thentic sample same conditions).

Preparation of Compounds Used in the Characterization of the Electrochemical Products. 2,2'-Bis[(diphenylmethyl)amino]biphenyl (18). A solution of 1.0 g of (0.001 96 mol) of **17** and 0.152 g (0.004 mol) of lithium aluminum hydride ($LiAlH_4$) in 125 mL of anhydrous ether was heated under reflux for 24 h. Ice was added slowly to destroy the excess $LiAlH_4$ and the solution then poured into a cold 20% sodium hydroxide solution. The two layers were separated and the aqueous layer extracted two additional times with 50 mL of ether. The combined ether extracts were dried over anhydrous $MgSO_4$ and filtered, and the ether was removed on a steam bath. The oil was dissolved in methylene chloride and diluted with methanol. The methylene chloride was slowly distilled from the solution. Cooling yielded two crops of compound **18**, 0.9 g (89%). The total yield of diamine **18** was 0.9 g (89%). Three recrystallizations from methanol–methylene chloride yielded a compound melting at 168.5–171.5 °C; the mixture melting point was identical with that of the compound obtained from the electrochemical reduction of the di-Schiff base **17**; the infrared spectra were also identical.

9-Acetyl-9a,18-dihydro-9*H*-dibenz[3,4:5,6]azepino[1,2-*a*]-dibenzo[*d*,*f*][1,3]diazepine (20a). To a stirred solution of 15 mL of acetic anhydride containing 0.2 mL of boron trifluoride etherate was added 0.4 g of **20**. The solution was stirred for 30 min, poured into water, and stirred to decompose the acetic anhydride. The precipitate that formed was filtered, washed with water, and air-dried. The material isolated, 0.4 g (89.5%), was used as obtained: mp 248–252 °C; NMR ($CDCl_3$) δ 1.60 (s, 3, $COCH_3$), 4.05 (s, 2, CH_2, br), 6.48 (s, 1, CH), 7.08–8.27 (m, 16, Ar H); mass spectrum (70 eV), *m/e* 402, 387, 359, 344.

9,18-Dihydrodibenzo[*e*,*g*]phenanthro[9,10-*b*][1,4]diazocine (21). A solution of 9.0 g (0.0253 mol) of dibenzo[*e*,*g*]-phenanthro[9,10–*b*][1,4]diazocine[37] and 2.0 g (0.0506 mol) of lithium aluminum hydride in 200 mL of anhydrous glyme was heated under reflux for 3 h. Ice was added to destroy the excess $LiAlH_4$. The solution was poured into a cold 20% sodium hydroxide solution. The two layers were separated, and the aqueous layer was extracted two additional times with 100-mL portions of ether. The combined extracts were dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness; 7.5 g (82.8%) of a light-tan solid was obtained. Several recrystallizations from benzene–petroleum ether yielded a fluffy, light-tan material identified as **21**, mp 272.5–273.5 °C. The infrared spectrum ($CHCl_3$) and mixture melting point proved this compound to be identical with one of the products isolated by the electrochemical reduction of **19**.

9,18-Dihydro-9,18-dimethyldibenzo[*e*,*g*]phenanthro[9,10-*b*][1,4]diazocine (21b). To a solution of 1.0 g (0.0028 mol) of **21** in 50 mL of glyme prepared under nitrogen was added 1.0 g of 60% suspension of sodium hydride in mineral oil. The mixture was stirred and heated under reflux for 30 min. After addition of 10 mL of methyl iodide, stirring and heating under reflux was continued for 2 h and the mixture was poured into ice–water. Extraction with methylene chloride and replacement of this solvent by ethanol gave 0.8 g (74%) of light-cream crystals. Recrystallization from a mixture of methylene chloride–ethanol gave off-white prisms melting at 180.5–183.5 °C: NMR ($CDCl_3$) δ 2.52 (s, 6, NCH_3), 6.68–8.92 (m, 16, Ar H).

Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.47; H, 5.75; N, 7.18.

Acknowledgment. We thank Firestone Tire and Rubber Co. and the National Science Foundation for partial support of this research.

Registry No. 5, 574-45-8; **6**, 1865-12-9; **6**·HCl, 2101-21-5; **7**, 104-71-2; **8**, 140-28-3; **8**·2HCl, 3412-76-8; **9**, 81577-03-9; **9**·2HCl, 83027-12-7; **10**, 64042-50-8; **11**, 83027-13-8; **12**, 7443-50-7; **13**, 3920-79-4; **14**, 83027-14-9; **15**, 83027-15-0; *dl*-**16**, 83027-16-1; *meso*-**16**, 83027-24-1; **17**, 83027-17-2; **18**, 83027-18-3; **19**, 7428-21-9; **20**, 83027-19-4; **20a**, 83027-22-9; **21**, 83027-20-7; **21b**, 83027-23-0; **22**, 7139-42-6; **23**, 83027-21-8; **24**, 3646-61-5; **25**, 10127-72-7; 2,2'-dibenzoylbiphenyl, 24018-00-6; aniline, 62-53-3; 2,2'-diaminobiphenyl, 1454-80-4; benzophenone, 119-61-9; dibenzo[*e*,*g*]phenanthro[9,10-*b*][1,4]diazocine, 214-45-9.

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Stereospecific Synthesis of the Phosphono Analogues of α- and β-D-Glucose 1-Phosphate

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The present paper describes the convenient stereospecific synthesis of the analogues of α- and β-D-glucose 1-phosphate. The β analogue, (1-deoxy-β-D-glucopyranosyl)methanephosphonic acid, was synthesized by treatment of 2,6-anhydro-1-bromo-1-deoxy-3,4,5,7-tetra-*O*-acetyl-D-*glycero*-D-*gluco*-heptitol with triethyl phosphite, followed by deethylation of the obtained diethyl (1-deoxy-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)methanephosphonate and deacetylation with ion-exchange resin. The α analogue, (1-deoxy-α-D-glucopyranosyl)methanephosphonic acid, was synthesized by starting from 2,3,4,6-tetra-*O*-benzyl-D-glucose through the following sequence: Wittig reaction with methylenetriphenylphosphorane, mercuriocyclization, bromodemercuriation, Arbuzov reaction, and removal of the protecting groups.

In recent years great interest has developed in the synthesis of phosphonic acids which might be considered isosteric analogues of naturally occurring phosphates.[1] These compounds, in which a substitution of methylene for oxygen occurs at the phosphonic ester group, may be able to inhibit or regulate metabolic processes. This is due to their geometrical similarity with the naturally occurring analogues and to the incapability of the carbon–phosphorous bond to be hydrolyzed.

In the carbohydrate field a number of phosphonate analogues have been synthesized,[1-7] although in many cases

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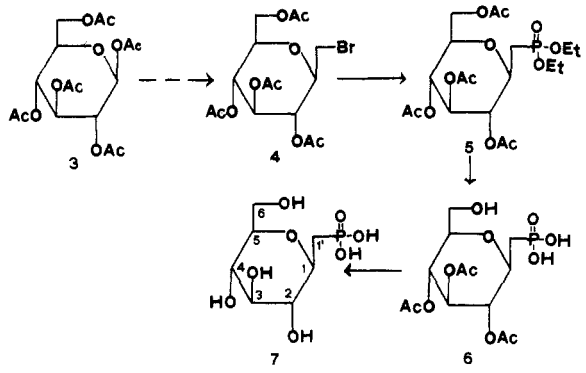
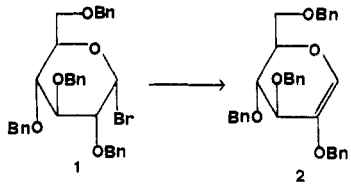
Scheme I



the analogy with the natural compounds was limited by the fact that they were not true isosteres or were in a protected form (e.g., the phosphonic group as an ester and the hydroxyl groups as esters or ethers).[1,7] In this connection, the phosphono analogues of pyranosyl 1-phosphates may be of great importance. In fact, these compounds are of both chemical and biological interest, as they have the phosphonic group linked to the anomeric center and as their natural isosteres play a central role in the carbohydrate metabolism.

In this paper we describe the stereospecific synthesis of (1-deoxy-α-D-glucopyranosyl)methanephosphonic acid (17) and (1-deoxy-β-D-glucopyranosyl)methanephosphonic acid (7), the phosphono analogues of α- and β-D-glucose 1-phosphate.

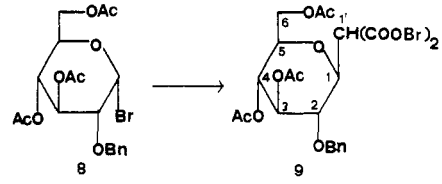
The most direct way to 7 and 17 appeared to us to be the introduction of the methylenephosphonic group on the carbohydrate moiety by reaction of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide (1) with $LiCH_2PO(OMe)_2$ in the presence of hexamethylphosphorotriamide to enhance the softness of the nucleophile.[8] Unfortunately, when 1 in tetrahydrofuran–hexamethylphosphorotriamide was treated at −78 °C with $LiCH_2PO(OMe)_2$, in the presence of tetraethylammonium bromide (to enhance the amount of the α-*C*-glucosyl product),[9] only the elimination product 2 was obtained (eq 1). We then



(1)

changed our synthetic plan and decided to prepare the *C*-glucosyl intermediate first and to link the phosphorous atom afterward. In order to synthesize both the α- and the β-*C*-glucosyl intermediates, the reaction of a glucopyranosyl bromide with a sodium malonate, as reported by Hanessian et al.,[10] appeared to be the most promising procedure as it can afford, depending on the substrate and the experimental conditions, either β-*C*-glucosyl malonates or a mixture of α and β derivatives. With this procedure, the synthesis of the (1-deoxy-β-D-glucopyranosyl)-methanephosphonic acid (7) was effected according to Scheme I: 2,6-anhydro-1-bromo-1-deoxy-3,4,5,7-tetra-*O*-acetyl-D-*glycero*-D-*gluco*-heptitol (4), obtained in 35% yield by starting from penta-*O*-acetyl-β-D-glucopyranose (3),[9] was refluxed with triethyl phosphite, affording in 90% yield diethyl (1-deoxy-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)methanephosphonate (5). Treatment of the phosphonic ester 5 with an excess of iodotrimethylsilane at 0 °C and a subsequent workup afforded (1-deoxy-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyl)methanephosphonic acid (6) in 67% yield. The structure of 6 is in agreement with its ^1H NMR spectrum (200 MHz) which shows the presence of only three acetoxy groups (singlets at δ 1.96, 2.01 and 2.03, each corresponding to three protons) located on carbons 2–4 of the sugar moiety. The deacetylation of 6 was effected in quantitative yield with a strong basic ion-exchange resin (Dowex 2, OH^- form) to yield, after chromatography on cellulose, (1-deoxy-β-D-glucopyranosyl)methanephosphonic acid (7) as the monoammonium salt, which was crystallized from ethanol. In the ^1H NMR spectrum (200 MHz) of 7, double-resonance experiments allowed us to determine a 9-Hz coupling constant between the protons 1 and 2. This coupling constant indicates an axial–axial relationship between the above protons, which is in agreement with the preferred $^4C_1$ conformation of 7 and the β orientation of the methanephosphonic group.

The synthesis of the biologically more interesting phosphono analogue of α-D-glucose 1-phosphate appeared less easy owing to the difficulty of obtaining the proper *C*-glucosyl intermediate with a high degree of stereospecificity. We first tried to utilize the reaction between a malonate nucleophile and a glucosyl bromide with the modifications which are described[9] to afford predominantly α-*C*-glucosyl compounds, namely, the use of a glucopyranosyl bromide bearing a nonparticipating group at C-2 in the presence of tetraethylammonium bromide. When we treated 2-*O*-benzyl-3,4,6-tri-*O*-acetyl-α-D-glucopyranosyl bromide[11] (8) in the presence of tetraethylammonium bromide with sodium dibenzylmalonate, the obtained *C*-glucosyl product appeared as a mixture of a higher R_f and a lower R_f (TLC on H_3BO_3–silica gel) product, the latter of which (9, eq 2) was predominant (90%) and was



(2)

isolated by crystallization. Unfortunately, this compound was again a β-*C*-glucosyl derivative, as indicated by the 10-Hz axial–axial coupling constant between the protons 1 and 2, determined by ^1H NMR (200 MHz) double-resonance experiments.

We then tried a different approach for the synthesis of the desired α-*C*-glucosyl compound, that is, the Wittig reaction between the aldehydic group of the sugar with (carboethoxymethylene)triphenylphosphorane followed by the cyclization of the obtained product, as reported by Moffat et al.[12] in the case of *C*-ribosides. The reaction between 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (10) and (carboethoxymethylene)triphenylphosphorane easily af-

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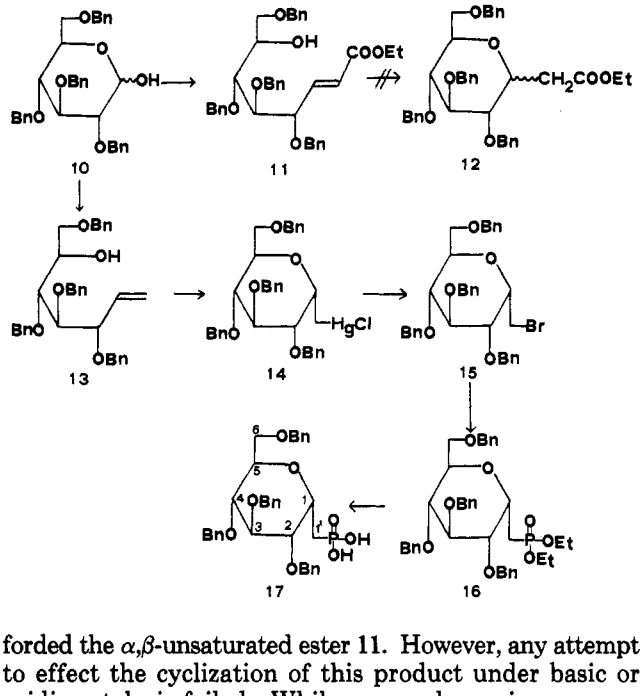
Scheme II



forded the α,β-unsaturated ester **11**. However, any attempt to effect the cyclization of this product under basic or acidic catalysis failed. While our work was in progress, Sinay et al.[13] reported the stereospecific mercuriocyclization of the product **13** of the Wittig reaction between 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**10**) and methylenetriphenylphosphorane, which afforded the mercurio derivative **14**. When we treated **14** with bromine, we obtained in 50% yield the bromo derivative **15**, which was refluxed with triethyl phosphite to afford, after chromatography, diethyl (1-deoxy-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)methanephosphonate (**16**) in 60% yield (Scheme II). Treatment of the phosphonic ester **16** with an excess of iodotrimethylsilane at 0 °C directly afforded, after the workup, the desired (1-deoxy-α-D-glucopyranosyl)methanephosphonic acid (**17**) in quantitative yield. This compound was purified by cellulose chromatography and was isolated as a crystalline hygroscopic monoammonium salt. In the ^{1}H NMR spectrum of **17**, double-resonance experiments allowed us to determine a 3-Hz coupling constant between the protons 1 and 2. This value indicates an axial–equatorial relationship between the above protons, in agreement with the α orientation of the methylenephosphonic group. Moreover, the chemical shift of proton 1 is at lower field (δ 4.38) than that of the corresponding proton in the β isomer **7** (δ 3.49). This is in agreement with the general fact that the equatorial protons come into resonance at lower fields than the chemically similar axial protons.

The syntheses here described afford the phosphono analogues of both α- and β-D-glucose 1-phosphate in nonprotected form and in reasonable (20–25%) overall yield from commerically available starting materials. The availability of these compounds may spread light on which is the more interesting anomer for the natural systems.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-100 spectrometer with Me_4Si as an internal reference, unless otherwise stated; ^{31}P NMR spectra were recorded on a Varian XL-200 spectrometer by using H_3PO_4 as a reference. Chromatographies were carried out on silica gel S (Riedel-De Haen AG) according to the flash procedure.[14] The reactions were monitored by thin-layer chromatography (TLC) on Merck HF_{254} silica gel plates unless otherwise stated, and the spots were detected under UV light and/or by spraying with 50% aqueous sulfuric acid and heating at 110 °C. Phosphate esters were detected with molybdate–perchloric acid reagent[15] and phosphoric acids with molybdate reagent.[16] The usual workup refers to dilution with water, extraction with an organic solvent, washing with water to neutrality, drying with Na_2SO_4, and evaporation of the solvent.

Reaction of 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl Bromide (1) with $LiCH_2PO(OMe)_2$. A solution of $LiCH_2PO(OMe)_2$, prepared by adding at −78 °C 6 mL of 1.6 M BuLi in hexane to 1.2 g of $CH_3PO(OMe)_2$ in 20 mL of THF and 2 mL of HMPTA, was added at −78 °C under argon atmosphere to a stirred solution of **1**[9] (1 g) in 10 mL of THF, to which 700 mg of Et_4NBr had been added. The usual workup afforded quantitatively 1,5-anhydro-2,3,4,6-tetra-*O*-benzyl-D-*arabino*-hex-1-enitol (**2**), which was crystallized from MeOH: mp 60–61 °C; ^{1}H NMR ($CDCl_3$) δ 3.6–4.4 (5 H, CH–O), 4.55, 4.67 (4 H, S, OCH_2Ph), 4.68 (4 H, s, OCH_2Ph), 6.35 (1 H, s, =CHO), 7.3 (20 H, PhH). Anal. Calcd for $C_{34}H_{35}O_5$: C, 78.18; H, 6.51. Found: C, 77.79; H, 6.43.

Diethyl (1-Deoxy-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)methanephosphonate (5). 2,6-Anhydro-1-bromo-1-deoxy-3,4,5,7-tetra-*O*-acetyl-D-*glycero*-D-*gluco*-heptitol (**4**,[10] 1.7 g) was refluxed for 6 h under an argon atmosphere with 20 mL of $P(OEt)_3$. The excess of reagent was removed under reduced pressure (0.5 mmHg), and the residue, dissolved in Et_2O–hexane and cooled overnight at −5 °C, afforded diethyl (1-deoxy-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)methanephosphonate (**5**; 1.7 g, 90% yield) in crystalline form. The product was crystallized from Et_2O: mp 59–60 °C; $[\alpha]^{20}_D$ +0.6° (*c* 1 in $CHCl_3$); ^{1}H NMR δ 1.26 (6 H, t, J = 7 Hz, OCH_2CH_3), 1.96 (4 H, dd, $J_{H,P}$ = 18 Hz, $J_{H,H}$ = 6 Hz, H-1′), 1.96, 1.99, 2.01, 2.03 (12 H, s, OAc), 4.08 (4 H, dd, $J_{H,P}$ = 9 Hz, $J_{H,H}$ = 7 Hz, $POCH_2$), 3.6–4.2 (5 H, H-1, H-2, H-5, H-6, H-6′), 4.86 (1 H, t, J = 8 Hz, H-4), 5.10 (1 H, t, J = 8 Hz, H-3); ^{13}C NMR ($CDCl_3$) 29.90 ppm (d, $J_{C,P}$ = 144 Hz, C-1′); ^{31}P NMR ($CDCl_3$) −26.52 ppm.

(1-Deoxy-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyl)methanephosphonic Acid (6). A solution of 1.7 g of **5** in 35 mL of dry CCl_4 was stirred under argon atmosphere at 0 °C with 2 mL of Me_3SiI. After 30 min 1 mL of water was added to the reaction mixture and the solvent was removed under reduced pressure. The brown residue was dissolved in Et_2O. On cooling overnight the solution afforded crystalline **6** (1 g, 67%) which was crystallized from EtOH: mp 190–192 °C; $[\alpha]^{20}_D$ +7.2° (*c* 1, MeOH); ^{1}H NMR (CD_3OD) δ 1.96, 2.01, 2.03 (9 H, s, OAc), 1.96 (2 H, H-1′), 3.5–3.7 (3 H, H-5, H-6, H-6′), 3.88 (1 H, m, H-1), 4.85 (1 H, t, J = 9 Hz, H-2), 5.00 (1 H, t, J = 9 Hz, H-4), 5.19 (1 H, t, J = 9 Hz, H-3); ^{31}P NMR (CD_3OD) −26.35 ppm. Anal. Calcd for $C_{13}H_{21}O_{11}P$: C, 40.63; H, 5.51. Found: C, 40.86; H, 5.32.

(1-Deoxy-β-D-glucopyranosyl)methanephosphonic Acid (7). A solution of 300 mg of **6** in 20 mL of MeOH was treated overnight at room temperature with 600 mg of Dowex 2 (OH^- form) resin. The resin was then filtered and washed with 5% HCl. The hydrochloric acid solution was evaporated under reduced pressure, affording 205 mg of **7**. The material, which exhibited a single spot at R_f 0.44 on cellulose TLC, developed with 1-propanol–ammonia–water (6:3:1) and visualized with molybdate reagent, was purified by chromatography on cellulose and crystallized from EtOH. The material is hygroscopic and analyzed for the monoammonium salt: ^{1}H NMR (D_2O, 200 MHz) δ 1.74 (1 H, m, $J_{1'a,1}$ = 9 Hz, $J_{1'a,P}$ = 16 Hz, $J_{1'a,1'b}$ = 16 Hz, H-1′a), 2.06 (1 H, m, $J_{1'b,1}$ = 4 Hz, $J_{1'b,P}$ = 18 Hz, $J_{1'b,1'a}$ = 16 Hz, H-1′b), 3.49 (1 H, $J_{1,2}$ = 9 Hz, $J_{1,1'a}$ = 9 Hz, $J_{1,1'b}$ = 4 Hz, H-1), 3.0–4.0 (7 H); ^{13}C NMR (D_2O, dioxane as reference −35.22 (d, $J_{C,P}$ = 134 Hz, C-1′); ^{31}P NMR (D_2O) −28.17 ppm. Anal. Calcd for $C_7H_{18}O_8PN$: C, 30.56; H, 6.59; N, 5.09. Found: C, 30.18; H, 6.42; N, 4.87.

Dibenzyl (2-*O*-Benzyl-1-deoxy-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl)malonate (9). A solution of sodium dibenzyl malonate, obtained from 1.12 mL of dibenzyl malonate in a 3.5 mL of DME and 90 mg of NaH, was added under an argon

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atmosphere to a stirred solution of 8[8] (540 mg) in 10 mL of DME to which 2.47 g of Et_4NBr had been added. After 40 h the usual workup and chromatography afforded 230 mg of pure **9**, which was crystallized from Et_2O: mp 106–107 °C; $[\alpha]^{20}_D$ +20.8 (*c* 0.5, $CHCl_3$); ^1H NMR (C_6D_6, 200 MHz) δ 1.88, 1.98, 2.00 (9 H, s, OAc), 3.42 (1 H, m, $J_{4,5}$ = 12 Hz, $J_{5,6}$ = 5 Hz, $J_{5,6'}$ = 2.5 Hz, H-5), 4.22 (1 H, dd, $J_{6,6'}$ = 13.5 Hz, $J_{5,6}$ = 2.5 Hz, H-6'), 4.25 (1 H, d, $J_{1',1}$ = 6 Hz, H-1'), 4.26 (1 H, dd, $J_{1,2}$ = 10 Hz, $J_{2,3}$ = 10 Hz, H-2), 4.39 (1 H, dd, $J_{1,1'}$ = 6 Hz, $J_{1,2}$ = 10 Hz, H-1), 4.52 (1 H, dd, $J_{6,6'}$ = 13.5 Hz, $J_{5,6}$ = 5 Hz, H-6), 4.90 (2 H, d, *J* = 1 Hz, OCH_2Ph), 5.20 (2 H, s, $PhCH_2COO$), 5.22 (2 H, s, $PhCH_2COO$), 5.5 0 (1 H, dd, $J_{3,4}$ = 10 Hz, $J_{4,5}$ = 12 Hz, H-4), 5.62 (1 H, dd, $J_{3,4}$ = 10 Hz, $J_{2,3}$ = 10 Hz, H-3), 7.46 (5 H, PhH); ^{13}C NMR ($CDCl_3$) 53.40 ppm (C-1').

(1-Deoxy-α-D-glucopyranosyl)methanephosphonic Acid (17). To a stirred solution of 5.8 g of the mercurio derivative 14[13] in 40 mL of CH_2Cl_2 was added 1.34 g of Br_2 in 40 mL of CH_2Cl_2 dropwise under an argon atmosphere. After 16 h at room temperature the solvent was removed under reduced pressure, and the residue was chromatographed, affording **15**: 2.3 g (50%); oily product; ^{13}C NMR (C_6D_6) 29.03 ppm (CH_2Br). The bromide **15** (2.3 g) was refluxed under an argon atmosphere with 35 mL of $P(OEt)_3$ for 7 h. The excess of reagent was then removed under reduced pressure (0.5 mmHg), and the residue afforded, after chromatography, 1.5 g (60%) of **16** as an oily product: ^1H NMR (C_6D_6) δ 1.02 (3 H, t, *J* = 7 Hz, OCH_2CH_3), 2.62 (2 H, m, H-1'), 4.50, 4.53, 4.66 (8 H, OCH_2Ph), 3.5–4.5 (7 H), 7.25 (20 H, PhH); ^{13}C NMR (C_6D_6) 16.31, 16.55 (OCH_2CH_3), 26.90 ppm (d, $J_{C,P}$ = 139 Hz, C-1'); ^{31}P NMR ($CDCl_3$) −27.02 ppm.

A solution of 520 mg of **16** in 2 mL of CCl_4 was treated at 0 °C with 1 mL of Me_3SiI. After 30 min, 1 mL of water was added to the reaction mixture, and the solvent was removed under reduced pressure. The residue (220 mg), which exhibited a single spot of R_f 0.41 on cellulose TLC [developed with 1-propanol–ammonia–water (4:3:1) and visualized with molybdate reagent], was chromatographed on cellulose. The recovered pure **17** (204 mg) was crystallized by rubbing under ethanol. The material is hygroscopic and analyzed for the monohydrate monoammonium salt: ^1H NMR (D_2O, 200 MHz) δ 1.95 (2 H, ABMX system, $J_{H,P}$ = 18 Hz, $J_{1,1'}$ = 7 Hz, H-1'), 3.5–4.5 (7 H), 4.38 (1 H, dd, $J_{1,2}$ = 3 Hz, $J_{1,1'}$ = 7 Hz, H-1); ^{13}C NMR (D_2O, dioxane as reference) −38.12 ppm (d, $J_{C,P}$ = 129 Hz, C-1'); ^{31}P NMR (D_2O) −20.41 ppm. Anal. Calcd for $C_7H_{18}O_8PN$, H_2O: C, 28.68; H, 6.87; N, 4.77. Found: C, 28.48; H, 6.86; N, 5.33.

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Regio- and Stereospecific [2 + 2] Photoaddition of Cycloalkenes to Pentafluoropyridine[1]

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Cyclohexane as a solvent plays an important role in the stereochemistry of photocycloaddition of cycloalkenes to pentafluoropyridine. [2 + 2] photoaddition of cyclopentene or cycloheptene to pentafluoropyridine in cyclohexane proceeds regiospecifically at positions C-3 and C-4 and is stereospecifically exo. The primary [2 + 2] adducts formed undergo further photochemical and thermal [2 + 4] cycloaddition with cycloalkenes. The quantum yield of [2 + 2] photocycloaddition depends on ring size and the concentration of cycloalkene.

The photochemical transformations and cycloaddition reactions of aromatic molecules and their derivatives have been widely investigated in the last 20 years.[2] On the other hand, reactions of heteroaromatic molecules have received much less attention.[3]

The use of fluorine as a convenient substituent for photochemical transformations of organic molecules has been variously reported and has been reviewed.[4] The photocycloaddition reaction of hexafluorobenzene with *cis*-cyclooctene gave various 1:1 cycloadducts which are formed via 1,2- and 1,3-addition processes.[5] On the other hand, we have demonstrated that cyclohexane as a solvent plays an important role in [2 + 2] photocycloaddition reactions of hexafluorobenzene with cycloalkenes, the stereochemistry depending also on the structure of the cycloalkene.[6] Recently, Haszeldine and co-workers[7] have shown that irradiation of a mixture of cycloalkenes and pentafluoropyridine gave two pairs of 2:1 adducts, which are formed by [2 + 2] addition at C-3 and C-4, and [4 + 2] addition at C-2 and C-5, the ratio of the products de-

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