1.3 Hz, 2 C, p-C_6H_5OP), 120.0, 119.9 (2d, J = 5.0 Hz, 4 C, o-C_6H_5OP), 76.4 (1 C, C5), 74.1, 73.7 (2d, J = 6.0 Hz, 2 C, C2, C3), 68.3 (d, J = 1.3 Hz, 1 C, C-4), 67.8 (d, J = 3.3 Hz, 1 C, C-1), 62.0 (1C, C-6), 20.7, 20.6, 20.5 (3 C, CH_3COO); ^{31}P NMR (C_6D_6) δ −11.7 (d, J = 7.5 Hz).

Kinetic Measurements. 3,4,6-Tri-O-acetyl-2-O-(diphenylphosphoryl)-α-D-glucopyranosyl bromide (**6**; 90 mg, 0.15 mmol) was dissolved in 1.8 mL of hexadeuteriobenzene. Six portions of 0.3 mL of this solution were transferred to NMR-tubes. Tri-n-butyltin hydride (80, 120, 160, 200, 240, and 280 μL) was added, and then hexadeuteriobenzene (320, 280, 240, 200, 160, and 120 μL) was added to make the sample volumes up to 0.7 mL. The solutions were mixed by shaking for 3 s. Each sample was irradiated individually with the filtered light of a Hanovia 977-B1 1-kW Hg–Xe high-pressure lamp for 30 s, and then the ^{31}P NMR spectrum was recorded. By integration the ratios [**15a**]/[13] were determined (10.0, 6.6, 5.3, 4.0, 3.1, 2.7) for the six different tin hydride concentrations (0.27, 0.41, 0.55, 0.68, 0.82, 0.96 M). The slope of a plot [**15a**]/[13] against $[Bu_3SnH]^{-1}$ gave the ratio k_R/k_H.

Preparation of the 2-Deoxydisaccharides. In a flask equipped with a magnetic stirring bar were placed the glycosyl acceptor (0.8 mmol) and anhydrous magnesium perchlorate (18 mg, 0.08 mmol). A solution of the glycosyl donor **15a** in diethyl ether or THF was added and the mixture stirred for 15 min. Triethylamine (0.5 mL, 5.0 mmol) was added to quench the reaction, and then the solvent was evaporated under reduced pressure and the residue dissolved in acetonitrile. After extraction with pentane and removal of the acetonitrile in vacuo the 2-deoxy disaccharide was isolated by flash chromatography. The yields are collected in Table II.

3,5-Di-O-benzoyl-2-deoxy-1-O-(diphenylphosphoryl)-α-D-*erythro*-pentofuranose (17). NMR spectroscopic characterization of the 2-deoxyribosyl phosphate **17**: 100 mg (0.15 mmol) of 3,5-di-O-benzoyl-2-O-(diphenylphosphoryl)-D-ribofuranosyl bromide (**9**) and 65 mg (0.15 mmol) of tri-n-butyltin hydride were dissolved in 0.7 mL of hexadeuteriobenzene, and the solution was transferred to an NMR tube. The sample was irradiated for 30 s with the filtered light (Schott UG-5) of a Hanovia 977-B1 1-kW Hg–Xe high-pressure lamp, and then the NMR spectra were immediately recorded: ^{1}H NMR (C_6D_6) δ 8.22–7.92 (m, 4 H, Ph), 7.35–6.84 (m, 16 H, Ph), 6.18 (t, J = 4.0 Hz, 1 H, H1), 5.15 (dd, J = 1.9, 6.7 Hz, 1 H, H3), 4.40–4.22 (m, 3 H, H4, H5a, H5b), 2.08 (d, J = 15.1 Hz, 1 H, H2a), 1.85 (m, 1 H, H2b, irrad. at 6.18 → ddd, J = 15.1, 6.7, 3.3 Hz); ^{13}C NMR (C_6D_6) δ 166.1, 165.9 (2 C, C_6H_5COO), 150.2, 149.9 (2 C, ipso-C_6H_5OP), 133.8–120.2 (Ph), 104.1 (d, $J \approx 9.0$ Hz, 1 C, C1), 84.9, 74.3 (2 C, C3, C4), 64.1 (1 C, C5), 40.1 (d, J = 8.6 Hz, 1 C, C2); ^{31}P NMR (C_6D_6) δ −13.3. The ^{1}H–^{31}P couplings were not discernible in the ^{31}P NMR.

General Procedure for the Preparation of the 2′-Deoxy Ribonucleosides. To a solution of 3,5-di-O-benzoyl-2-O-(diphenylphosphoryl)-D-ribofuranosyl bromide (**9**) (1 mmol) in absolute THF or diethyl ether was added tri-n-butyltin hydride (1.2 equiv) in one portion. The nucleophilic base (1.1 equiv) was added, and the mixture was photolyzed immediately. The best yields were achieved by irradiation of the mixture in a round-bottom flask of regular pyrex glass for 4 min with the filtered light of a Hanovia 977-B1 1-kW Hg–Xe high-pressure lamp. Using a lamp of lower power resulted in a poorer yield of the deoxy nucleoside as direct substitution of the bromide by the nucleophile competes with the radical reaction. For workup the solvent was evaporated and the residue dissolved in acetonitrile and extracted with pentane. The acetonitrile was evaporated, and the deoxy nucleoside was purified by flash chromatography.

Registry numbers supplied by authors: **26α**, 50705-73-2; **26β**, 50705-72-1; **27β**, 125085-00-9; **28β**, 125084-95-9.

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Supplementary Material Available: Spectral data and specific procedures of 2-deoxy disaccharides **26–29** and 2-deoxy nucleosides **31–36** (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.