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Preliminary communication

Synthesis of a 6-nitro-D-glucopyranose having phosphorus in the hemiacetal ring

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The synthesis of sugar analogs[1] in which the ring-oxygen atom is replaced by a heteroatom is interesting, not only from the point of view of the chemistry, but also from that of the utility of the biological activities. Concerning sugar analogs having phosphorus in the hemiacetal ring, only a few reports[2] have been published; moreover, all of them discussed pentopyranose-type compounds prepared from 5-deoxy-5-halo derivatives *via* a Michaelis–Arbuzov reaction, reduction, and hydrolysis. We have now succeeded in the synthesis of a hexopyranose having phosphorus in the hemiacetal ring by using the addition reaction of a phosphine to an active olefinic sugar, namely, 3-*O*-acetyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-nitro-α-D-*xylo*-hex-5-enofuranose[3] (**1**).

Treatment of **1** with a large excess of phenylphosphine for 1 h at 40–50° afforded two major compounds (**2** and **3**), which were separated by column chromatography on silica gel. Compound **2** thus obtained was a syrup (63 % yield), but most of it was crystallized (by the addition of a small amount of methanol or ethanol) as colorless needles (**2a**); m.p. 105.5–106°, $[\alpha]^{29}_{D}$ −15.8° (*c* 1.14, methanol). The melting point did not change on several further recrystallizations. Optical circular dichroism measurements with **2a** showed it to be the D-*gluco* isomer[4]; $[\theta]_{296nm}$ −12,640 (trough) (*c* 0.2, methanol). In the p.m.r. spectrum (chloroform-*d*), a characteristic P–H peak was observed having a J_{P-H} value of 218 Hz at δ 4.38, and the i.r. spectrum (KBr) showed P–H absorption at 2280 and 2250 cm^{-1}, but no P=O group absorption was found. Treatment of **2a** in methanol with[5] an equivalent of H_2O_2 gave, almost quantitatively, the crystalline compound **4**; m.p. 169–171°, $[\alpha]^{24}_{D}$ −35.6° (*c* 1.35, methanol). The p.m.r. spectrum (chloroform-*d*) of **4** showed a characteristic J_{P-H} value of 520 Hz at δ 7.85; the absorption disappeared on deuteration. The i.r. spectrum (KBr) of **4** showed the absorption due to a P–H group at 2376 cm^{-1} and that due to a P=O group at 1210 cm^{-1}. These results indicated that compound **2a** was (3-*O*-acetyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-nitro-α-D-glucofuranose-5-yl)-

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