Applied Organometallic Chemistry (1989) 3 417–424

0268-2605/89/03506417/$03.50

Preparation and properties of triorganostannylmethyl 2,3:5,6-di-*O*-isopropylidene-α-*D*-mannofuranosides; pesticidal and fungicidal activities of triphenylstannyl-carbohydrate derivates

Christine R McDonough, Oonah J Taylor and James L Wardell*
Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, Scotland, UK

Received 13 April 1989 *Accepted 19 June 1989*

The synthesis of trioganostannylmethyl 2,3:5,6-di-*O*-isopropylidene-α-*D*-mannofuranoside (compound 3, R*OCH_2SnR_2R':R=R′=Me or Ph) from *D*-mannose is reported. The compound 3 (R=R′=Ph) is transmetallated by PhLi to compound 5, R*OCH_2Li, which can be trapped by $HgCl_2$ [as $(R^*OCH_2)_2Hg$] and by ketones, R^3COMe [as compound 7, R*OCH_2CR^3MeOH]. Two stereoisomers of this compound (7a, R^3=Ph) were formed in a ratio of 40:60, indicating some asymmetric induction, arising from the chiral R* moiety. Reactions of compound 3, (R=R′=Ph), with I_2, HO_2CCF_3 and Cl_2PtCOD result in Ph–Sn bond cleavage and formation of compound 3 with R=Ph; R′=I, $OCOCF_3$ and Cl respectively. Reactions of compound 3 (R=R′=Me) with electrophiles can lead to cleavage of either or both types of C–Sn bonds present (e.g. by I_2, Br_2, Cl_2PtCOD or $SnCl_4$) or to attack at the C_5–C_6 protecting group with release of acetone (e.g. by CF_3CO_2H, SO_2 or CH_3COCl). Pesticidal and fungicidal activities of compound 3(R=R′=Ph) as well as of 1,2:5,6-di-*O*-isopropylidene-3-*O*-(triphenylstannylmethyl)-α-*D*-glucofuranose (compound 2, R=Ph) and methyl 4, 6-*O*-benzylidene-2-deoxy-2-triphenylstannyl-α-*D*-altropyranoside (compound 1, R=Ph) are reported.

Keywords: Triorganotin, sugars, pesticidal, fungicidal

INTRODUCTION

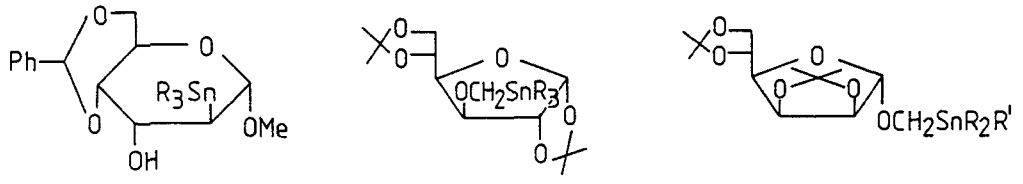
Organotin compounds have uses[1] as far-ranging as reagents in organic synthesis[2] to biologically active species. These applications have given a great impetus to the study of organotin chemistry. One persistent goal of the research effort has been the synthesis of new organotin species. As shown in recent reviews,[3–5] organotin–carbohydrate derivatives have attracted some attention, especially over the last decade or so; oxygen–tin linked derivatives have had the major share of the activity and their utility in carbohydrate synthesis is now well established.[4] Carbon–tin linked carbohydrate compounds, e.g. Scheme 1, compound **1**,[6] have been less well studied[7–14] and their potential remains essentially untapped.

The preparation of 1,2:5,6-di-*O*-isopropylidene-3-*O*-triorganostannylmethyl-α-*D*-glucofuranose (**2**, $R_SOCH_2SnR_3$) and its reaction to R_SOCH_2Li were recently reported;[11] unfortunately these had only limited value in organic synthesis. Other *O*-triorganostannylmethyl furanose derivatives, namely trioganostannylmethyl 2,3:5,6-di-*O*-isopropylidene-α-*D*-mannofuranoside (**3**), have now been studied. We wish to report the synthesis and reactions of compound **3**; the pesticidal and fungicidal activities of **3** (R=R′=Ph), **1** (R=Ph) and **2** (R=Ph) are also reported.

RESULTS AND DISCUSSION

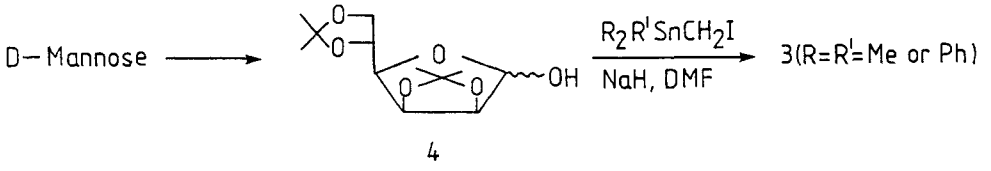
The compounds **3** (R*OCH_2SnR_2R': R=R′=Me or Ph) were synthesized from *D*-mannose via alkylation of the anomeric hydroxyl of 2,3:5,6-di-*O*-isopropylidene-α-*D*-mannofuranose (**4**) by $R_2R'SnCH_2I$ (Scheme 2). Exclusive formation of the α-anomer (**3**) was achieved.

* Author to whom correspondence should be addressed.



1, R=Ph 2 3

Scheme 1



4

Scheme 2

The H and ^{119}Sn NMR spectra of **3** are given in Tables 1 and 2. Compound **3** (R=R′=Ph) was stable to moist air at ambient temperature for at least one year. In contrast, **3** (R=R′=Me) decomposed over a few months to trimethyltin formate and the derivative sugar **4** (Eqn [1]).

$$\mathbf{3}\ (R=R'=Me) \xrightarrow{O_2,H_2O} Me_3SnOCOH + \mathbf{4} \quad [1]$$

The $Me_3SnOCOH$ product appeared on the sides of the containing vessels of **3** (R=R′=Me) as fine needle-shaped crystals. An analogous decomposition of **2** (R=Me) has already been reported.[11]

In general, alkoxymethylstannyl derivatives, $R'OCH_2SnR_3$, are useful precursors[15–17] of synthetically valuable alkoxymethyllithiums (Eqn [2]).

$$R'OCH_2SnR_3 + RLi \xrightarrow{-R_4Sn} R'OCH_2Li \quad [2]$$

The tin–sugar derivative **2** ($R_SOCH_2SnR_3$; R=Ph), as previously reported,[11] underwent transmetallation with PhLi; the product, R_SOCH_2Li, could be trapped by organotin halides [e.g. by $R^2{}_3SnCl$ as $R_SOCH_2SnR^2{}_3$(R^2=Me or cyclohexyl)] but not unfortunately by ketones, R^3R^4CO. Instead of the desired alcohol product, $R_SOCH_2CR^3R^4OH$, the major species isolated was the parent sugar, R_SOH. More success has now been realized with **3** (R=R′=Ph:R*OCH_2SnPh_3). This was readily transmetallated by PhLi and the lithium product **5** (R*OCH_2Li) reacted successfully with both metal halides and ketones (Scheme 3). Reactions with ketones (R^3COMe, R^3=Me or Ph) provided the alcohols **7** and showed that the R*OCH_2 unit could be transferred from tin to carbon. The yields quoted for **7** are for isolated products; however, these were not optimized. Two stereoisomers of **7a** were obtained, as an oily mixture, in a ratio of 60:40. This indicates that the chiral moiety, R*, in **5** is inducing asymmetry at the carbonyl carbon of the attacking ketone. In **7b**, the two methyl groups (at C_8) have slightly different δ^1H values and thus are in different environments. The diorganomercural (**6**) was formed as an oil in modest yield from **3** (R=R′=Ph); it decomposed on standing, forming a deposit of mercury. Further work on **5** with ketones and other electrophiles is underway, to investigate both the extents of asymmetric induction and further uses in carbohydrate synthesis. Compounds **3** (R=R′=Me) underwent a similar transmetallation, as did compound **3** with R=R′=Ph; however, it stores less well and there are no advantages of using it over compound **3** with R=R′=Ph.

Direct reactions of compound **3** (R=R′=Ph: R*OCH_2SnPh_3) with electrophiles were studied to determine whether the R*OCH_2 unit could be transferred to other centres. However, as reactions with Cl_2PtCOD, I_2 and CF_3CO_2H all showed, the most readily cleaved group is a phenyl; quantitative formation of compound **3** (R=Ph,R′=Cl) and PhClPtCOD, compound **3** (R=Ph,R′=I) and PhI, and compound **3** (R=Ph,R′=$OCOCF_3$) and PhH, respectively resulted.

This parallels findings obtained[18] for $Ph_3SnCH_2OC_6H_4Me$-*p* towards halogens and $HgCl_2$. The ^{1}H NMR and ^{119}Sn NMR data for the tin products are given in Tables 1 and 2.

The transfer of the R*OCH_2 unit from compound

Table 1 ^{1}H NMR spectra of compound **3**

	δ′H(rpm) (*J*(Hz))									
R_2R' (Solvent)	H_1	H_2 ($J_{2,3}$)	H_3 ($J_{3,4}$)	H_4 ($J_{4,5}$)	H_5 ($J_{5,6}$) [$J_{5,6'}$]	H_6 ($J_{6,6'}$)	H_6'	CH_2Sn ($J_{H,H}$) [$J^{119}Sn-^1H$]	CMe_2	Me–Sn or Ph–Sn ($J^{119}Sn-^1H$)
Ph_3	4.76	4.40	4.53	3.64	4.19 (5.6)	3.95 (8.3)	3.78	4.46; 4.06 (10.3)	1.34, 1.26	7.30 m
(CCl_4)		(5.8)	(3.3)	(7.2)	[6.3]				1.25, 1.19	7.48 m
Ph_3 ($CDCl_3$)	4.91	4.54 (5.5)	4.69 (3.8)	3.81 (8.2)	4.39 (4.8) [6.5]	4.1 (9.1)	3.99	4.50; 4.11 (10.1)	1.45, 1.41 1.37. 1.31	7.35 m 7,53 m
Ph_3 (CD_2Cl_2)	4.87	4.52 (5.8)	4.64 (3.5)	3.76 (7.5)	4.29 (4.9) [6.3]	4.03 (8.4)	3.92	4.49; 4.11 (10.5)	1.35, 1.31 1.27, 1.23	7.35 m 7.54 m
Ph_2I (CCl_4)	4.83	4.44 (5.9)	4.57 (3.3)	3.73 (7.2)	4.16 (6.1) [6.7]	3.82 (8.3)	3.57	4.47; 4.33 (10.2)	1.34, 1.21 1.21, 1.20	7.34 m 7.57 m
Ph_2Cl (CD_2Cl_2)	4.96	4.56 (5.9)	4.66 (3.7)	3.83 (8.4)	4.19 (5.7) [6.3]	3.72 (8.5)	3.52	4.43; 4.42 (10.3)	1.35, 1.22 1.18, 1.13	7.44 m 7.65 m
Me_3 ($CDCl_3$)	4.77	4.51 (6.2)	4.72 (4.1)	3.84 (7.4)	4.38 (6.7) [4.8]	4.10 (8.4)	4.02	3.81; 3.50 (10.8) [16.8]	1.43 1.43 1.37 1.30	0.12 (50)
Me_3[a] ($(CD_3)_2CO$)	4.71(s)	4.47(d)	4.72(dd)	8.35(dd)	4.31(m)	4.01(dd)	3.93(dd)	3.84(d); 3.54(d) [17]	1.34(s) 1.32(s) 1.26(s) 1.24(s)	0.08 (53)
Me_3[a] (C_6D_6)	4.99(s)	4.51(d)	4.50(dd)	4.12(dd)	4.63(m)	4.25(dd)	4.20(dd)	3.87(d); 3.43(d) [17]	1.51(s) 1.41(s) 1.35(s) 1.09(s)	0.13 (50)
Me_3[a] (CD_2Cl_2)	4.74(s)	4.49(d)	4.69(dd)	3.85(dd)	4.33(m)	4.06(dd)	3.97(dd)	3.83(d); 3.53(d) [17]	1.43(s) 1.40(s) 1.34(s) 1.29(s)	0.12 (50)
Me_2Cl (CD_2Cl_2)	4.88	4.57 (6.5)	4.73 (4.3)	4.30 (7.2)	4.37 (7.2) [6.7]	3.97 (7.4)	3.87	4.00: 3.88 (12.0)	1.40 1.40, 1.39 1.35	0.78 (61)
Me_2Br ($CDCl_3$)	4.88	4.56 (6.2)	4.73 (4.3)	4.26 (3.7)	4.38 (6.7) [4.8]	4.02[b]	3.90[b]	4.07; 3.92 (11.5)	1.42 1.43 1.31 1.27	0.89 (58)

[a] Couplings not measured; (s) singlet; (d) doublet, (m) multiplet. [b] Couplings not resolved.

3 (R=R′=Me) in direct reactions with electrophiles was also investigated (Table 3). In comparison with the electrophilic reactions of **3** (R=R′=Ph), reactions with **3** (R=R′=Me; $R^*OCH_2SnMe_3$) are more varied, giving rise to cleavage of both or either of the R^*OCH_2-Sn and Me–Sn bonds (e.g. using I_2, Br_2, Cl_2PdCOD or $SnCl_4$), Scheme 4, or to initial reaction at the C_5-C_6 protecting group with release of acetone (e.g. using CF_3CO_2H, SO_2 or CH_3COCl). Benzoyl chloride and $ClCO_2Et$ did not react

Table 2 ^{119}Sn chemical shifts for **3** (R=Ph)

R′	Solvent	δ ^{119}Sn (rel. to Me_4Sn)
I	CCl_4	−123.4
Cl	CD_2Cl_2	− 54.4
Ph	CCl_4	−136.3
Ph	$CDCl_3$	−138.5

3 (R=R′=Me; $R^*OCH_2SnMe_3$)

$$+\ E{-}Y \rightarrow \begin{cases} Me{-}E + \mathbf{3}\ (R{=}Me, R'{=}Y) \\ R^*OCH_2E + Me_3SnY \end{cases}$$

The selectivity in the C−Sn bond cleavages depends greatly on the electrophile (see Table 3), e.g. the degree of R^*OCH^2−Sn cleavage ranged from 0% (with $SnCl_4$) to 100% (with I_2). Unfortunately the iodine reaction product, R^*OCH_2I, did not survive the reaction conditions. Based on the ^1H NMR spectrum, both (R^*OCH_2)ClPdCOD (**8**) and MeClPdCOD (in a ratio of 1:3) were obtained from the reaction of compound **3** (R=R′=Me) with Cl_2PdCOD. Compound **8** was however neither isolated nor used further. The ^1H NMR data for **3** (R=Me, R′=Cl or Br) are given in Table 1. A general feature of the direct electrophilic reactions of compound **3** (R=R′=Me) is that prolonged reaction times (e.g. over period of days) led to complex mixtures of tin and carbohydrate products.

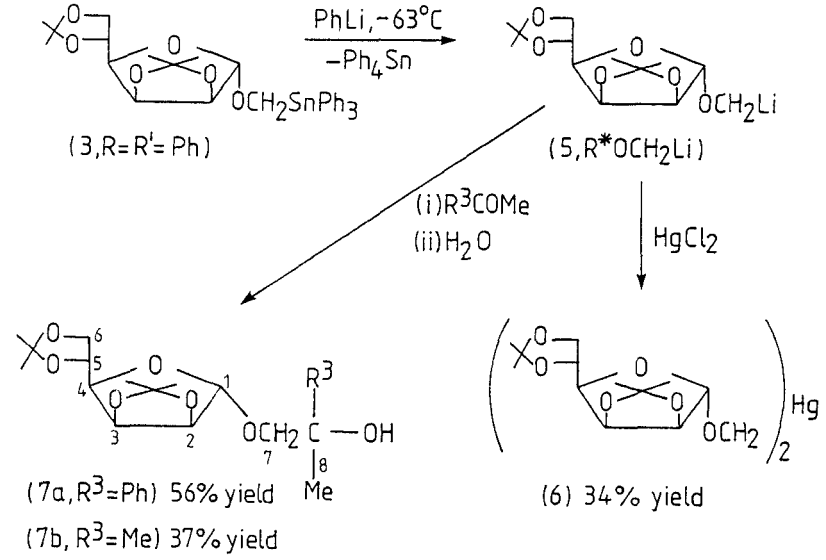
Biological activity

The evaluation of the stannylated sugar derivatives **1** (R=Ph), **2** (R=Ph) and **3** (R=R′=Ph) for pesticidal, fungicidal and herbicidal activities was performed at the ICI Plant Protection (Agrochemical) Division, Bracknell. Moderate pesticidal activity was observed, especially against mites (*Tetranychus urticae*) (Table 4). Fungicidal and herbicidal activity were generally poor; see Table 5 for fungicidal data. All three derivatives tested were tetraorganotins; these generally have very much reduced activity compared with trioganotin species. It is a possibility that some carbon−tin cleavage could be occurring after administration, thereby converting these species to active triorganotins. As already indicated, cleavage of compound **3** (R=R′=Ph), of **2** (R=Ph)[11] and of **1** (R=Ph)[12] occurs most readily at a Ph−Sn bond. Such cleavages could be happening after administration of the tetraorganotins.

EXPERIMENTAL

Iodomethyltrimethyltin and iodomethyltriphenyltin were prepared as previously[11] described.

D-Mannose was converted to 2,3:5,6-di-*O*-



Scheme 3

Table 3 Equimolar reactions of **3** (R=R′=Me: R*OCH_2SnMe_3) with electrophilic reagents [1.3–1.5 mol dm^{-3}]

Electrophilic reagent	Solvent	Reaction conditions	Products	Yield (%)	^1H NMR spectral data: δ^1H	Relative ease of cleavage Me–Sn: R*OCH_2–Sn
I_2	$CDCl_3$	RT	Me_3SnI[a]	100	0.86 ($J^{119}Sn-^1H$ 56 Hz)	
			Me_2CO	40	2.14	0:100
Br_2	$CDCl_3$	−10°C, dark	Me_3SnBr	5	0.73 ($J^{119}Sn-^1H$ 56 Hz)	
			3 (R=Me,R′=Br)	95	See Table 1	90:10
			MeBr	95	2.62	
$Cl_2Pd(COD)$	CD_2Cl_2	RT, 12 h	Me_3SnCl	25	0.63 ($J^{119}Sn-^1H$ 57 Hz)	
			3 (R=Me,R′=Cl)	75	See Table 1	50:50
			MeClPdCOD	75	1.04 (s,Me), 2.45(m), 2.55(m), 5.10(m), 5.80(m)	
			$(R*OCH_2)ClPdCOD$[b]	25		
$SnCl_4$	CD_2Cl_2	RT, 20 min	$MeSnCl_3$	100	1.70 ($J^{119}Sn-^1H$ 96 Hz)	
			3 (R=Me,R′=Cl)	100	See Table 1	100:0
			Me_2CO	5	2.14	
$ClSO_2OH$	$CDCl_3$	−10°C, 1 h	MeH		0.19	
			Me_2CO	25	2.16	
			Other[c]			
CF_3CO_2H	$CDCl_3$	RT, <2 h	Me_2CO			
			Other[d]			

[a] Only methyltin species detected; primary sugar product decomposed. [b] ^1H NMR spectrum partially hidden: δ 5.01 (H-1); 4.56 (H-2); 4.65 (H-3); 4.47 (H-4) ppm; some decomposition of Pd species occurred. [c] Major methyl–tin product, δ 0.80 ppm $J^{119}Sn-^1H$ 60 Hz: a little Me_3SnCl also detected (δ 0.65ppm); sugar absorption complex not resolved. [d] Deprotected tin–sugar formed: δ^1H 0.11 (s, H-1), 1.31 (s) and 1.45 (s, CMe_2) ppm.

Table 4 Pesticidal activity

Compound	Rate (ppm)	*Tetranychus* C	Ov.	G	*Myzus* C	*Musca* C	K	*Heliothis* R	G	*Spodoptera* R	G	*Diabrotica* R	*Blattela* R	*Meloidogyne* R
1 (R=Ph)	500	9	0	9	0	0	0	0				0	0	
	250													0
2 (R=Ph)	500	9	9	—	9	0	9	0	0	9	—	9	0	
	380	0	0	0	0	0	0			0	0	0		
	250													5
3 (R=R′=Ph)	500	9	9	—	5	0	0	0	0	0	0	0	0	
	250													9

Key: C contact; Ov. ovicide; G growth; K knockdown; R residual

O 0.49% kill; 5 50–79% kill; 9 80–100% kill; — unassessable

isopropylidene-α-*D*-mannofuranose (**4**) using acetone and concetrated sulphuric acid. DMF was dried over BaO, decanted and distilled prior to use. Diethyl ether was dried over sodium wire. Dichloro(cycloocta-1,5-diene)-platinum and palladium were samples obtained in previous studies.[11]

Preparation of triphenylstannylmethyl 2,3:5,6-di-*O*-isopropylidine-α-*D*-mannofuranoside, 3 (R = R′ = Ph)

To a solution of 2,3:5,6-di-*O*-isopropylidene-α-*D*-mannofuranose (**4**) (2.60 g; 0.01 mol) in dry DMF

Table 5 Fungicidal and bactericidal activity *in vitro*

Organism	Compound at 25 ppm		
	1(R=Ph)	**2**(R=Ph)	**3**(R=R′=Ph)
Cladosporium sphaerospermum	2	2	2
Aerobasidium pullulans	0	2	0
Alternaria tenuis	0	4	0
Aspergillus niger	0	2	0
Trichoderma viride	0	2	0
Penicillium digitatum	0	2	0
Colletotrichum musae	0	2	0
Botrytis cinerea	0	0	0
Fusarium culmorum	0	0	0
Geotrichum candidum	0	0	0
Verticillum albo-atrum	4	2	0
Erwinia carotovora	0	0	0
Xanthomonas campestris malvacearum	0	0	0
Pseudomonas solanacearum	0	0	0
Phytophthora cinnamomi	2	2	2
Colletotrichum coffeanum	2	2	2
Cercospora beticola	4	2	2
Septoria nodorum	2	2	2
Pseudocercosporella herpotrichoides	2	2	2

Key: 4 no disease
3 trace–5% disease
2 6–25% disease
1 26–60% disease
0 >60% disease

(25 cm^3) under a nitrogen atmosphere was slowly added excess sodium hydride (50% suspension in mineral oil) until evolution of hydrogen ceased. Iodomethyltriphenyltin (4.9 g; 0.01 mol) in dry DMF (20 cm^3) was added dropwise. After 2 h stirring, TLC showed some unreacted starting materials still to be present. More sodium hydride was added and stirring continued for a further 30 min before the careful addition of methanol (10 cm^3) to destroy any excess sodium hydride. The reaction mixture was diluted with chloroform (250 cm^3), washed with water (4 × 100 cm^3) and dried over magnesium sulphate, before removal of the solvent by rotary evaporation. The product was isolated by use of a chromatotron (eluant: diethyl ether–hexane) as a colourless syrup; yield 4.2 g, 67%, $[\alpha]_D^{20}$ +20.42 ($CHCl_3$).

Analysis. Found:C, 60.1; H, 5.9. Calculated for $C_{31}H_{36}O_6Sn$: C, 59.7; H, 5.8%.

The ^1H NMR and ^{119}Sn NMR spectra are given in Tables 1 and 2.

MS (20 eV) *m/z* (%, fragment): 609 (2,$M^+ - Me$), 547 (<1, $M^+ - Ph$), 535 (1), 489 (<1, $M^+ - Ph - Me_2CO$), 463 (1), 446 (<1, $M^+ - Ph - CH_2CHOCMe_2O$), 409 (3), 381 (<1, $Ph_3SnCH_2O^+$), 197 (14, $PhSn^+$), 120 (9, Sn^+) 101 (14, $CH_2CHOCMe_2O^+$), 78 (23, PhH^+).

Preparation of trimethylstannylmethyl 2,3:5,6-di-*O*-isopropylidene-α-*D*-mannofuranoside, 3 (R = R′ = Me)

This was prepared from iodomethyltrimethyltin (3.50 g; 0.01 mol), 2,3:5,6-di-*O*-isopropylidene-α-*D*-mannofuranose (2.60 g; 0.01 mol) and excess sodium hydride by an analogous procedure to that described for the triphenylstannyl derivative. The product was isolated by the use of a chromatotron as a colourless syrup; yield 2.33 g, 53%.

Analysis. Found: C, 43.7; H, 7.0. Calculated for $C_{16}H_{30}O_6Sn$: C, 44.0; H, 6.9%.

The ^1H NMR spectra details are in Table 1.

MS (20 eV) *m/z* (%., fragment): 423 (15, M^+-15, 365 (7, $M^+-Me-Me_2CO$), 349 (2), 307 (1, M^+-2Me, $-\overline{CH_2CHOCMe_2O}$), 277(9), 261(3), 245(6), 223(12), 195 (20, $Me_3SnCH_2O^+$), 185 (12, $M^+-Me_3SnCH_2O$, $-Me_2CO$), 179 (3, $Me_3SnCH_2^+$) 165 (100, Me_3Sn^+), 135 (6, $MeSn^+$), 127 (10, $M^+-Me_3SnCH_2O$, $-\overline{CH_2CHOCMe_2O}$, $-Me$), 101 (35, $\overline{CH_2CHOCMe_2O^+}$).

Transmetallation reactions of 3 (R = R′ = Ph) with phenyllithium

(a) Trapping with acetone

A solution of **3** (R=R′=Ph) (1.418 g; 2.28 × 10^{-3} mol) in dry Et_2O (40 cm^3) under nitrogen was cooled to −64°C. Phenyllithium (1.2 molar ratio equiv., 1.6 cm^3 of 1.7 mol dm^{-3} solution in cyclohexane–ether; 2.72 × 10^{-3} mol) was added slowly by syringe and the reaction mixture stirred at −64°C for 1 h before the addition of anhydrous acetone (2 cm^3 *ca* 10-fold excess). The reaction was allowed to warm up to room temperature overnight, then hydrolysed (60 cm^3 of aqueous pH (6.6) buffer solution) and extracted into diethyl ether (3 × 20 cm^3). The combined ethereal extracts were dried over magnesium sulphate and chilled in an ice-bath before filtration to remove the bulk of the tetraphenyltin. The residue on removal of the solvent was chromatographed on a chromatotron, leading to isolation of the expected acetone adduct (**7b**) (0.28 g, 37%) as white crystals, m.p. 63–66°C.

2-Hydroxy-2-methylpropyl 2,3:5,6-di-*O*-isopropylidene-α-*D*-mannofuranoside (7b)

^{1}H NMR ($CDCl_3$, 220 MHz): δ 4.99 (s, 1H, H-1), 4.78 (dd, 1H, $J_{2,3}$ 5.5 Hz, $J_{3,4}$ 3.6 Hz, H-3), 4.63 (d, 1H, $J_{2,3}$ 5.5 Hz, H-2), 4.38 (m, 1H, $J_{4,5}$ 7.2 Hz, $J_{5,6}$ 7.0 Hz, $J_{5,6'}$ 4.8 Hz, H-5), 4.09 (dd, 1H, $J_{5,6}$ 7.0 Hz, $J_{6,6'}$ 8.9 Hz, H-6), 3.98 (dd, 1H, $J_{5,6'}$ 4.8 Hz, $J_{6,6'}$ 8.9 Hz, H-6′), 4.04 (dd, 1H, $J_{3,4}$ 3,6 Hz, $J_{4,5}$ 7.2 Hz, H-4), 3.47 (d, 1H, $J_{8,8'}$ 9.6 Hz, H-8′), 3.26 (d, 1H, $J_{8,8'}$ 9.6 Hz, H-8), 2.27 (broad s, 1H, OH), 1.43, 1.41, 1.34 and 1.30 (all s, 4 × 3H, 2 × CMe_2), 1.18 and 1.17 (both s, 2 × 3H, $Me_2C(OH)$—).

(b) Trapping with acetophenone

By an analogous procedure to that described above, **3** (R=R′=Ph) (1.800 g; 2.89 × 10^{-3} mol) in dry Et_2O (30 cm^3), phenyllithium (1.2 molar ratio equiv., 2.0 cm^3 of a 1.7 mol dm^{-3} solution in cyclohexane–ether, 3.40 × 10^{-3} mol) and acetophenone (1.5 equiv., 0.5 cm^3; 4.27 × 10^{-3} mol) gave a mixture of two stereoisomers (60:40 ratio) as a syrup, viz. 2-hydroxy-2-phenylpropyl 2,3:5,6-di-*O*-isopropylidene-α-*D*-mannofuranoside (**7a**).

Stereoisomer A (40%)

^{1}H NMR ($CLCl_3$, 220 MHz): δ 7.48–7.17 (m,5H,Ph), 4.99 (s,1H,H-1), 4.63 (dd, 1H, $J_{2,3}$ 5.5 Hz, $J_{3,4}$ 3.6 Hz, H-3) 4.52 (d, 1H, $J_{2,3}$ 5.5 Hz, H-2), 4.33 (m, 1H, $J_{4,5}$ 7.2 Hz, $J_{5,6}$ 6.5 Hz, $J_{5,6'}$ 4.8 Hz, H-5), 4.06 (dd, 1H, $J_{5,6}$ 6.5 Hz, $J_{6,6'}$ 7.7 Hz, H-6), 3.95 (dd, 1H, $J_{5,6'}$ 4.8 Hz, $J_{6,6'}$ 7.7 Hz, H-6′), 3.72 (d, 1H, $J_{8,8'}$ 7.2 Hz, H-8), 3.63 (dd, 1H, $J_{3,4}$ 3.6 Hz, $J_{4,5}$ 7.2 Hz, H-4), 3.44 (d, 1H, $J_{8,8'}$ 7.2 Hz, H-8′), 2.32 (s, 1H, OH), 1.37 (s, 3H, Me(Ph)C(OH)—), 1.40, 1.40, 1.34, 1.24 (all s, 4 × 3H, 2 × CMe_2).

Stereoisomer B (60%)

^{1}H NMR ($CDCl_3$, 220 MH_z): δ 7.48–7.17 (m, 5H, Ph), 4.47 (s, 1H, H-1), 4.69 (dd, 1H, $J_{2,3}$ 6.2 Hz, $J_{3,4}$ 4.1 Hz, H-3) 4.53 (d, 1H, $J_{2,3}$ 6.2 Hz, H-2), 4.33 (m, 1H, $J_{4,5}$ 7.0 H, $H_{5,6}$ 6.5 Hz, $J_{5,6'}$ 4.8 Hz, H-5), 4.06 (dd, 1H, $J_{5,6}$ 6.5 Hz, $J_{6,6'}$ 7.7 Hz, H-6), 3.95 (dd, 1H, $J_{5,6'}$ 4.8 Hz, H-6′), 3.88 (d, 1H, $J_{8,8'}$ 9.6 Hz, H-8), 3.79 (dd, 1H, $J_{3,4}$ 4.1 Hz, $J_{4,5}$ 7.0 Hz, H-4), 3.51 (d, 1H, $J_{8,8'}$ 9.6 Hz, H-8′), 3.07 (s, 1H, OH) 1.47 (s, 3H, MePhC(OH)—), 1.40, 1.40, 1.32 and 1.24 (all s, 4 × 3H, 2 × CMe_2).

(c) Trapping with mercury chloride

By an analogous procedure to that used for acetone, **3** (R=R′=Ph) (1.175 g; 1.89 × 10^{-3} mol) in dry Et_2O (20 cm^3), phenyllithium (1.1 molar ratio equiv.; 1.2 cm^3 of a 1.7 mol dm^{-3} solution in cyclohexane–ether, 2.08 × 10^{-3} mol) and mercury chloride (0.5 molar ratio equiv.; 0.256 g; 0.94 × 10^{-3} mol) gave, after separation on the chromatotron, methyl 2,3:5,6-di-*O*-isopropylidene-α-*D*-mannofuranoside (16%) and the diorganomercury species **6** (34%). The mercury product slowly decomposed in $CDCl_3$ solution to give a deposit of mercury.

Methyl 2,3:5,6-di-*O*-isopropylidene-α-*D*-mannofuranoside

^{1}H NMR ($CDCl_3$, 220 MHz): δ 4.87 (s, 1H, H-1), 4.75 (dd, 1H, $J_{2,3}$ 5.5 Hz, $J_{3,4}$ 4.3 Hz, H-3), 4.55 (d,

1H, $J_{2,3}$ 5.5 Hz, H-2), 4.40 (m, 1H, $J_{4,5}$ 7.7 Hz, $J_{5,6}$ 6.2 Hz, $J_{5,6'}$ 4.8 Hz, H-5), 4.11 (dd, 1H, $J_{5,6}$ 6.2 Hz, $J_{6,6'}$ 8.6 Hz, H-6), 4.03 (dd, 1H, $J_{5,6'}$ 4.8 Hz, $J_{6,6'}$ 8.6 Hz, H-6′), 3.79 (dd, 1H, $J_{3,4}$ 4.3 Hz, $J_{4,5}$ 7.7 Hz, H-4), 3.30 (s, 3H, OCH_3), 1.43, 1.43, 1.35 and 1.30 (all s, 4 × 3H, 2 × CMe_2).

Bis(2,3:5,6-di-*O*-isopropylidene-α-*D*-mannofuranosylmethyl)mercury (6)

^{1}H NMR ($CDCl_3$, 220 MHz): δ 4.84(s, 1H, H-1), 4.74 (dd, 1H, $J_{2,3}$ 5.3 Hz, $J_{3,4}$ 4.1 Hz, H-3), 4.53 (d, 1H, $J_{2,3}$ 5.3 Hz, H-2), 4.39 (m, 1H, $J_{4,5}$ 7.7 Hz, $J_{5,6}$ 6.5 Hz, $J_{5,6'}$ 4.8 Hz, H-5), 4.10 (dd, 1H, $J_{5,6}$ 6.5 Hz, $J_{6,6'}$ 9.1 Hz, H-6), 4.05 (dd, 1H, $J_{5,6'}$ 4.8 Hz, $J_{6,6'}$ 9.1 Hz, H-6′), 3.88 (dd, 1H, $J_{3,4}$ 4.1 Hz, $J_{4,5}$ 7.7 Hz, H-4), 1.42, 1.41, 1.34, and 1.29 (all s, 4 × 3H, 2 × CMe_2).

Direct reactions of 3 with electrophiles

Solutions containing equimolar ratios of **3** and the electrophile were prepared and the reaction investigated by ^{1}H NMR spectroscopy at 30°C.

With **3** (R=R′=Ph), the following electrophiles (solvents) were used:

(i) I_2 (CCl_4); (ii) CF_3CO_2H ($CDCl_3$); and (iii) Cl_2PtCOD (CD_2Cl_2).

In each case, phenyl–tin bond cleavage resulted in the quantitative formation of (i) PhI, (ii) PhH and (iii) PhClPt(COD) as well as the appropriate tin–carbohydrate derivative **3** (R=Ph; R′=I, $OCOCF_3$ and Cl, respectively).

PhClPt(COD)

^{1}H NMR (CD_2Cl_2, 220 MH_z): 2.46 (m, 8H, CH_2), 4.51 (t, 2H, J^{195}Pt–^{1}H 7.5 Hz), 5.72 (t, 2H, CH, J^{195}Pt–^{1}H 34 Hz), 6.7–7.4 (m, 5H, phenyl); lit.[20] value ($CDCl_3$): 2.58 (m, 8H, CH_2), 4.60 (t, 2H, J^{195}Pt–^{1}H 76 Hz), 5.81 (t, 2H, CH, J^{195}Pt–^{1}H 34 Hz), 6.8–7.5 (m, 5H, phenyl).

Tables 1 and 2 list the NMR parameters for the tin products. Confirmation of the quantitative cleavage of a Ph–Sn bond in **3** (R=R′=Ph) by I_2 with formation of PhI, was obtained using GC (with PhBr as internal standard).

The following electrophiles were used with **3** (R=R′=Me):

(i) CF_3CO_2H, (ii) I_2, (iii) Br_2 (at −10°C in the dark), (iv) CH_3COCl, (v) PhCOCl, (vi) $ClCO_2Et$, (vii) SO_2, (viii) $SnCl_4$ (in CD_2Cl_2) and (ix) Cl_2PdCOD (in CD_2Cl_2).

Except where indicated, the solvent used was $CDCl_3$ at a temperature of 30°C.

The results for **3** (R=R′=Me) reactions are given in Table 3. ^{1}H NMR data for **3** (R=Me, R′]Br and Cl) are in Table 1.

Acknowledgements We wish to thank the SERC (OJT) and the University of Aberdeen (CRMcD) for research grants and Professor J S Brimacombe for measuring the optical rotations. ICI Plant Protection (Agrochemicals) is also thanked for carrying out the evaluation of the biological activity.

REFERENCES

1. Davies, A G and Smith, P J In: *Comprehensive Organometallic Chemistry*, Wilkinson, G, Stone, F G A and Abel, E W (eds), Pergamon, Oxford, 1982, chapter 11
2. Pereyre, M, Quintard, J-P, and Rahm, A *Tin in Organic Synthesis*, Butterworths, London, 1987
3. Blunden, S J, Cusack, P A and Smith, P J, *J. Organomet. Chem.*, 1987, 325:141
4. David, S and Hanessian, S *Tetrahedron*, 1985, 141:643
5. Patel, A and Poller, R C *Rev. Si, Ge, Sn, Pb Compds*, 1985, 8:264
6. Hall, L D, Steiner, P R and Miller, D C *Can. J. Chem.*, 1979, 57:38
7. Hall, L D and Neeser, J R *J. Chem. Soc., Chem. Comm.*, 1982:887
8. Beau, J M and Sinay, P *Tetrahedron Lett*, 1985, 26:6165
9. Lisimple, P, Beau, J M, Jaurand, G and Sinay, P *Tetrahedron Lett.*, 1986, 27:6201
10. Taylor, O J and Wardell, J L *Recl. Trav. Chim. Pays-Bas*, 1988, 107:267
11. Taylor, O J and Wardell, J L *J. Chem. Res (S)*, 1989, 98; *J. Chem. Res (M)*, 1989, 852
12. Taylor, O J, Wardell, J L and Mazhar, M *Main Group Metal Compounds*, 1989, (in press)
13. Cox, P J, Doidge-Harrison, S M S V, Howie, R A, Nowell, I W, Taylor, O J and Wardell, J L *J. Chem. Soc., Perkin Trans 1*, 1989, (to be published)
14. Hale, K J, Hough, L and Richardson, A C *Carbohydr. Res.*, 1988, 177:259
15. Ref. 2, p 60
16. Wardell, J L In: *Inorganic Reactions and Methods*, Zuckerman, J J (ed), VCH Publishers, New York, 1988, vol. II, Section 552.31, p 39
17. Wardell, J L In: *The Chemistry of the Metal Carbon Bond*, Hartley, F R (ed), Wiley, New York, 1987, vol 4, chapter 1
18. Taylor, R D and Wardell, J L *J. Chem. Soc., Dalton Trans.*, 1976:1345
19. Schmidt, O T In: *Methods in Carbohydrate Chemistry* Whistler, R L and Wolfrom, N L (eds) Academic Press, New York, vol 2, p 38
20. Eaborn, C, Odell, K T and Pidcock, A *J. Chem. Soc., Dalton Trans.*, 1978:357