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C-Stannylated carbohydrate derivatives. Part 1. 6-Deoxy-1,2-*O*-isopropylidene-6-(triorganostannyl)-α-D-glucofuranose#

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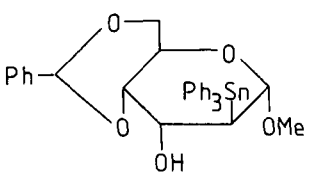
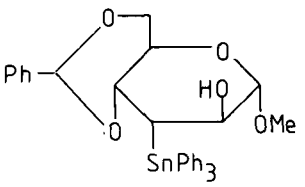
Abstract. The synthesis of 6-deoxy-1,2-*O*-isopropylidene-6-(triorganostannyl)-α-D-glucofuranose (**4**) is reported. Compound **4a** (R = R′ = Me), reacts with halogens (I_2 and Br_2) or with $Pd(COD)Cl_2$ to give **4** (R = Me, R = X (X = I, Br or Cl) and MeY [Y = I, Br or Pd(CODCl]. The unsaturated sugar, 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose (**6**) is formed in the reaction of **4a**(-R = R′ = Me) with CF_3CO_2H, ClC(O)Z (Z = Ph, Me or OEt), SO_2 or $(NC)_2C{=}C(CN)_2$.
Phenyl–tin bond cleavage is the predominant, if not sole, reaction of **4b** (R = R′ = Ph) with CF_3CO_2H or I_2.

Introduction

Various stannylated compounds are known[1], including compounds containing organotin and carbohydrate moieties[2]. In the majority of these compounds, the organotin unit is bound to the sugar via oxygen[3]. Only a few compounds have been reported with tin bound to a carbon of the sugar[4]; some examples of these species are **1–3**.



(1)[4]

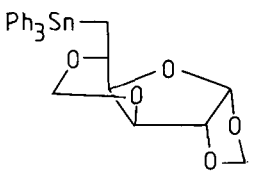


(2)[4]

We have begun a study of tin–carbon-bonded carbohydrate molecules and now wish to report the syntheses and reactions of 6-deoxy-1,2-*O*-isopropylidene-6-(triorganostannyl)-α-D-glucofuranose compounds (**4**).

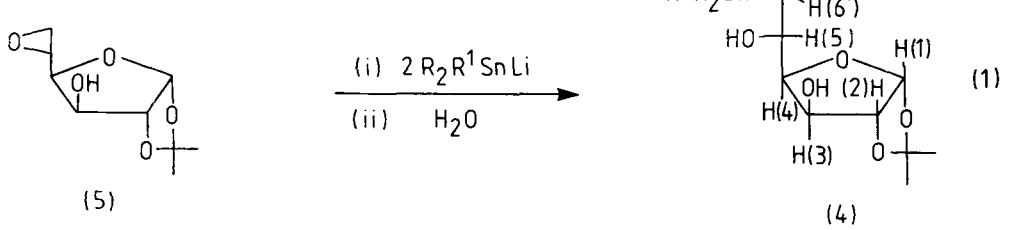
Results and discussion

The two stannyl derivatives 4a (R = R′ = Me) and 4b (R = R′ = Ph) were readily obtained from reactions of $R_2R'SnLi$ with the epoxy-substituted sugar **5** (Eqn. 1). A pH-6.6 buffer solution had to be used in the hydrolysis step in order to prevent decomposition of **4**. Compounds **4** were unstable both at high and low pH, **4b** (R = R′ = Ph) being more sensitive. The two compounds were however stable to air and moisture and to at least 100°C.



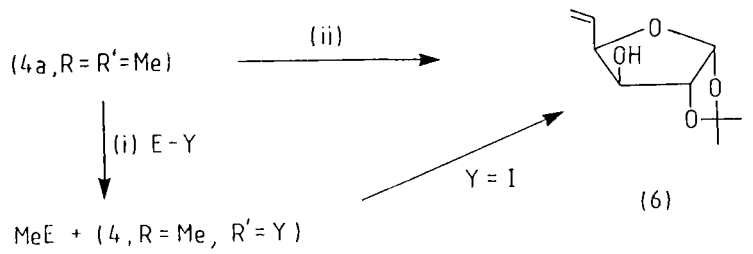
(3)[4]

The stannyl derivatives were considered to have potential both as precursors of other sugar compounds and as con-



(5) (4) (1)

Dedicated to Prof. *G. J. M. van der Kerk* on the occasion of his 75th birthday.



Reagents: *(i)* E–Y = Br–Br, I–I or Cl–Pd(COD)Cl;
(ii) R″COCl(R″ = Me or Ph), CF_3CO_2H, Cl–CO_2Et, SO_2 or $(NC)_2C{=}C(CN)_2$.

Scheme 1

trolled sources (via elimination reactions) of triorganotin species. For these reasons, a series of reactions of **4a** (R = R′ = Me) were carried out with a number of reagents, including electrophiles (covering a wide range of reactivities), an electron acceptor and transmetalling agents. Two distinct types of reaction were realized: *(i)* cleavage of a Me–Sn bond and *(ii)* formation of the unsaturated sugar, 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose (**6**) via a β-elimination reaction. Compound **6** has been obtained[5] from 1,2-*O*-isopropylidene-α-D-glucofuranose (**7**) via its cyclic 5,6-carbonothioate derivative as well as from 1,2-*O*-isopropylidene-5,6-bis(4-methylbenzenesulphonyloxy)-α-D-glucofuranose and NaI.

The halogens, Br_2 and I_2, lead to cleavage of a Me–Sn bond in **4a** (R = R′ = Me). While the Br_2 reaction occurs quantitatively at −10°C, the 1:1 reaction with I_2 at *ca.* 20°C apparently also produced a little **6**. However, the cleavage product **4c** (R = Me, R′ = I) was shown to be unstable in solution at 20°C and to slowly decompose over a period of days to **6** and formally [$Me_2Sn(OH)I$]. Thus the small amount of **6** initially detected in the reaction of **4a** (R = R′ = Me) and I_2 need not have arisen directly.

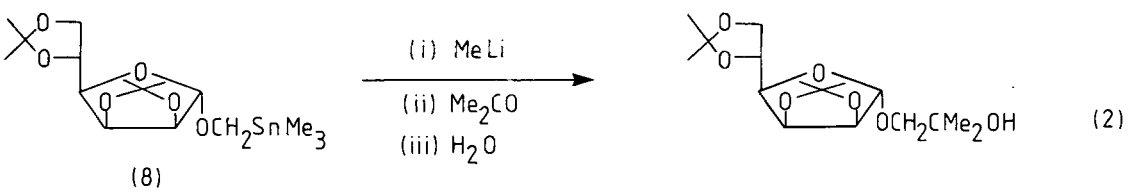
The species **4d** (R = Me, R′ = Br) reacts with 1 equivalent of Br_2; however the reaction is not clean as shown by three different chemical shift values for H(1) in the ^{1}H NMR spectrum. The major sugar products are **4e** (R = Br, R′ = Me) [δ 1.35, s, 3, Me–Sn, $J(^{119}Sn-^1H)$ 58 Hz); 2.40–2.15, m, 2H, H(6) + H(6′)] and **6**.

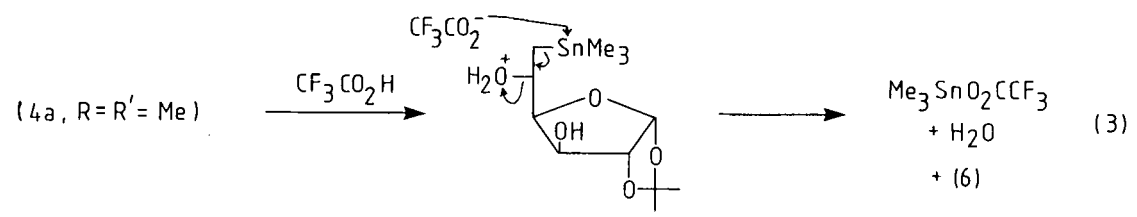
Route *(i)* in Scheme 1 was also followed in the $Pd(COD)Cl_2$ reaction which produced **4f** (R = Me, R′ = Cl) and MePd(COD)Cl. The product **4f** (R = Me, R′ = Cl) remained unchanged in solution for several days, and is considerably more stable in solution than the iodide analogue. In contrast to this reaction, methylation of $Pd(COD)Cl_2$ by Me_2CuLi or MeLi provides the dimethylated product, $Me_2Pd(COD)$. Attempts to limit the methylation to the mono-stage using Me_2CuLi did not succeed.

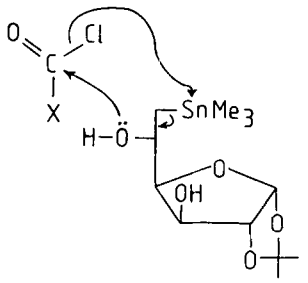
From the substitution reactions of **4a** (R = R′ = Me) it is clear that the Me group is transferred in preference to the sugar unit and hence, disappointingly, a Pd-catalysed reaction of an organic halide or ester with **4** is unlikely to yield a cross-coupled product containing the carbohydrate unit.

Treatment of **4a** (R = R′ = Me) with MeLi (4 equivalents) at −64°C, followed by the addition of PhCHO led after hydrolysis to the recovery of **4a** in 72% yield and the isolation of PhCH(OH)Me. Again transfer of the sugar unit from **4** from Sn to Li did not occur. If any exchange took place, it must have involved the Me groups, with no net change in the reagents, MeLi then reacting with the added PhCHO. There have been several reports of the transfer of alkoxyalkyl groups (especially in α- but also in γ-positions) from tin to lithium in transmetallation reactions involving alkyllithiums and alkyl(alkoxyalkyl)Sn compounds[7]. Indeed the reaction of **8** with MeLi did lead[8] to transfer of the sugar unit (Eqn. 2).

The unsaturated sugar **6** was obtained from **4a**(R = R′ = Me) on reaction with the following electrophilic species: CF_3CO_2H, RC(O)Cl (R = Me or Ph), $ClCO_2$Et and SO_2. The trifluoroacetic acid reaction is particularly fast and probably occurs via protonation of the β-OH group (Eqn. 3). A concerted reaction, which must occur with RC(O)Cl or $ClCO_2R$ (Eqn. 4), is also a possibility.







$$\longrightarrow \quad Me_3SnCl + HO-\overset{\overset{O}{\|}}{C}-X + (6) \qquad (4)$$

X ▫ Ph, Me or OEt

Acyl chlorides [like RO–C(O)Cl] are weak electrophiles and do not generally react with organotins, unless activated by a strong *Lewis* acid. Sulphur dioxide is a more powerful electrophilic reagent, and its insertions into tin–carbon bonds are well-known[9]. The trimethyltin product of the SO_2 reaction has a chemical shift value in the ^1H NMR spectrum of 0.50 with $J(^{119}Sn-^1H)$ 62.4 Hz. The initial Me_3Sn product will be $Me_3SnOS(O)OH$ but this will change to $(Me_3SnO)_2SO$ and $(Me_3SnO)_2SO_2$, especially as oxygen was not excluded.

All these β-elimination reactions of **4a** are with reagents able to interact with the β-OH group. β-Elimination reactions involving organotin compounds have been variously reported, *e.g.* with such β-substituents[10], NR_2, SR and PR_2 as well as the OH group.

The reaction of tetracyanoethene (TCNE) with **4a** (R = R′ = Me) has a parallel with its initial reaction[11] with $Ph_3SnCH_2CH_2SAr$ (Eqn. 5), which proceeds via a charge-transfer complex and an electron-transfer step. The proposed course of the TCNE reaction is given in Scheme 2.

$$(4a, R = R' = Me) \xrightarrow{TCNE} [Me_3SnCH_2\overset{*}{C}HROH, TCNE]$$

$$[Me_3SnCH_2\overset{*}{C}HROH, TCNE^{\cdot-}] \xrightarrow{-TCNE} Me_3SnOH + (6)$$

Scheme 2. R = sugar residue.*

The Me_3Sn signal in the ^1H NMR spectra was broad, due to interaction with $TCNE^{-\cdot}$; treatment with water destroyed the radical anion and led to sharpened Me_3SnOH signals. Other reported interactions of TCNE with organotin compounds include stable charge-transfer complexes as well as insertions into carbon–tin bonds[11].

$$Ph_3SnCH_2CH_2SAr \xrightarrow{TCNE} [Ph_3SnSAr] + CH_2=CH_2 \qquad (5)$$

Both the $SnCl_4$ and $ClSO_3H$ reactions with **4a** (R = R′ = Me) led to considerable amounts of decomposition of the sugar moiety; no sugar derivatives could be identified.

In addition to the reactions of **4a** (R = R′ = Me), a few reactions of **4b** (R = R′ = Ph) were carried out. Some differences between **4a** (R = R′ = Me) and **4b** (R = R′ = Ph) were realized in keeping with the increased reactivity of a Ph–Sn bond over an alkyl–tin bond[1]. In contrast to the reaction of **4a** (R = R′ = Me) with CF_3CO_2H, which gave **6** and $Me_3SnO_2CCF_3$, that of **4b** (R = R′ = Ph) produced mainly PhH and **4g** (R = Ph, R′ = O_2CCF_3); however this substitution product was unstable and decomposed completely over 4 days at 20°C to **6**, an insoluble material $[PhSn(O)O_2CCF_3]_n$ [ν(CO) 1630 cm^{-1}] and a further equivalent of PhH (Scheme 3). It is of interest that the decomposition of **4g** (R = Ph, R′ = O_2CCF_3) involved a phenyl–tin cleavage. A little **6** was also detected in the early stages of the reaction but this could have arisen from the decomposition of **4g** (R = Ph, R = O_2CCF_3) rather than being formed directly.

With I_2, Ph–Sn cleavage of **4b** (R = R′ = Ph) resulted (Eqn. 6); the initial product **4h** (R = Ph, R′ = I) is much more stable in solution than is **4c** (R = Me, R′ = I).

$$\textbf{4b}\ (R = R' = Ph) \xrightarrow{I_2} \textbf{4h}\ (R = Ph, R' = I) + PhI \qquad (6)$$

Experimental

Melting points were uncorrected. ^1H NMR spectra were recorded on a Perkin Elmer R34 (220 MHz) spectrometer. Mass spectra were obtained using an AEI MS 30 instrument; *m*, based on ^{120}Sn. Tetrahydrofuran was dried over $LiAlH_4$. Table I lists the ^1H NMR spectral data for products **4**.

1,2,5,6-Di-*O*-isopropylidene-α-D-glucofuranose, prepared from D-glucose using a standard procedure[12], was partially deprotected on treatment with 0.8% H_2SO_4 in MeOH to 1,2-*O*-isopropylidene-α-D-glucofuranose **7**. Treatment of **7** with tosyl chloride and pyridine in $CHCl_3$, followed by sodium methoxide gave[13] the epoxide, 5,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose **5**.

*6-Deoxy-1,2-O-isopropylidene-6-(trimethylstannyl)-α-D-glucofuranose (**4a**, R = R′ = Me)*

Lithium wire (1.95 g) was extruded directly into a flask containing THF 20 ml). After cooling to 0°C, a solution of Me_3SnCl (5.58 g, 0.028 mol) in THF (25 ml) was added dropwise under nitrogen. The green reaction mixture was stirred for $3\frac{1}{2}$ h (with the occasional use also of an ultrasonic bath). After cooling to −74°C, a solution of **5** (2.02 g, 0.010 mol) in THF (15 ml) was slowly added. The mixture was allowed to warm-up to room temperature overnight and then was filtered through glass wool, to remove excess

$$(4b, R = R' = Ph) + CF_3CO_2H \xrightarrow[fast]{-PhH} (4g, R = Ph, R' = O_2CCF_3)$$

$$(4g, R = Ph, R' = O_2CCF_3) \xrightarrow[slow]{-(6)} [Ph_2Sn(OH)O_2CCF_3]$$

$$[Ph_2Sn(OH)O_2CCF_3] \longrightarrow PhH + {}^1/_n[PhSn(O)O_2CCF_3]_n$$

Scheme 3

Table I ^1H *NMR spectral data for* **4** *in* $CDCl_3$ *solution.*

R/R′	δ										
	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(6′)	OH at C(5)	OH at C(3)	CMe_2	$R_2R'Sn$
Me/Me	5.97 *J*(1)–*J*(2) 3.6	4.51 *J*(2)–*J*(3) 0	4.35 *J*(3)–*J*(4) 2.5	3.94 *J*(4)–*J*(5) 2.5	4.30 *J*(5)–*J*(6) 9.0 *J*(5)–*J*(6′) 7.3	1.24 *J*(6)–*J*(6′) 13.4	1.12	4.36(s)	2.77(s)	1.46 and 1.30	0.13 *J*(^{119}Sn–^{1}H) 53.8 Hz
Me/Br	5.78 *J*(1)–*J*(2) 3.6	4.51 *J*(2) – *J*(3) 0	4.34 *J*(3)–*J*(4) 2.7	3.89 *J*(4)–*J*(5) 8.2	4.18 *J*(5)–*J*(6) 5.4 *J*(5)–*J*(6′) 11.7	1.86 *J*(6)–*J*(6′) 11.7	1.68	3.18 (d)	2.68 (br)	1.46 and 1.29	0.79 *J*(^{119}Sn–^{1}H) 61.0 Hz
Me/I	5.82 *J*(1)–*J*(2) 3.0	4.51 *J*(2)–*J*(3) 0	4.36 *J*(3)–*J*(4) 2.7	3.91 *J*(4)–*J*(5) 8.0	4.20 *J*(5)–*J*(6) 5.6 *J*(5)–*J*(6′) 11.5	1.95 *J*(6)–*J*(6′) 11.5	1.76	3.34 (br)	2.83 (br)	1.46 and 1.29	0.92 *J*(^{119}Sn–^{1}H) 61.0 Hz
Me/Cl in CD_2Cl_2	5.80 *J*(1)–*J*(2) 3.0	4.54 *J*(2)–*J*(3) 0	4.35 *J*(3)–*J*(4) 2.9	3.88 *J*(4)–*J*(5) 9.3	4.16 *J*(5)–*J*(6) 6.1 *J*(5)–*J*(6′) 12.5	1.71 *J*(6)–*J*(6′) 12.5	1.65	3.47 (br)	3,07 (br)	1.46 and 1.30	0.66 *J*(^{119}Sn–^{1}H) 63.5 Hz
Ph/Ph	5.94 *J*(1)–*J*(2) 3.6	4.50 *J*(2)–*J*(3) 0	4.45[a]	4.06[a]	4.45[a]	1.90[a]	1.82[a]	4.20 (d)	2.93 (br)	1.41 and 1.29	7.58(m) *o*-protons 7.37(m) *m*-protons
Ph/ O_2CCF_3	5.42 *J*(1)–*J*(2) 2.8	4.36 *J*(2)–*J*(3) 0	4.36 *J*(3)–*J*(4) 2.8	4.10[a]	4.60 *J*(5)–*J*(6′) 4.9 *J*(5)–*J*(6′) 12.2	2.24 *J*(6)–*J*(6′) 12.2	2.05	3.20		1.19 and 1.13	7.55(m) *o*-protons 7.34 *m*-protons
Ph/I	5.73 *J*(1)–*J*(2) 3.2	4.42 *J*(2)–*J*(3) 0	4.35 *J*(3)–*J*(4) 2.7	4.00 *J*(4)–*J*(5) 6.6	4.40 *J*(5)–*J*(6) 7.3 *J*(5)–*J*(6′) 8.6	2.27 *J*(6)–*J*(6′) 13.2	2.14	3.32 (d)	3.13 (br)	1.31 and 1.21	7.67(m) *o*-protons 7.36 *m*-protons
(3) [b,c] (C_6D_6)	5.86 *J*(1)–*J*(2) 3.8	4.25 *J*(2)–*J*(3) 0	3.95 *J*(3)–*J*(4) 2.4	3.68 *J*(4)–*J*(5) 2.3	4.41 *J*(5)–*J*(6) 11.3 *J*(5)–*J*(6′) 6.1	1.63 *J*(6)–*J*(6′) 13.3	1.32				7.67(m) *o*-protons 7.67(m) *m*-/*p*-protons

[a] Coupling unresolved. [b] Ref. 4a. [c] $-O-CH_2-O-$: δ ^1H 4.69 and 4.40.

lithium, into an aqueous buffer solution at pH 6.6 (600 ml). The product was extracted with CH_2Cl_2 (3 × 150 ml); the combined organic fractions were dried over $MgSO_4$ and the solvent removed by rotatory evaporation. The residue was chromatographed on a chromatotron using hexane/Et_2O as the eluant. Recrystallisation of the crude product (3.40 g) from hexane gave pure **4a** (R = R′ = Me), 2.91 g, m.p. 91.5–92.5°C. $C_{12}H_{24}O_5Sn$ calcd.: C 39.3, H 6.6; found: C 39.2, H 6.6%. ^{1}H NMR data are given in the Table. MS (20 eV) *m/z* (%, fragment): 353 (1, M^+ – Me), 277 (5, $M^+ - Me_2CO - H_2O$ – Me); 219 (12), 165 (75, Me_3Sn^+); 150 (8, Me_2Sn^+); 135 (20, $MeSn^+$).

In a similar manner, 6-deoxy-1,2-*O*-isopropylidene-6-(triphenylstannyl)-α-D-glucofuranose (**4b**, R = R′ = Ph) was prepared from Ph_3SnLi and **5**; m.p. 172–176°C. $C_{27}H_{30}O_5Sn$ calcd.: C 58.6, H 5.5; found: C 59.1, H 5.6%. ^{1}H NMR data are given in the Table.

Reactions of **4** *(R = R′ = Me)*

^{1}H NMR spectral data for tin products **4** are listed in the Table.

With trifluoroacetic acid. To a solution of **4a** (R = R′ = Me) (28.7 mg, 7.83 × 10^{-5} mol) in $CDCl_3$ (0.5 ml) was added CF_3CO_2H (6.0 µl, 7.83 × 10^{-5} mol). Reaction occurred immediately, as shown by ^{1}H NMR, to form quantitatively $Me_3SnOCOCF_3$ [^{1}H NMR: δ 0.65 [s, 9H, $J(^{119}Sn-^1H)$ 61.0 Hz]] and 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose (**6**). ^{1}H NMR ($CDCl_3$): δ 5.92, d, 1H, H(1), J[H(1)–H(2)] 4.6 Hz; 5.86, m, 1H, H(5), J[H(4)–H(5)] 5 Hz, J[H(5)–H(6)] 18.3 Hz, J[H(5)–H(6′)], 12.2 Hz; 5.52, d, t, 1H, H(6), J[H(6)–H(5)] 18.3 Hz, J[H(6)–H(6′)] = J[H(4)–H(6)] ≈ 1.5 Hz; 5.39, d, t, 1H, H(6′), J[H(6′)–H(5)] 12.2 Hz, J[H(6)–H(6′)] = J[H(4)–H(6′)] 1.5 Hz; 4.71, broad s, 1H, H(4); 4.54, d, 1H, H(2), J[H(1)–H(2)] 4.6 Hz; 4.07, d, 1H, H(3), J[H(33–H(4)], 2.5 Hz; 2.67, s, 3H, OH + H_2O; 1.48, s, 3H, CMe_2; 1.30, s, 3H, CMe_2.

With bromine. To a solution of **4a** (R = R′ = Me) (28.7 mg, 7.83 × 10^{-5} mol) in $CDCl_3$ (0.5 ml) at −10°C was added dropwise bromine (4.0 µl, 7.83 × 10^{-5} mol). Reaction was indicated by the decolourization of the bromine and gave MeBr (^{1}H NMR: δ 2.62, s) and **4d** (R = Me, R′ = Br).

With iodine. Iodine (20.0 mg, 7.88 × 10^{-5} mol) was added to a solution of **4a** (R = R′ = Me) (28.9 mg, 7.88 × 10^{-5} mol) in $CDCl_3$ (0.5 ml) at room temperature. Reaction was complete within 15 min and produced MeI (^{1}H NMR: δ 2.13, s) and **4c** (R = Me, R′ = I).

Compound **4c** (R = Me, R′ = I) slowly decomposed in $CDCl_3$ solution to the unsaturated sugar **6**.

With tetrachlorostannane. Tetrachlorostannane (9.2 µl, 7.83 × 10^{-5} mol) was added to a solution of **4a** (R = R′ = Me) (28.7 mg, 7.83 × 10^{-5} mol) in $CDCl_3$ (0.5 ml). A white precipitate formed immediately. After centrifuging the reaction mixture, the supernatant layer was shown by ^{1}H NMR to contain Me_3SnCl [δ 0.66, $J(^{119}Sn-^1H)$ 57.2 Hz] and acetone (δ 2.17). The residue was dissolved in acetone-d_6 and was found to contain a mixture of several sugars.

With acetyl chloride. To a solution of **4a** (R = R′ = Me) (28.9 mg, 7.88 × 10^{-5} mol) in $CDCl_3$ (0.5 mol) was added MeCOCl (5.6 µl, 7.88 × 10^{-5} mol). The reaction mixture was left for 16 h. ^{1}H NMR spectrocopy indicated the quantitative formation of Me_3SnCl [δ 0.65, s, $J(^{119}Sn-^1H)$ 57.3 Hz], **6** and $MeCO_2H$ (δ 2.06, s, 3H, Me); 2.20, s, 2H, OH from **6** and H from $MeCO_2\underline{H}$.

With benzoyl chloride. Benzoyl chloride (9.3 µl, 7.88 × 10^{-5} mol) was added to a solution of **4a**, (R = R′ = Me) (28.9 mg, 7.88 × 10^{-5} mol) in $CDCl_3$ (0.5 ml). The reaction was complete after 14 d; the products were **6**, Me_3SnCl and $PhCO_2H$ (^{1}H NMR: δ 8.14, d, 2H, *J* 7.4 Hz; 7.66, t, 1H, *J* 7.4 Hz; 7.52, t, 2H, *J* 7.4 Hz; 2.25, broad s, 2H, OH from **6**, H from $PhCO_2H$).

With ethyl carbonochloridate. To a solution of **4a** (R = R′ = Me) (28.9 mg, 7.88 × 10^{-5} mol) in $CDCl_3$ (0.5 ml) was added $ClCO_2Et$ (7.5 µl, 7.88 × 10^{-5} mol). After 11 days at room temperature reaction was only 50% complete with formation of **6** and Me_3SnCl.

With sulphur dioxide. A SO_2-saturated solution of $CDCl_3$ (0.4 ml) was added to a solution of **4a** (R = R′ = Me) (28.9 mg, 7.88 × 10^{-5} mol) in $CDCl_3$ (0.1 ml). ^{1}H NMR spectroscopy indicated the immediate formation of **6** (δ 2.28, OH) and a trimethyltin compound [δ 0.50, $J(^{119}Sn-^1H)$ 62.4 Hz)].

With tetracyanoethene. Tetracyanoethene (9.9 mg, 7.74 × 10^{-5} mol) was added to a solution of **4a** (R = R′ = Me) (28.4 mg, 7.74 × 10^{-5} mol) in CD_2Cl_2 (0.5 ml). After 1½ h, the ^{1}H NMR spectra of the yellow solution indicated the formation of **6** [δ 3.89 (OH)] and a trimethyltin species [δ 0.76, broad s, $J(^{119}Sn-^1H)$ 62.8 Hz; 1.99, broazd s, OH]. Addition of D_2O resulted in sharpening of the Me_3Sn peak and change in δ (0.66) as well as removal of absorption at δ 1.99.

6. ^{1}H NMR of (CD_2Cl_2): δ 5.88, d, 1H, H(1), J[H(1)–H(2)] 4.9 Hz; 5.88, m, 1H, H(5), J[H(5)–H(6)] 12.2 Hz, J[H(5)–H(6′)] 17.1 Hz, J[H(4)–H(5)] 5.1 Hz; 5.48, d, t, 1H, H(6′), J[H(5)–H(6′)] 17.1 Hz, J[H(6)–H(6′)] = J[H(4)–H(6′)] ≃ 1.5 Hz; 5.37, d, t, 1H, H(6), J[H(5)–H(6)] 12.2 Hz, J[H(6)–H(6′)] = J[H(4)–H(6)] ≃ 1.5 Hz; 4.67, broad m, 1H, H(4), J[H(3)–H(4)] ≃ 2 Hz, J[H(4)–H(5)] 5.1 Hz; 4.53, d, 1H, H(2), J[H(1)–H(2)] 5.1 Hz; 4.06, d, 1H, H(3), J[H(3)–H(4)] ≃ 2 Hz; 3.89, s, 1H, OH; 1.46, s, CMe_2; 1.30, s, CMe_2.

With dichloro[(1,2,5,6-η)-1,5-cyclooctadiene]palladium, Pd(COD)Cl_2. To a solution of **4a**(R = R′ = Me) (27.4 mg, 7.47 × 10^{-5} mol) in CD_2Cl_2 (0.5 ml) was added $Pd(COD)Cl_2$ (21.3 mg, 7.47 × 10^{-5} mol). After 2 days, the solution was colourless with a slight precipitation of black metallic Pd; ^{1}H NMR spectroscopy revealed the presence of MePd(COD)Cl and **4f** (R = Me, R′ = Cl). MePd(COD)Cl. ^{1}H NMR (CD_2Cl_2): δ 5.80, broad, m, 2H; 5.13, broad, m, 2H; 2.56, broad m, 4H; 2.46, broad, m, 4H (all COD); 1.08, s, 3H, Me. Lit.[6] ^{1}H NMR (CCl_4): δ 5.85, m, 2H; 5.00, m, 2H; 2.50, m, 8H; 0.86, s, 3H, Me. Lit.[6] ^{1}H NMR (PhH): δ 5.50, m, 2H; 4.10, m, 2H; 1.35, m, 8H; 1.00, s, 3H, Me.

With chlorosulphuric acid. Chlorosulphuric acid (5.2 µl, 7.88 × 10^{-5} mol) was added to a solution of **4a** (R = R′ = Me) (28.9 mg, 7.88 × 10^{-5} mol) in $CDCl_3$ (0.5 mol) at −10°C. The reaction mixture was maintained at −10°C for 30 min. Considerable charring occurred with the formation of a dark solid. The decanted colourless supernatant liquid was shown by ^{1}H NMR spectroscopy to contain Me_3SnCl [δ 0.64, s, $J(^{119}Sn-^1H)$ 59.7 Hz] and acetone (δ 2.15, s).

With methyllithium. To a solution of **4a** (R = R′ = Me) (169 mg, 4.60 × 10^{-4} mol) in sodium-dried ether (5 ml) at −64°C under N_2, was added methyllithium (4 equivs. 1.84 × 10^{-3} mol, 1.23 ml of a 1.5 M solution in ether) by syringe. The reaction mixture was stirred at −64°C for 1 h. A white precipitate was formed which disappeared on the addition of PhCHO (0.19 ml, 1.84 × 10^{-3} mol). The reaction mixture was allowed to reach room temperature overnight, hydrolyzed using a pH-6.6 buffer solution, extracted with chloroform (3 × 15 ml) and dried over $MgSO_4$. The solvent was removed and the residue chromatographed using the chromatotron. This led to the isolation of **4a** (R = R′ = Me) (121 mg, 72%) and PhCH(Me)OH (129 mg, 57%). ^{1}H NMR (220 MHz, $CDCl_3$): δ 7.35, m, 5H, C_6H_5; 4.86, q, 1H, CH, *J* 7.5 Hz; 1.87, broad s, 1H, OH; 1.45, d, 3H, CH_3.

Reactions of **4b** *(R = R′ = Ph)*

With trifluoroacetic acid. To a solution of **4b** (R = R′ = Ph) (27.9 mg, 5.04 × 10^{-5} mol) in $CDCl_3$ (0.5 ml) was added CF_3CO_2H (3.9 µl, 5.04 × 10^{-5} mol). The reaction was immediate; ^{1}H NMR spectra indicated the formation of PhH (δ 7.37 ppm), the substitution product (4 g, R = Ph, R′ = $OCOCF_3$) and a little of the unsaturated sugar **6**.

The substitution product (4 g, R = Ph, R′ = $OCOCF_3$) decomposed in solution over 4 days to **6**, PhH and a white solid [IR (KBr): ν(CO) 1630 cm^{-1}].

With iodine. To a solution of **4b** (R = R′ = Ph) (29.5 mg, 5.33 × 10^{-5} mol) in $CDCl_3$ (0.5 ml) was added I_2 (13.5 mg, 5.33 × 10^{-5} mol) at room temperature. After decolourisation, ^{1}H NMR spectra indicated the quantitative formation of PhI and **4h** (R = Ph, R′ = I).

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