3-*O*-Benzyl-5-deoxy-5-(ethylphosphinyl)-D-xylopyranose

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There has been a great deal of activity in recent years in connection with the syntheses of sugar analogs with nitrogen or sulfur in the hemiacetal ring.[1] Concerning sugar analogs with phosphorus in the ring, however, only one short report has been published, by Whistler and Wang,[2] who prepared 5-deoxy-3-*O*-methyl-5-(phosphinyl)-D-xylopyranose and 5-deoxy-3-*O*-methyl-5-(hydroxyphosphinyl)-D-xylopyranose in poor yields.

The present paper will report on the synthesis of 3-*O*-benzyl-5-deoxy-5-(ethylphosphinyl)-D-xylopyranose in 27% yield from **1**.

As a starting material, we used 3-*O*-benzyl-5-deoxy-5-iodo-1,2-*O*-isopropylidene-α-D-xylofuranose (**1**) (mp 76—76.5°C,[3] $[\alpha]^{14}_{D}$ −59.8° (*c* 4.5, acetone)), which has been prepared from 3-*O*-benzyl-1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose through the sequence of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose, 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranose, and 3-*O*-benzyl-5-*O*-tosyl-1,2-*O*-isopropylidene-α-D-xylofuranose. The Michaelis-Arbuzov reaction of **1** with diethyl ethylphosphonite gave, in an 87% yield, 3-*O*-benzyl-5-deoxy-5-(ethoxyethylphosphinyl)-1,2-*O*-isopropylidene-α-D-xylofuranose (**2**) (bp 105—110°C/10^{-2}—10^{-3} mmHg, syrup, $[\alpha]^{14}_{D}$ −15.3° (*c* 3.9, chloroform)). The reduction of **2** with lithium aluminum hydride, followed by oxidation with air, afforded, in an 85% yield, 3-*O*-benzyl-5-deoxy-5-(ethylphosphinyl)-1,2-*O*-isopropylidene-α-D-xylofuranose (**3**) (bp 120—130°C/10^{-2}—10^{-3} mmHg, syrup, $[\alpha]^{15}_{D}$ −34.5° (*c* 4.6, chloroform)). The structure of **3** was established by studies of the PMR and IR spectra. The PMR spectrum (chloroform-*d*) showed a characteristic *J*(P–H) value[4] of 462 Hz at τ 3.1 (one-proton multiplet, disappearing upon the addition of D_2O). The IR spectrum showed the absorption of a P–H group at 2350 cm^{-1} and that of a P=O group at 1260 and 1220 cm^{-1}. The methanolysis of **3** in a methanol solution containing hydrochloric acid did not afford a methyl glycoside with phosphorus in the ring, but methyl 3-*O*-benzyl-5-deoxy-5-(ethylphosphinyl)-D-xylofuranoside (syrup) (**4**) in an 82% yield. The PMR spectrum (chloroform-*d*) showed a *J*(P–H) value of 462 Hz at τ 3.1 (one-proton multiplet, disappearing upon the addition of D_2O), and the IR spectrum showed the absorption of a P–H group at 2350 cm^{-1}. The structure of **4** was then identified as a methyl furanoside. On the hydrolysis of **3** in 50% aqueous methanol containing sulfuric acid (2 N), two major spots (R_f 0.70 and 0.55) and one minor spot (R_f 0.15) could be observed on a thin-layer chromatogram (chloroform-methanol, 5 : 1 v/v). The constitution of the two major components was about 1 : 1. The component **5**, with R_f 0.70, was easily separated, in a 45% yield, from the mixture by extraction with chloroform. The PMR spectrum (chloroform-*d*) showed a *J*(P–H) value of 462 Hz at τ 3.1 (one-proton multiplet, disappearing upon the addition of D_2O), and the IR spectrum showed the absorption of a P–H group at 2350 cm^{-1}. The component **5** was then identified as 3-*O*-benzyl-5-deoxy-5-(ethylphosphinyl)-D-xylofuranose (syrup). The component **6**, with R_f 0.55, was separated, in a 37% yield, by alumina-column chromatography (chloroform-methanol, 5 : 1 v/v). In the PMR (dimethyl sulfoxide-d_6) and IR spectra of **6**, the absorption showing the presence of a P–H group completely disappeared and the absorption of a one-proton multiplet at τ about 5 assigned to H-1 appeared. Moreover, by the treatment of **5** with 2 N sulfuric acid, half of the **5** was led to **6**. Therefore, **6** was identified as 3-*O*-benzyl-5-deoxy-5-(ethylphosphinyl)-D-xylopyranose (syrup, $[\alpha]^{11}_{D}$ −7.0° (*c* 2.6, methanol)).

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1) For example, H. Paulsen and K. Todt, *Advan. Carbohyd. Chem.*, **23**, 116 (1968).

2) R. L. Whistler and C.-C. Wang, *J. Org. Chem.*, **33**, 4455 (1968).

3) R. C. Young, P. W. Kent, and R. A. Dwek, *Tetrahedron*, **1970**, 3984.

4) H. R. Hays, *J. Org. Chem.*, **33**, 3690 (1968).