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Preliminary communication

Stannane derivatives of carbohydrates

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As part of a general programme[1–3] to synthesize carbohydrate derivatives that are joined to a metal substituent, we now describe examples of two general routes to synthesize derivatives that have an organo-tin substituent attached to either a primary or a secondary carbon atom.

Primary *p*-toluenesulfonates are sufficiently reactive to be displaced by a tin-nucleophile. For example, 1,2:3,5-di-*O*-methylene-6-*O*-tosyl-α-D-glucofuranose[4] (**1**), in anhydrous tetrahydrofuran under dry nitrogen, reacted during 2 h at 20° with triphenyltin lithium[5] in anhydrous tetrahydrofuran to give, after processing, (1,2:3,5-di-*O*-methylene-α-D-glucofuranos-6-yl)triphenylstannane (**2**) as white granules, in 43% yield, m.p. 108–110° [from chloroform–light petroleum (b.p. 30–60°)], $[\alpha]_D^{25}$ + 60.0° (*c* 2.3, acetone)*.

Tin substituents can be easily attached to a secondary carbon atom by reaction of a suitably blocked epoxide with a tin nucleophile. Thus methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside (**3**), in dry tetrahydrofuran under dry nitrogen, reacted almost instantaneously at 20° with triphenyltin lithium; the reaction mixture was stirred for 1 h and then processed to give (methyl 4,6-*O*-benzylidene-α-D-altropyranoside-2-yl)-triphenylstannane (**4**) as a fine, colourless powder, yield 75%, m.p. 67–69° [from chloroform–light petroleum (b.p. 30–60°)], $[\alpha]_D^{25}$ + 5.9 (*c* 2.15, acetone).

In like fashion, methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside[7] (**5**) afforded (methyl 4,6-*O*-benzylidene-α-D-altropyranoside-3-yl)triphenylstannane (**6**) as a foamy syrup; this solidified under vacuum to give **6** in 94% yield, m.p. 166–168° [from toluene–light petroleum (b.p. 30–60°)], $[\alpha]_D^{25}$ + 91.0° (*c* 2, acetone).

The *vicinal* ^{1}H–^{1}H coupling constants of **6** ($J_{1,2}$ 4.0 Hz, $J_{2,3}$ 2.1 Hz, $J_{3,4}$ 5.9 Hz, and $J_{4,5}$ 8.8 Hz) are sufficiently different from those reported[8] for other derivatives of methyl 4,6-*O*-benzylidene-α-D-altropyranoside to suggest that **6** is distorted by the steric interactions of the triphenyltin moiety. This, and other aspects of *C*-stannyl sugars will be discussed elsewhere.

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*All derivatives reported here had elemental microanalyses and n.m.r. spectra in entire accord with the assigned structures.

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