C-Stannylated Carbohydrate Derivatives, Part 5.† 1,2:5,6-Di-*O*-isopropylidene-3-*C*-(organostannyl)- and -3-*C*-(phenylstannyl)methyl-α-D-allofuranose Compounds. X-Ray Crystal and Molecular Structure of 1,2:5,6-Di-*O*-isopropylidene-3-*C*-(triphenylstannylmethyl)-α-D-allofuranose

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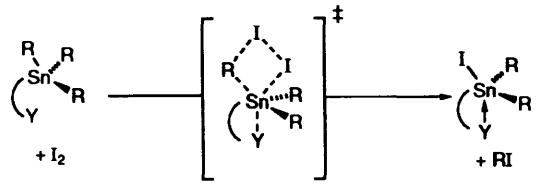
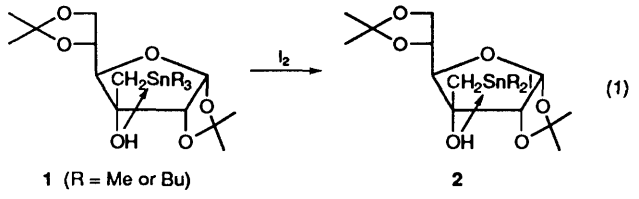
The crystal structure and the solid state (^{13}C and ^{119}Sn) and solution (^{1}H, ^{13}C and ^{119}Sn) NMR spectra of 1,2:5,6-di-*O*-isopropylidene-3-*C*-triphenylstannylmethyl-α-D-allofuranose (**1**; R = Ph) have been obtained. The structure of compound (**1**; R = Ph) is similar in both phases and contains a slightly distorted tetrahedral tin atom [C–Sn–C valency angles range from 103.8(3) to 114.9(5)°]. The β-oxygen atom at C(3) in compound (**1**; R = Ph) is 3.01(1) Å distant from Sn and is ideally sited to take part in nucleophilic assistance during Ph–Sn bond-cleavage reactions. Reactions of compound (**1**; R = Ph) and 1,2:5,6-di-*O*-isopropylidene-3-*C*-R_3Sn-α-D-allofuranose with electrophiles (*e.g.*, I_2 or CF_3CO_2H) are also reported.

A number of stannyl carbohydrate derivatives have been studied. These include compounds having β-hydroxyalkylstannyl fragments;[1,2] among the reactions studied for these compounds have been tin–carbon bond cleavages and β-eliminations. The reactivities of tin–carbon bonds towards electrophiles (*e.g.*, I_2) can be enhanced on nucleophilic assistance[3,4] by neighbouring donor groups (Y), see Scheme 1.



Scheme 1

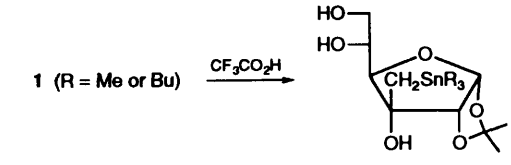
This appears to be the case for 1,2:5,6-di-*O*-isopropylidene-3-*C*-(trialkylstannylmethyl)-α-D-allofuranoses (**1**; R = Me or Bu) which undergo a more ready R–Sn bond cleavage than does R_4Sn [eqn. (1)]. The product of this reaction was shown

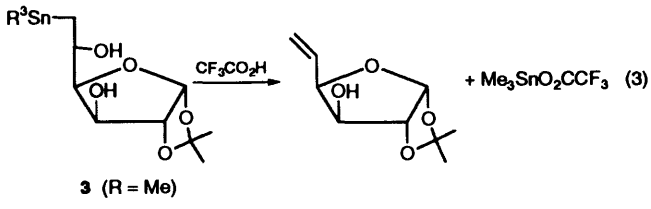


1 (R = Me or Bu) **2**

by NMR spectroscopy [for (**2**; R = Me)] and by X-ray crystallography [for (**2**; R = Bu)] to contain 5-coordinate-tin, as a result of Sn ← OH intramolecular coordination. For maximum nucleophilic assistance, it has been stated that the participating group should be able to approach[4] the tin centre *trans*-axially to the leaving group.

For β-elimination, the stereochemistry of the β-hydroxyalkylstannyl fragment must also play an important role; the reaction of F_3CCO_2H with compound (**1**; R = Me) occurs at the O^5–O^6 isopropylidene group in contrast to the ready β-elimination reaction with another stannyl-sugar (**3**) which



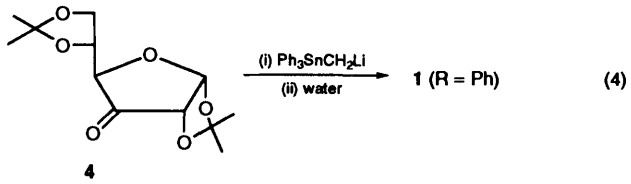


3 (R = Me)

contains an acyclic β-hydroxyalkylstannyl unit, eqns. (2) and (3). To confirm the spatial arrangements of the β-HO and R_3Sn units in compound **1** an X-ray crystallographic study of a compound **1** was undertaken; suitable crystals were grown for (**1**; R = Ph). The results of this study are now reported, as are some reactions and spectral data for compound (**1**; R = Ph) and related compounds.

Results and Discussion

Compound (**1**; R = Ph) was produced from Ph_3SnCH_2Li [prepared *in situ* from Ph_3SnCH_2I and BuLi] and 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose **4**, obtained from D-glucose[5] [eqn. (4)]; only the allose addition product of Ph_3SnCH_2Li was obtained.



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Crystal Structure of Compound **1** (R = Ph).—A suitable crystal for X-ray crystallography was obtained after recrystallisation from hexane. Single-crystal data are consistent with the atomic arrangements in Fig. 1; the cell content is shown in Fig. 2. The bond lengths and valency angles in Table 1. The

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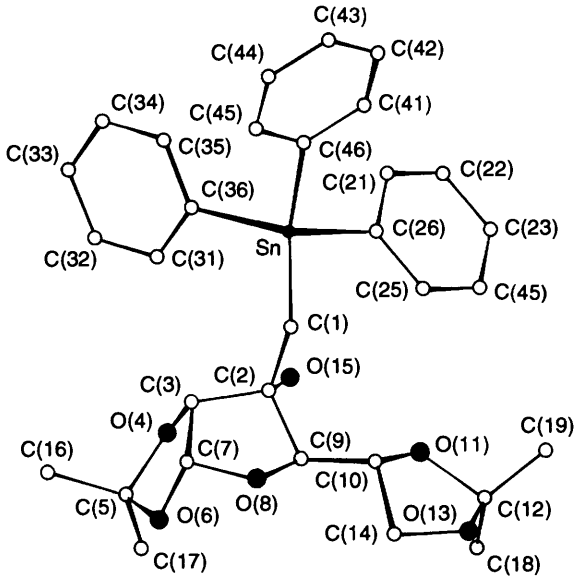


Fig. 1

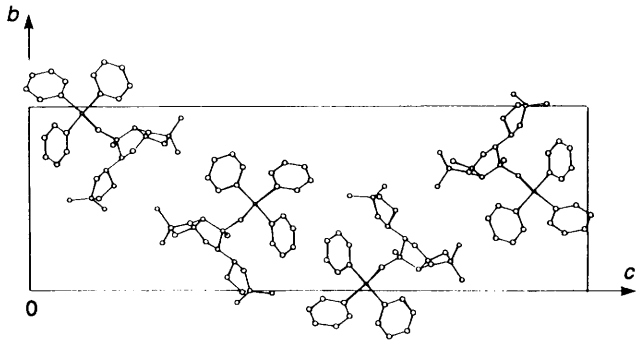


Fig. 2

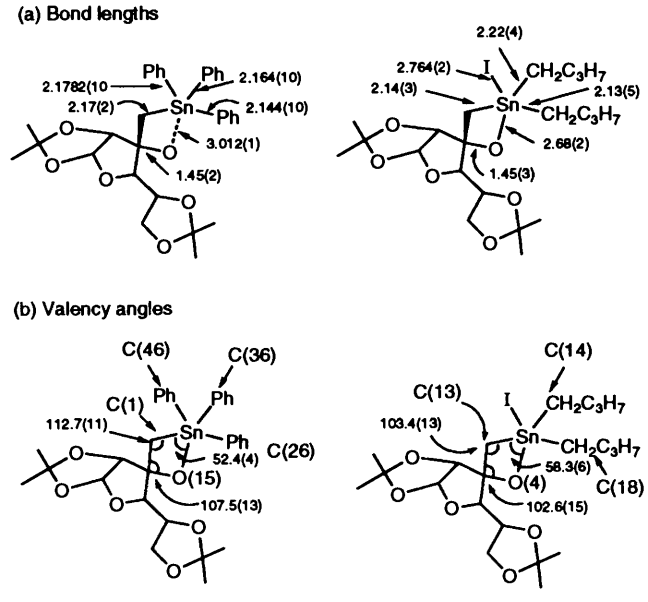


Fig. 3

asymmetric unit of the structure consists of discrete molecules. The C–Sn–C valency angles range from 103.8(3) to 114.9(5)° and the C–Sn bond lengths are 2.17(2) Å (tin–alkyl carbon) and from 2.14 (1) to 2.18(1) Å (tin–aryl carbon); all are within the usual ranges found for such bonds. The β-HO oxygen atom [O(15)] is 3.01(1) Å distant from the tin atom; this distance is well within the sum of the van der Waals radii (3.70 Å) but considerably greater[6] than a normal Sn–O covalent bond (*ca.* 2.0 Å). Intramolecular Sn–O distances ranging from 2.263(6) to 3.071(2) Å have been reported with varying degrees of confidence and assertion to indicate Sn–O bonding.[7]

The Sn–O(15) distance in compound (**1**; R = Ph) is taken here as indicating a weak Sn · · · O interaction and the geometry about tin is regarded as being distorted away from tetrahedral towards trigonal bipyramidal, with atoms O(15) and C(46) in quasi-axial sites [O(15) · · · Sn–C(46) 160.8(3)°].

The bond lengths and valency angles within the carbohydrate rings are as expected. The three rings in compound (**1**; R = Ph) adopt envelope conformations with flap atoms C(5), C(9) and C(10).

Comparison of the Sold-state Structures of Compounds (**1**; R = Ph) *and* (**2**; R = Bu) *from X-Ray Crystallography.*—As was mentioned earlier, the crystal structure of compound (**2**; R = Bu) has also been determined.[1] The tin atom in compound (**2**; R = Bu) has clearly a trigonal bipyramidal geometry with a Sn–O coordinate bond length of 2.68(3) Å. Some comparative data for the molecular structures of compounds (**1**; R = Ph) and (**2**; R = Bu) are provided in Fig. 3. Despite the shorter Sn–O distance in compound (**2**; R = Bu) (and the differences in certain valency angles), the axial ligand–Sn–axial ligand valency angles in compounds (**1**; R = Ph) and (**2**; R = Bu) are similar [160.8(3) and 158.3(4)° respectively]. If the solid-state structures can be taken to be good guides of the solution structures—and that the difference in R groups has only a minimal affect—then the β-HO oxygen atom in compounds **1** is ideally sited to take part in nucleophilic assistance during

Table 1 Selected bond lengths (Å) and bond angles (°) in compound (**1**; R = Ph) with esds in parenthesis

C(1)–Sn	2.17(2)	C(26)–Sn	2.14(1)
C(36)–Sn	2.16(1)	C(46)–Sn	2.18(1)
C(2)–C(1)	1.54(2)	C(3)–C(2)	1.51(2)
C(9)–C(2)	1.53(2)	O(15)–C(2)	1.45(2)
O(4)–C(3)	1.43(2)	C(7)–C(3)	1.52(2)
C(5)–O(4)	1.47(2)	O(6)–C(5)	1.42(2)
C(16)–C(5)	1.47(2)	C(17)–C(5)	1.50(2)
C(7)–O(6)	1.43(2)	O(8)–C(7)	1.41(2)
C(9)–O(8)	1.46(2)	C(10)–C(9)	1.53(2)
O(11)–C(10)	1.41(2)	C(14)–C(10)	1.52(3)
C(12)–O(11)	1.48(2)	O(13)–C(12)	1.39(3)
C(18)–C(12)	1.43(3)	C(19)–C(12)	1.49(3)
C(14)–O(13)	1.45(2)		
C(26)–Sn–C(1)	108.5(5)	C(36)–Sn–C(1)	114.9(5)
C(36)–Sn–C(26)	114.4(4)	C(46)–Sn–C(1)	109.5(5)
C(46)–Sn–C(26)	105.2(4)	C(46)–Sn–C(36)	103.8(4)
C(2)–C(1)–Sn	112.7(11)	C(3)–C(2)–C(1)	111.6(13)
C(9)–C(2)–C(1)	112.8(13)	C(9)–C(2)–C(3)	102.3(13)
O(15)–C(2)–C(1)	107.5(13)	O(15)–C(2)–C(3)	112.1(14)
O(15)–C(2)–C(9)	110.6(14)	O(4)–C(3)–C(2)	108.6(13)
C(7)–C(3)–C(2)	104.9(14)	C(7)–C(3)–O(4)	106.7(13)
C(5)–O(4)–C(3)	105.8(15)	O(6)–C(5)–O(4)	105.2(16)
C(16)–C(5)–O(4)	110.2(17)	C(16)–C(5)–O(6)	112.2(18)
C(17)–C(5)–O(4)	105.9(17)	C(17)–C(5)–O(6)	108.5(17)
C(17)–C(5)–C(16)	114.3(19)	C(7)–O(6)–C(5)	108.8(14)
O(6)–C(7)–C(3)	105.2(14)	O(8)–C(7)–C(3)	107.9(14)
O(8)–C(7)–O(6)	110.2(13)	C(9)–O(8)–C(7)	106.3(14)
O(8)–C(9)–C(2)	103.4(13)	C(10)–C(9)–C(2)	122.2(14)
C(10)–C(9)–O(8)	106.6(14)	O(11)–C(10)–C(9)	106.4(16)
C(14)–C(10)–C(9)	115.1(16)	C(14)–C(10)–O(11)	106.3(17)
C(12)–O(11)–C(10)	109.1(16)	O(13)–C(12)–O(11)	102.2(18)
C(18)–C(12)–O(11)	105.9(21)	C(18)–C(12)–O(13)	113.8(23)
C(19)–C(12)–O(11)	108.6(18)	C(19)–C(12)–O(13)	108.7(21)
C(19)–C(12)–C(18)	116.6(24)	C(14)–O(13)–C(12)	112.4(21)
O(13)–C(14)–C(10)	97.7(17)	C(25)–C(26)–Sn	121.2(2)
C(41)–C(46)–Sn1	120.4(2)	C(45)–C(46)–Sn	119.2(2)
C(21)–C(26)–Sn	118.8(1)	C(35)–C(36)–Sn	117.9(2)
C(31)–C(36)–Sn	122.0(2)		

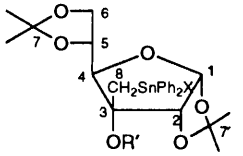


Table 2 NMR Spectral details for 1,2:5,6-di-*O*-isopropylidene-3-*C*-organostannylmethyl-α-D-allofuranose compounds in $CDCl_3$ solutions at 25 °C

(a) ^1H NMR

X/R′	$\delta(H^1)$ [$J(H^1–H^2)$]	$\delta(H^2)$ [$J(H^2–H^3)$]	$\delta(H^4)$ [$J(H^4–H^5)$] [[$J(^{119}Sn–^1H)$]]	$\delta(H^5)$ [$J(H^5–H^6)$] [[$J(H^5–H^{6'})$]]	$\delta(H^6$ and $H^{6'})$ [$J(H^6–H^{6'})$]	δ(OH) [J(OH–$H^{8'}$)]	$\delta(H^8$ and $H^{8'})$ [$J(H^8–H^{8'})$] [$J(^{119}Sn–^1H)$]	$\delta(CMe_2)$	$\delta(H_{aryl})$
Ph/H (≡**1**; R = Ph)	5.61 [3.7]	4.05	3.86 [7.9][[15.6]]	4.25 [6.20][[5.2]]	4.10 and 3.97 [8.5]	3.08 [1.3]	2.16 and 1.50 [13.3][[65]]	1.50, 1.38, 1.32, 1.06	7.61(m) *o* 7.34(m) *m* + *p*
I/H (≡**2**; R = Ph)	5.73 [3.7]	4.12	3.83 [8.0][[21]]	4.14 [6.9][[4.7]]	4.17 and 3.97 [8.3]	3.58 [1.6]	2.72 and 1.90 [13.1][[76]]	1.54, 1.36, 1.36, 1.18	7.80(m) *o* 7.40(m) *m* + *p*
CF_3CO_2/H	5.30 [3.8]	4.32	3.73 [9.1]	4.14 [6.7][[4.1]]	4.05 and 3.95 [9.5]	3.63	2.59 and 1.99 [13.7]	1.52, 1.28, 1.10, 1.02	8.01–7.30
Ph/CH_2OMe[a]	5.51 [3.8]	4.23	4.35 [5.5]	4.19 [6.0][[7.0]]	4.00 and 3.93 [7.9]		1.97 and 1.48 [13.4]	1.48, 1.39, 1.24, 1.03	7.85–7.25

(b) ^{13}C NMR

X/R′	δ(C-1)	δ(C-2) [$J(^{119}Sn–^{13}C)$]	δ(C-3) [$J(^{119}Sn–^{13}C)$]	δ(C-4) [$J(^{119}Sn–^{13}C)$]	δ(C-5)	δ(C-6)	δ(C-7, -7′)	δ(C-8) [$J(^{119}Sn–^{13}C)$] [[$J(^{117}Sn–^{13}C)$]]	δ(Me)	δ(C-aryl) [$J(^{119}Sn–^{13}C)$]
Ph/H (≡**1**; R = Ph)	103.5	84.3 [14]	79.7 [32.1]	82.4 [35.2]	74.0	67.5	109.2 112.3	18.3 [377][[360]]	25.1, 25.8 26.5, 26.5	139.2[519]C^i 137.1[38.1]C^o 128.3[49.6]C^m 128.6[11.4]C^p
Ph/H (≡**1**; R = Ph) (solid state)	104.9(br)	85.4, 85.0, 84.8	79.1(br)	83.8(br), 82.9	72.7(br)	70.1, 69.4, 69.4	110.2, 109.6, 109.6 111.8, 111.5, 111.3	15.4(br)	25.2(1), 25.9(2), 26.8(1) 27.1(3), 28.8(1)[b]	138.7(m) C^i + C^o 127.8(m), C^m + C^p
I/H (≡**2**; R = Ph)	103.5	84.2 [18.4]	79.9 [38.6]	81.9 [33.9]	73.9	67.8	109.7 112.8	27.6 [423][[405]]	25.1, 26.1 26.5, 26.6	138.7, 137.5 C^i 136.2, 136.1[50.8]C^o 128.6, 128.4[65.6]C^m 129.6[14.1]C^p

(c) ^{119}Sn NMR

X/R′	$\delta(^{119}Sn)$
Ph/H (≡**1**; R = Ph)	−111.3
(solid state)	−102.3, −103.5, −104.8
I/H (≡**2**; R = I)	−96.7

[a] OCH_2 δ 5.06, 4.71; J(H–H) 7.0 Hz; OMe 3.07. [b] Numbers in parentheses = number of Me groups.

Table 3 Anisotropy, asymmetry and shielding tensors for the tin signals in the solid-state ^{119}Sn NMR spectrum of (**1**; R = Ph)

	Shielding tensors				
$\delta(^{119}Sn)$	σ_{11}	σ_{22}	σ_{33}	Anisotropy (ppm)	Asymmetry
−102.3	146.575	108.447	51.878	−50	+0.76
−103.5	151.058	111.623	47.819	−56	+0.71
−104.8	144.90	116.360	53.140	−52	+0.55

Table 4 Values of $^2J(^{119}Sn-^{13}C)$ for β-hydroxyalkyltriphenylstannanes in $CDCl_3$ solution

Compound	$^2J(^{119}Sn-^{13}C^{\alpha})$ [a] (Hz)	$^2J(^{119}Sn-^{13}C^{ipso})$ [b] (Hz)
(**1**; R = Ph)	377	518
5	379	519
(**3**, R = Ph)	375	517
6	329	519

[a] C^{α} = aliphatic carbon. [b] C^{ipso} = aromatic carbon.

Table 5 Values of $\delta(^{13}C)$ for phenyl carbons in compound (**2**; R = Ph) in $CDCl_3$ at different temperatures

	$\delta(^{13}C)$			
T/°C	*ipso*	*ortho*	*meta*	*para*
55	138.0	136.3	129.6	128.6
24	138.7, 137.5	136.2, 136.1	129.6	128.6
−30	138.5, 136.5	136.1, 135.8	129.7	128.6, 128.2
−55	138.5, 136.0	136.0, 135.6	129.6(br)	128.5, 128.3

the R–Sn bond cleavage, *i.e.* in compounds **1**, the O atom is already on the ideal approach to tin to give compounds **2**.

NMR Spectra of Compound (**1**; R = Ph).—Both the ^{13}C and ^{119}Sn solid-state and solution NMR spectral data for compound (**1**; R = Ph) are displayed in Table 2. The number of lines in the solid-state spectra (both ^{13}C and ^{119}Sn) indicate the presence of 3 structural variations in the solid state (in the proportions 1:1:1), probably differing in the orientation of the three phenyl rings. The structural variations must be slight; the X-ray crystallography data were analysed to an acceptable *R*-value (0.066) in terms of a single structure with several atoms having relatively large thermal parameters. The anisotropies and asymmetry of the three tin signals are given in Table 3.

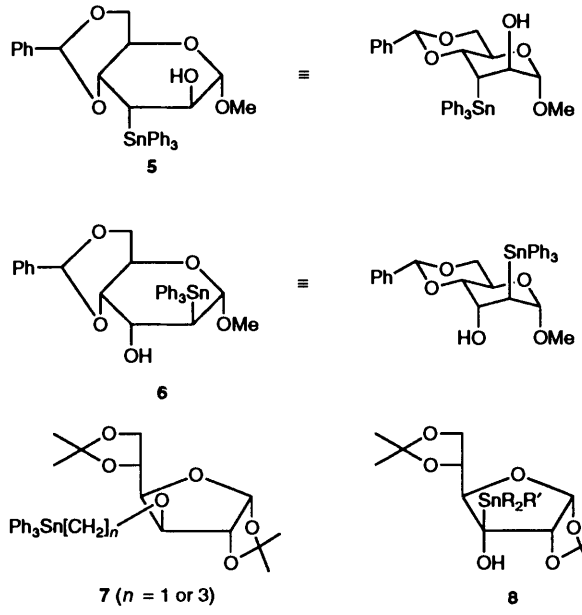
The similarities in the δ_C-values for corresponding carbons as well as the closeness of the δ_{Sn}-values for the two phases clearly point to similar structures in the two phases. Thus, the crystal structure of compound (**1**; R = Ph) can be taken as an excellent guide to the structure in solution.

Values of the coupling constants, $^2J(^{119}Sn-^1H)$ and $^1J(^{119}Sn-^{13}C)$, have been used to indicate coordination numbers at tin centres.[8,9] The $^2J(^{119}Sn-^1H)$, $^1J(^{119}Sn-^{13}C_{alkyl})$ and $^1J(^{119}Sn-^{13}C_{aryl})$ values for compound (**1**; R = Ph) in $CDCl_3$ solution are 65, 377 and 519 Hz, respectively; these values are indicative of essentially a tetrahedral tin atom in compound (**1**; R = Ph) in solution.

The coupling constant values for various (oxyalkyl)triphenylstannanes [especially for $^1J(^{119}Sn-^{13}C_{alkyl})$] show influences of the neighbouring oxygen atoms on the tin centre.

The $^1J(^{119}Sn-^{13}C)$-values for other (β-hydroxyalkyl)triphenylstannanes—compounds **5**, **6** and (**3**; R = Ph)—are provided in Table 4. The values of $^1J(^{119}Sn-^{13}C_{alkyl})$ for the four β-hydroxyalkylstannanes are the same (518 ± 1 Hz); however, $^1J(^{119}Sn-^{13}C_{alkyl})$ for compound **6** (329 Hz) is significantly lower than the corresponding values for compounds (**1**; R = Ph), **5** and (**3**; R = Ph) (377 ± 2 Hz).

Values of $^1J(^{119}Sn-^{13}C)$ for (α-oxyalkyl)triphenylstannanes [*e.g.*, Ph_3SnCH_2OR (R = Me, Et, *etc.*), (**7**; *n* = 1) and (**8**; R = R′ = Ph)] are more dependent [10] on the substituents, but fall in the regions 450 ± 25 (C_{alkyl}) and 515 ± 10 Hz (C_{aryl}); for (γ-oxyalkyl)triphenylstannanes [*e.g.*, $Ph_3Sn[CH_2]_3OR$ (R = H or CH_2Ph) and (**7**; *n* = 3)] the corresponding coupling constants [10] are 397 ± 7 (C_{alkyl}) and 492 ± 3 Hz (C_{aryl}).



Reactions of Compound (**1**; R = Ph).—It is of interest that the lowest $^1J(^{119}Sn-^{13}C_{alkyl})$-value for the four (β-hydroxyalkyl)triphenylstannanes given in Table 4 is for the compound having the lowest Ph–Sn bond reactivity towards I_2. [Relative reactivities [11] for (**1**; R = Ph), (**3**; R = Ph), **5** and **6** are 1.0:1.4:0.35:0.003].

For compound **5** [as for (**1**; R = Ph)] X-ray crsytallography showed that neighbouring oxygens [in particular O(4)] are in close and suitable sites [12] with respect to tin to take part in nucleophilic assistance in I_2 reactions; for compound (**3**; R = Ph), the critical $Ph_3SnCH(OH)$- unit, being acyclic, can readily adopt a suitable conformation for nucleophilic assistance. On the other hand it was concluded from an NMR spectral study [12] that the conformation of compound **6** in solution did not allow for short Sn···O intramolecular contracts and hence no nucleophilic assistance could be offered.

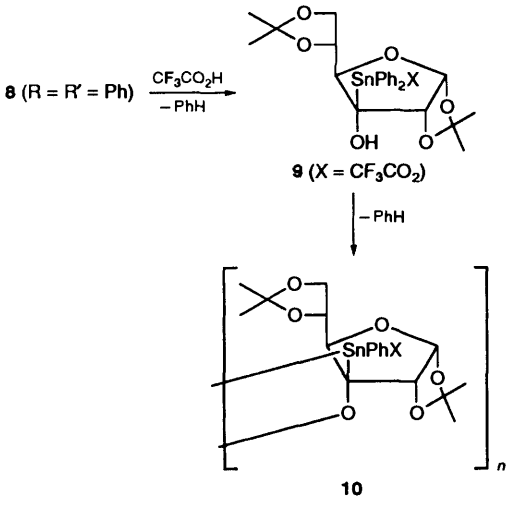
The NMR spectra of products of Ph–Sn bond cleavages in (**1**; R = Ph) by I_2 and CF_3CO_2H (TFA) are displayed in Table 2. Tin–oxygen coordination in compound (**2**; R = Ph) in $CDCl_3$ solution at temperatures below 47 °C is indicated not only by the $^2J(^{119}Sn-^1H)$- and $^1J(^{119}Sn-^{13}C_{alkyl})$-values (76 and 423 Hz, respectively, at 25 °C) but also by the inequivalent phenyl groups (as shown by two sets of $\delta(^{13}C_{aryl})$-values (see Table 5). Coalescence of the phenyl signals occurs at temperatures above 47 °C, as a result of elimination of Sn ← HO coordination and a rapid iodide-exchange reaction. The ν(OH)-values in CCl_4 solution at 25 °C and in a KBr disc for compound (**2**; R = Ph) [3538 and 3439 cm^{-1}] are different to those for compound (**1**; R = Ph) [3584 and 3517 cm^{-1}]. The greater reactivity of a Ph–Sn bond over a Me–Sn one is reflected

by the fact that TFA causes Ph–Sn cleavage in compound (**1**; R = Ph) whereas reaction with compound (**1**; R = Me) occurs at the O^5–O^6 protecting group.

The free HO group in compound (**1**; R = Ph) can be readily alkylated under basic conditions; *e.g.*, by $MeOCH_2Br$.

1,2:5,6-*Di*-O-*isopropylidene*-3-C-*triorganostannyl*-α-D-*allofuranose Compounds* **8**.—Compounds **8** were obtained from ketone **4** and $R_2R'SnLi$ (R = R′ = Me or Ph); these α-hydroxyalkyltin analogues of compounds **1** were shown to be less reactive towards electrophiles[11] than were compounds **1**; *e.g.*, relative rates of cleavage of Ph–Sn bonds in compounds (**1**; R = Ph) and (**8**; R = R′ = Ph) are 1.00:0.008. Reaction of compound (**8**; R = Me) with I_2 occurred at either type of carbon–tin bond although the major extent was at the Me–Sn bond. A cross-coupling reaction of compound (**8**; R = R′ = Me) with PhCOCl in the presence of $[(Ph_3P)_4Pd]$, however, was regiospecific with formation of PhCOMe. As with compound (**1**; R = Me), TFA reacted with compound (**8**; R = R′ = Me) at the O(5)–O(6) isopropylidene group.

In contrast, compound (**8**; R = R′ = Ph) reacted with equimolar TFA at the Ph–Sn bond to initially give compound (**9**; X = O_2CCF_3); however. this initial product was unstable and decomposed to give the polymer **10** on release of PhH (Scheme 2).



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Scheme 2

Experimental

M.p.s are uncorrected and were measured on a Kofler hot-stage apparatus. NMR spectra were obtained on a Bruker 250 MHz instrument; IR spectra were recorded on a Philips Analytical PU9800 Fourier-transform spectrometer; mass spectra were obtained on an AEI M30 instrument; *m/z*-values for tin-containing peaks are based on ^{120}Sn.

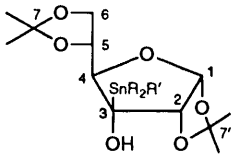
The compound $[(Ph_3P)_4Pd]$ was prepared by a published procedure.[14]

Preparation of 1,2:5,6-*Di*-O-*isopropylidene*-3-C-*triphenylstannyl*-α-D-*allofuranose* (**8**; R = R′ = Ph).—A solution of triphenylstannyllithium [prepared from Ph_3SnCl (5.00 g, 0.013 mol) and Li (0.91 g, 0.13 mol)] in dry tetrahydrofuran (THF) (50 cm^3) was cooled to −63 °C under nitrogen and a solution of 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose **4**[2] (2.0 g, 7.0 × 10^{-3} mol) in THF (15 cm^3) was added dropwise. The reaction mixture was allowed to warm to room temperature overnight and was then hydrolysed using an aq. pH 6.6 buffer (500 cm^3). The product was extracted into chloroform (3 × 150 cm^3); the extracts were given a backwash with water (100 cm^3), and were then dried over sodium sulfate before removal of the solvent. The residue was dissolved in cold Et_2O and the insoluble $Ph_3SnSnPh_3$ was removed by filtration. The solvent was removed from the filtrate and the title product was isolated by use of a Chromatotron [eluent Et_2O–hexane, 1:1(v/v)], as a crystalline solid, which was recrystallised from hexane (2.87 g, 61%), m.p. 104–105 °C (Found: C, 58.9; H, 5.8. $C_{30}H_{34}O_6Sn$ requires C, 59.15; H, 5.62%); ^1H, ^{13}C and ^{119}Sn NMR spectral data are given in Table 6; *m/z* (20 eV) (%, fragment), 610 (< 1, M^+), 595 (1, M^+ − Me), 551 (11, M^+ − Me_2CO_2 − H), 535 (3, M^+ − Me_2CO_2 − OH), 475 (4, M^+ − Ph − Me_2CO), 421 (7), 409 (6), 351 (100, Ph_3Sn^+), 291 (7, Ph_2SnOH^+), 274 (6, Ph_2Sn^+), 243 (6, M^+ − Ph_3Sn − Me − H), 201 (12, M^+ − Ph_3Sn − Me_2CO), 197 (9, $PhSn^+$) and 101 (59, $CH_2CHOCMe_2O^+$); ν_{max}(KBr disc)/cm^{-1} 3414, 3059–2853, 1427–1368, 1257, 1215, 1070, 1057, 1044, 1022, 997, 986, 839, 737 and 698.

Preparation of 1,2:5,6-*Di*-O-*isopropylidene*-3-C-*trimethylstannyl*-α-D-*allofuranose* (**8**; R = R′ = Me).—A solution of trimethylstannyllithium [prepared from trimethyltin chloride (3.98 g, 0.02 mol) and lithium (1.39 g, 0.20 mol)] in dry THF (30 cm^3) under nitrogen was cooled to −63 °C and a solution of 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexafuranos-3-ulose **4**[1] (3.70 g, 0.014 mol) was added dropwise. The reaction mixture was allowed to warm to room temperature overnight, then was filtered through glass wool (to remove unchanged lithium) into aq. pH 6.6 buffer (500 cm^3) and extracted into CH_2Cl_2 (3 × 150 cm^3). The combined extracts were washed with water (100 cm^3) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the residue was chromatographed using a Chromatotron (eluent Et_2O–hexane). The title product was isolated as a crystalline solid (1.85 g, 31%), m.p. 55–59 °C (Found: C. 42.2; H, 6.5. $C_{15}H_{28}O_6Sn$ requires C, 42.6; H, 6.7%); ^1H, ^{13}C and ^{119}Sn NMR spectral data are in Table 6; *m/z* (20 eV) (%, fragment) 424 (1, M^+), 377 (3, M^+ − 2Me − OH), 363 (3, M^+ − 4Me − H), 259 (< 1, M^+ − Me_3Sn), 243 (7), 231 (7), 170 (100), 104 (28) and 58 (36, Me_2CO^+).

Preparation of 1,2:5,6-*Di*-O-*isopropylidene*-3-C-(*triphenylstannylmethyl*)-α-D-*allofuranose* (**1**; R = Ph).—To a solution of triphenylstannylmethyllithium [prepared from (iodomethyl)-triphenyltin[15] (4.91 g, 0.01 mol) and butyllithium (1.0 mol equiv.; 7.0 cm^3 of 1.5 mol dm^{-3} solution in hexanes] in dry Et_2O (30 cm^3) at −63 °C under nitrogen was added dropwise a solution of 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose **4** (2.58 g, 0.01 mol) in dry Et_2O (915 cm^3). The reaction mixture was warmed to room temperature, hydrolysed with aq. pH 6.6 buffer (300 cm^3) and extracted into CH_2Cl_2 (3 × 150 cm^3). The combined extracts were dried over $MgSO_4$ and the solvent was removed by rotary evaporation to leave a syrupy residue. Purification by use of a Chromatotron [eluent Et_2O–hexane, 1:1 (v/v)], led to isolation of the title product as a solid [3.86 g, 62% (crude)], which was recrystallised from hexane (2.40 g, 39%), m.p. 121–123 °C (Found: C, 59.8; H, 6.0. $C_{31}H_{36}O_6Sn$ requires C, 59.73; H, 5.82%); ^1H, ^{13}C and ^{119}Sn NMR spectral data are in Table 2; *m/z* (20 eV) (%, fragment) 547 (4, M^+ − Ph), 489 (3, M^+ − Ph − Me_2CO), 465 (1, M^+ − Me_2CO − $CH_2CHOCMe_2O$), 431 (3, M^+ − Ph − 2Me_2-CO), 409 (2), 371 (3), 351 (100, Ph_2Sn^+), 291 (30, Ph_2SnOH^+), 274 (4, Ph_2Sn^+), 197 (23, $PhSn^+$), 120 (20, Sn^+), 101 (59, $CH_2CHOCMe_2O^+$) and 78 (42, PhH); ν_{max}(KBr)/cm^{-1} 3517, 3063, 3048, 2988–2859, 1429, 1372, 1215, 1074, 1042, 1019, 997, 878, 849, 731 and 700; ν_{max}(CCl_4 soln.)/cm^{-1} 3584.

Preparation of 1,2:5,6-*Di*-O-*isopropylidene*-3-O-*methoxymethyl*-3-C-(*triphenylstannylmethyl*)-α-D-*allofuranose*.—The reaction of triphenylstannylmethyllithium [prepared from (iodomethyl)triphenyltin[15] (4.01 g, 0.004 mol) and butyllithium



8

Table 6 NMR Spectral details for 1,2:5,6-di-*O*-isopropylidene-3-*C*-organostannyl-α-D-allofuranose compounds in $CDCl_3$ solution at 25 °C

(a) ^1H NMR

8 R/R′	$\delta(H^1)$ $[J(H^1–H^2)]$	$\delta(H^2)$ $[J(^{119}Sn–^1H)]$	$\delta(H^4)$ $[J(H^4–H^5)]$	$\delta(H^5)$ $[J(H^5–H^6)]$ $[[H(H^5–H^{6'})]]$	$\delta(H^6$ and $\delta(H^{6'})$ $[J(H^6–H^{6'})]$	δ(OH) $[J^{119}Sn–^1H)]$	δ(Me)	$\delta(H_{aryl})$	Other
Ph/Ph	5.52	4.85	4.00	4.13	4.02, 3.83	3.18	1.56, 1.32,	7.72(m),	*o*-H
	[3.5]	[28.9]	[8.7]	[5.8][[6.0]]	[8.6]	[49.2]	1.26, 0.91	7.41(m)	*m* + *p*-H
Ph/I	5.83	5.19	4.14	~4.00	4.07, 3.86	3.40	1.59, 1.39,	7.76(m),	*o*-H
	[3.7]	[45]	[7.4]	[5.9][[5.2]]	[8.1]	[68]	1.09, 1.00	7.39(m)	*m* + *p*-H
Me/Me	5.63	4.62	*a*	4.14	*a*	2.58	1.52, 1.42,	0.26	Me_3Sn
	[3.6]					[45]	1.36, 1.36	[51]	
Me/I	5.78	5.13	4.02	4.15	4.18, 3.86	2.89	1.57, 1.46,	1.02	$Me_2(I)Sn$
	[3.8]	[39]	[4.8]	[11.8][[7.4]]	[6.2]	[86]	1.39, 1.38	[59]	

(b) ^{13}C NMR

R/R′	$\delta(C^1)$	$\delta(C^2)$ $[J(^{119}Sn–^{13}C)]$	$\delta(C^3)$ $[J(^{119}Sn–^{13}C)]$ $[[J(^{117}Sn–^{13}C)]]$	$\delta(C^4)$ $[J(^{119}Sn–^{13}C)]$	$\delta(C^5)$ $[J(^{119}Sn–^{13}C)]$	$\delta(C^6)$	$\delta(C^7)$ and $\delta(C^{7'})$	δ(Me)	Others $[J(^{119}Sn–^{13}C)]$ $[[J(^{117}Sn–^{13}C)]]$	
Ph/Ph	103.5	83.5	86.5	84.2	77.7	68.6	112.9, 109.9	24.5, 26.3,	137.1[495][[473]]	C^i
		[44.9]	[484][[463]]	[19.1]	[25.2]			26.4, 26.5	137.3[35]	C^o
									128.6[51]	C^m
									129.1[11]	C^p
Ph/I	104.0	83.8	86.1	85.1	76.4	68.4	110.8, 113.3	24.7, 25.9,	137.4[668][[636]]	C^i
		[49.6]	[584][[559]]	[40.5]	[24.8]			26.5, 26.8	136.4[44]	C^o
									128.7[63.4]	C^m
									129.8[—]	C^p

(c) ^{119}Sn NMR

R/R′	
Ph/Ph	−43.6

[a] δ 3.94–3.81 [3 H, m, H^4, H^6 and $H^{6'}$].

(1.0 mol equiv.; 5.3 cm^3 of 1.5 mol dm^{-3} solution in hexanes)] and 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose **4**[1] (2.11 g, 0.008 mol) was repeated as described above. After stirring of the reaction mixture at −63 °C for 1 h, bromomethyl methyl ether (1.5 mol equiv.; 1 cm^3, 0.012 mol) was added and the reaction was allowed to continue as before. The product was isolated from the Chromatotron as a syrup (2.1 g, 39%). ^1H NMR spectral data are in Table 2.

Reactions of Compound (**8**; R = R′ = Me).—(1) *With TFA.* To a solution of compound (**8**; R = R′ = Me) (32.6 mg, 7.71×10^{-5} mol) in $CDCl_3$ (0.5 cm^3) was added TFA (5.9 mm^3, 7.71×10^{-5} mol). As shown by ^1H NMR spectroscopy, a slow initial reaction led to formation of acetone (δ_H 2.18; 100% yield).

(2) *With iodine.* To a solution of compound (**8**; R = R′ = Me) (29.4 mg, 6.95×10^{-5} mol) in $CDCl_3$ (0.5 cm^3) was added I_2 (17.6 mg, 6.95×10^{-5} mol). Reaction was complete after 2 days at room temp. Products indicated by ^1H NMR spectroscopy were MeI (δ 2.15) and 3-*C*-iododimethylstannyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (see Table 6) as major products with Me_3SnI as a minor product *ca.*, 10% [δ 0.88 $J(^{119}Sn–^1H)$ 55 Hz].

(3) *With* PhCOCl *in the presence of* [$Pd(PPh_3)_4$]. A mixture of $P(PPh_3)_4$ (1 mg, 4.33×10^{-4} mol dm^{-3}), compound (**8**; R = R′ = Me) (0.268 g, 6.3×10^{-4} mol) and PhCOCl (0.089 g, 6.34×10^{-4} mol) in hexamethylphosphoric triamide (2 cm^3) was maintained at 65 °C overnight. The reaction mixture was diluted with water (2 cm^3) and extracted into Et_2O (3 × 10 cm^3). The combined extracts were washed with water (2 × 10 cm^3), dried over $MgSO_4$, and the solvent was removed. The residue was chromatographed on a Chromatotron [eluent Et_2O–hexane, 1:1 (v/v)]. Acetophenone was isolated in 40% yield.

Reactions of Compound (**8**; R = R′ = Ph).—(1) *With TFA.* To a solution of compound (**8**; R = R′ = Ph) (33.2 mg, 5.45×10^{-5} mol) in CH_2Cl_2 (2.5 cm^3) was added TFA (4.2 mm^3, 5.45×10^{-5} mol). GLC indicated formation of PhH (199.5%).

(2) *With* I_2. To a solution of compound (**8**; R = Ph) (32.5 mg, 5.33×10^{-5} mol) in CCl_4 (2.5 cm^3) was added I_2 (12.7 mg, 5.00×10^{-5} mol) and the mixture was maintained in the dark at room temperature. Analysis by GLC of the reaction mixture, after decolorisation, showed formation of PhI (100%).

The reaction was repeated on a 0.61 mmol scale in $CHCl_3$ solution. After complete reaction, the solvent was removed under reduced pressure to leave a residue, which was recrystallised from hexane to give 3-*C*-(iododiphenylstannyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**9**; X = I). ^1H and ^{13}C NMR spectral data are in Table 6; ν_{max}(KBr)/cm^{-1} 3472, 3067–2870, 1481–1375, 1254, 1217, 1057, 1013, 870, 833, 729, 696 and 654.

Reactions of Compound (**1**; R = Ph).—(1) *With TFA.* To a solution of compound (**1**; R = Ph) (32.0 mg, 5.13×10^{-5} mol) in CH_2Cl_2 (2.5 cm^3) was added TFA (4.0 mm^3, 5.13×10^{-5} mol). Analysis by GLC showed the formation of PhH (98%). Removal of the volatiles left a residue of 3-*C*-[diphenyl(trifluoroacetato)stannylmethyl]-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose. ^1H spectral data are listed in Table 2.

(2) *With* I_2. To a solution of compound (**1**; R = Ph) (0.38 g, 0.61 mmol) in $CHCl_3$ (10 cm^3) was added a solution of I_2 (0.15 g, 0.61 mmol) in $CHCl_3$ (30 cm^3). The mixture was kept in the dark until complete decolorisation. The solvent was removed under reduced pressure to leave a residue of 3-*C*-(iododiphenylstannyl)methyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**2**; R = Ph), which was recrystallised from hexane, m.p. 90 °C. NMR spectral data are listed in Table 2; ν_{max}(KBr)/cm^{-1} 3439, 3048–2886, 1431, 1379, 1262, 1217, 1165, 1074, 1042, 1020, 997, 729, 696, 580, 460, 380, 225, 173, 150, 115 and 105; ν_{max}(CCl_4 soln.)/cm^{-1} 3439.

Crystal Structure Determination of Compound (**1**; R = Ph).—*Crystal data.* $C_{31}H_{36}O_6Sn$, M_r = 623.3, orthorhombic, $P2_12_12_1$, a = 6.070(4), b = 13.074(12), c = 37.687(32) Å, Z = 4, D_x = 1.384 Mg m^{-3}, V = 2990(4) Å, room temperature, Mo-Kα, λ = 0.710 69 Å, μ = 0.89 mm^{-1}. $F(000)$ = 1280 e^-, R = 0.066 for 1863 observed reflections with $I > 2\sigma(I)$.

Data collection and processing. X-Ray diffraction data were obtained from a crystal (0.08 × 0.05 × 0.16 mm) on a Nicolet P3 four-circle diffractometer with Mo-Kα radiation and graphite monochromator. Cell dimensions were determined using 14 reflections at 9–10° in 2θ. The intensities of 3111 reflections with $2\theta \leqslant 50°$ and $0(0,0) \leqslant h(k, l) \leqslant 7(15,44)$ were measured from ω scans with a fixed width of 0.6°, scan rates in the range 1.0–29.3° min^{-1} related to pre-scan intensity and stationary crystal–stationary counter background counts taken at ±1.0° in ω from the calculated position of the Bragg peak. No correction for absorption or extinction was applied. Two reference reflections, monitored periodically, showed no significant variation in intensity. The data were reduced to structure amplitudes in the usual way to yield a total of 2600 unique reflections (R_{int} = 0.014).

The structure was solved by Patterson methods[16] to yield the position of Sn. The positions of the remaining non-H-atoms were obtained from a succession of difference maps.[17] Full-matrix least-squares refinement minimising $\Sigma w(\Delta F)^2$, with isotropic thermal parameters for all atoms except Sn, H in calculated positions with separate group isotropic thermal parameters for phenyl, methyl and alkyl H-atoms, and phenyl and methyl groups treated as rigid bodies (137 parameters) converged at R = 0.066 and wR = 0.061 with $w = 1.8/[\alpha^2(F_o) + 0.000\,678\,(F_o)^2]$, max. shift/esd = 0.02 (0.2 for certain rigid group rotational parameters) and Δmin(max) = 0.73 (0.60) e^- $Å^{-3}$. Despite a diligent search of the final difference map it proved impossible to determine the position of the hydroxy group H-atom associated with O(15). Calculations were carried out on a SUN SPARC 480 system of the Computing Centre of the University of Aberdeen. The scattering curves installed in SHELX76 were used.

The final values for R_g for the atomic coordinates and for a model with all the coordinates changed in sign (0.066 and 0.069 respectively) suggest that the model presented here represents the absolute configuration of the sugar component with better than 99.5% certainty.[18]

Lists of fractional coordinates, hydrogen atom coordinates and anisotropic thermal parameters have been deposited with the CCDC.*

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* For the details of the Cambridge Crystallographic Data Centre deposition scheme, see *J. Chem. Soc., Perkin Trans. 1*, 1993, Issue 1, 'Instructions for Authors.'

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