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Note

6-Deoxy-6-(dimethylphenylsilyl)-1,2:3,4-di-*O*-isopropylidene-β-L-altropyranose: Synthesis *via* hydrosilation, and reactivity

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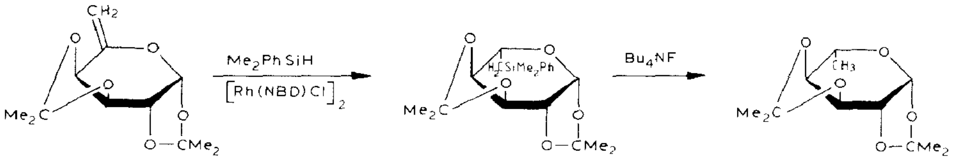
Hydrosilation of 5,6-unsaturated sugars is attractive as a method by which to prepare 6-*C*-silylated sugars. Such silylated sugars could serve as intermediates in reactions that exploit the unique reactivity of organosilanes, such as Petersen elimination[1] which we hoped would open the pyranose ring, providing a substrate suitable for chiral synthesis. We now report the hydrosilation of 6-deoxy-1,2:3,4-di-*O*-isopropylidene-β-L-*arabino*-hex-5-enopyranose (**1**), which is readily prepared from the corresponding 6-iodo-D-galactose derivative[2], to give 6-deoxy-6-(dimethylphenylsilyl)-1,2:3,4-di-*O*-isopropylidene-β-L-altropyranose (**2**). Compound **2** was formed in 70% yield when **1** was treated with dimethylphenylsilane and a catalytic amount of rhodium norbornadiene chloride. Some other catalysts, namely, oxygenobistriphenylphosphineplatinum(II), bistriethylphosphinediethylplatinum(II)[3], and norbornadienebistriphenylphosphinerhodium(I) hexafluorophosphate[4], resulted in formation of very little or no silylated product.



1 **2** **3**

A preliminary investigation into the chemistry of **2** involved its treatment with tetrabutylammonium fluoride in hexamethylphosphoramide (HMPA) which resulted in a 94% yield of **3**, the result of protiodesilylation. The ^{1}H-n.m.r. spectrum of **3** differs significantly, in chemical shifts and coupling constants, from that of 6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, which has now been reported twice[5]. However, the spectra of **3** and **2** are similar to that of 6-bromo-6-deoxy-1,2:3,4-di-*O*-isopropylidene-β-L-altropyranose, which Hall and co-

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workers[6] obtained, along with the isomeric α-D-galactopyranose derivative, by bromination of the hydroboration product from **1**, and it is on this basis that the configuration of **3**, and thus of **2**, are assigned. The *altro* configuration of **2** and **3** can be rationalized as the result of addition of H-Si to the side of **1** *anti* to O-1, which would be axial in a chair conformation, whereas addition to the other side, giving the *galacto* configuration, would be hindered by a *syn*-1,3-diaxial interaction with O-1.

EXPERIMENTAL

*6-Deoxy-6-(dimethylphenylsilyl)-1,2:3,4-di-*O*-isopropylidene-β-*L*-altropyranose* (**2**). — 6-Deoxy-1,2:3,4-di-*O*-isopropylidene-β-L-*arabino*-hex-5-enopyranose (**1**; 52 mg, 0.22 mmol), dimethylphenylsilane (0.65 mL, 4.3 mmol), and (norbornadiene)rhodium chloride dimer (1 mg, 4 μmol) were placed in a 5-mL round-bottomed flask equipped for reflux and having a dry nitrogen atmosphere. Preparation of **1** was achieved in 65% yield by treatment of commercial 6-deoxy-6-iodo-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose in Me_2SO with potassium *tert*-butoxide[2]. The reaction mixture was heated for 24 h at 80°, cooled, and evaporated under high vacuum (to remove volatile compounds), and the residue was chromatographed on silica gel (230–400 mesh) by eluting with 1:9 ether–pentane, to yield 56 mg (70%) of oily product; ^{1}H-n.m.r. data: δ 0.32 (s, 3 H, $SiCH_3$), 0.36 (s, 3 H, $SiCH_3$), 1.0 (m, 2 H, H-6), 1.31 (s, 3 H), 1.32 (s, 3 H), 1.37 (s, 3 H), 1.51 (s, 3 H), 3.13 (m, 1 H, H-5), 3.81 (dd, 1 H, $J_{4,5}$ 9.3, $J_{3,4}$ 5.4 Hz, H-4), 4.18 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-2), 4.47 (d, 1 H, $J_{3,4}$ 5.4 Hz, H-3), 5.05 (d, 1 H, $J_{1,2}$ 2.4 Hz, H-1), 7.3–7.4 (m, 3 H, Ph), and 7.5–7.6 (m, 2 H, Ph).

Anal. Calc. for $C_{20}H_{30}O_5Si$: C, 63.46; H, 7.99. Found: C, 63.41; H, 8.13.

*6-Deoxy-1,2:3,4-di-*O*-isopropylidene-β-*L*-altropyranose* (**3**). — A dry 5-mL round-bottomed flask fitted with a stirring bar, and maintained with a dry nitrogen atmosphere was first charged with 1.5 mL of M Bu_4NF in tetrahydrofuran (THF). The THF was removed under vacuum, 0.75 mL of HMPA was added, and then 63 mg (0.17 mmol) of **2** was added. The mixture was heated for 2 h at 75°, cooled, poured into ether (20 mL), successively washed with water (three times), 10% $NaHCO_3$ solution, and brine, dried (Na_2SO_4), evaporated, and the residue chromatographed on silica gel (230–400 mesh) by eluting with 1:9 ether–pentane, to give an oily product (40 mg, 94%); ^{1}H-n.m.r. data: δ 1.25 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6s), 1.33 (s, 3 H), 1.36 (s, 3 H), 1.42 (s, 3 H), 1.51 (s, 3 H), 3.27 (m, 1 H, H-5), 3.78 (dd, 1 H, $J_{4,5}$ 9.6, $J_{3,4}$ 5.4 Hz, H-4), 4.21 (d, 1 H, $J_{1,2}$ 2.1 Hz, H-2), 4.48 (d, 1 H, $J_{3,4}$ 5.4 Hz, H-3), and 5.21 (d, 1 H, $J_{1,2}$ 2.4 Hz, H-1); *m/z* (M^+) Calc.: 244.13095: Found: 244.1301.

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