ELSEVIER

Journal of Organometallic Chemistry 498 (1995) 275–282

Journal of Organometallic Chemistry

2-Diphenylarsino-, 2-diphenylphosphinyl-, and 2-triphenylstannyl-derivatives of methyl 4,6-O-benzylidene-2-deoxy-α-D-altropyranoside. Crystal structure of the phosphinyl derivative

Martyn A. Brown [a], Philip J. Cox [b], R. Alan Howie [a], Olga A. Melvin [b], Oonah J. Taylor [a], James L. Wardell [a,*]

[a] *Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, AB9 2UE, UK*
[b] *School of Pharmacy, The Robert Gordon University, Schoolhill, Aberdeen, AB9 1FR, UK*

Received 22 February 1995

Abstract

Reaction of methyl 2,3-anhydro-4,6-O-benzylidene-α-D-allopyranoside (3) with Ph_nMLi [M = As or P, $n = 2$; M = Sn, $n = 3$] gives methyl 4,6-O-benzylidene-2-deoxy-2-M-α-D-altropyranoside (4; M = Ph_2As, Ph_2P or Ph_3Sn). Compound (4, M = Ph_2P) is readily oxidised in air to the phosphinyl derivative (4, M = $Ph_2P(O)$). Characterisation of (4, M = Ph_2As, $Ph_2P(O)$, or Ph_3Sn) was achieved by NMR spectroscopy, including solid state NMR spectroscopy, for (4, M = Ph_2As) and (4, M = Ph_3Sn), and by X-ray crystallography for [4, M = $Ph_2P(O)$]. In the solid state both the benzylidene and pyranose rings in [4, $Ph_2P(O)$], adopt chair conformations. The pentavalent phosphorus atom has a distorted tetrahedral geometry with C–P–C valency angles in the narrow range from 105.7(3) to 106.0(3)° and the C–P–O valency angles ranging from 111.3(3) to 115.6(2)°; the P–C_{aryl} bond lengths are 1.808(5) and 1.815(6) Å, while the P–C_{alkyl} bond length is slightly larger, being 1.829(6) Å. Intermolecular H-bonding, involving HO and O(P) centres, links the molecules in the crystal.

Keywords: Tin; Phosphorus; Arsinic; Pyranosides; Crystal structure

1. Introduction

The monosaccharide derivatives, methyl 4,6-O-benzylidene-3-deoxy-3-M-α-D-altropyranoside (**1**; M = Ph_2As, Ph_2P and Ph_3Sn) have been obtained by opening of the epoxide ring in methyl 2,3-anhydro-4,6-O-benzylidene-α-D-mannopyranoside (**2**) on reaction with Ph_2AsLi [1], Ph_2PLi [2] and Ph_3SnLi [3,4], respectively [Eq. (1)].Compound (**1**, Ph_2P) is very readily oxidised in air to give the diphenylphosphinyl derivative [**1**, $Ph_2P(O)$]. Crystal structures of (**1**, Ph_2As) [1], [**1**, $Ph_2P(O)$] [2] and (**1**, Ph_3Sn) [3] have been reported.

Hall et al. [4] have reported that an isomer of (**2**), methyl 2,3-anhydro-4,6-O-benzylidene-α-D-allopyranoside (**3**), also underwent an epoxide ring-opening reaction with Ph_3SnLi to give methyl 4,6-O-benzylidene-2-deoxy-2-M-α-D-altropyranoside (**4**, M = Ph_3Sn), (Eq. (2)).

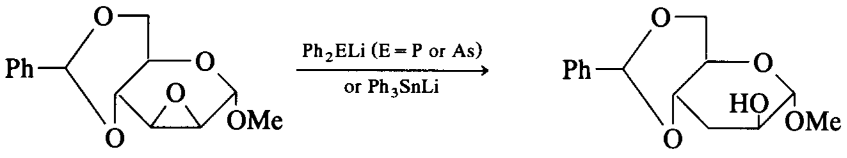
We now report on the ring opening of (**3**) by Ph_2AsLi or Ph_2PLi and the formation of (**4**, M = Ph_2As or Ph_2P). Compound (**4**, M = Ph_2P) was readily oxidised in air to [**4**, M = $Ph_2P(O)$]. Some NMR spectral data for [**4**, M = Ph_2As, $Ph_2P(O)$, and Ph_3Sn] are presented and the crystal structure of [**4**, M = $Ph_2P(O)$] is reported.

2. Experimental details

Solution NMR spectra were recorded on a Bruker 250 MHz instrument. Solid state NMR spectra were recorded by the SERC service based at Durham. IR spectra were recorded on a Phillips Analytical PU 9800 Fourier-transform spectrometer. Mass spectra were recorded on an AEI MS30 instrument or were recorded

* Corresponding author.

SSDI 0022-328X(95)05529-0



(1)

(2) (1: M = Ph_2P, Ph_2As or Ph_3Sn)

by the SERC MS service based at Swansea. In the case of tin-containing fragments, the quoted m/z values are based on ^{120}Sn.

2.1. Methyl 4-6-O-benzylidene-α-D-glucopyranoside (5) [5]

Methyl α-D-glucopyranoside (10.0 g) was shaken with anhydrous zinc chloride (9 g) and freshly distilled benzaldehyde (30 g) for 3 h. The resulting viscous material was added to ice-water, whereupon crystallisation took place. The solid was filtered off, washed with water and recrystallised twice from either water or benzene–chloroform; yield 8.1 g (52%), m.p. 161–162°C, literature [5] m.p. 161–163°C.

2.2. Methyl 4,6-O-benzylidene-2,3-di-O-p-toluenesulphonyl-α-D-glucopyranoside (6) [6]

A solution of compound (5) (5.0 g) in anhydrous pyridine (40 ml) was stirred as *p*-toluenesulphonyl chloride (10 g) was added at room temperature. The mixture was kept at room temperature for 48 h then poured onto ice, upon which crystallisation occurred. After the ice had melted, the solid was filtered off, washed with water and recrystallised twice from ethanol; Yield 6.9 g (66%); m.p. 153–154°C, literature [6] m.p. 154–155°C.

2.3. Methyl 2,3-anhydro-4,6-O-benzylidene-α-D-allopyranoside (3) [6]

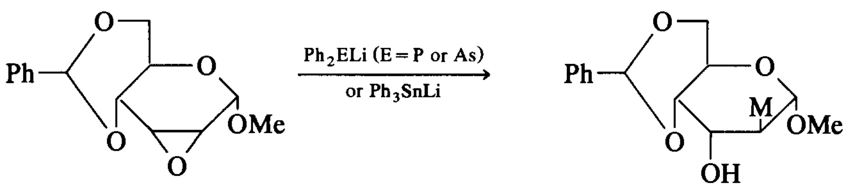
Compound (6) (10.0 g) was dissolved in dry chloroform (100 ml) and a solution sodium (1.2 g) in dry methanol (30 ml), was added. The mixture was allowed to stand at room temperature for 48 h, then diluted with water (100 ml). The organic layer was separated, washed with water and dried over anhydrous calcium chloride. The solvent was removed under reduced pressure to leave solid (3), which was recrystallised from chloroform–ethanol. Yield: 4.0 g (96%); m.p. 200–201°C, literature [6] m.p. 199–200°C.

2.4. Methyl 4,6-O-benzylidene-2-deoxy-2-C-diphenylphosphinyl-α-D-altropyranoside [4, M = $Ph_2P(O)$]

A solution of (3) (2.50 g, 9.5 mmol) in anhydrous THF (20 ml) was added dropwise under dinitrogen to a cooled stirred solution of lithium diphenylphosphinide [2] (10 mmol) in anhydrous THF (50 ml). The solution became colourless immediately after complete addition. The mixture was allowed to attain room temperature and was then stirred for a further 1 h. Water (100 ml) was added and the THF removed under reduced pressure. The aqueous solution was extracted with benzene (3 × 80 ml) and the combined extracts were washed with water (2 × 100 ml) and dried over magnesium sulphate then filtered and the filtrate was evaporated to leave crude [4, M = $Ph_2P(O)$].

Recrystallisation (twice) from ethyl acetate–methanol afforded the pure product: Yield 3.5 g (76%); m.p. 253–256°C (dec). Anal. Found: C, 67.2; H, 5.7%. $C_{26}H_{27}O_6P$ Calc.: C, 67.0; H, 5.8%.

^1H NMR ($CDCl_3$). δ(ppm): 7.87 (m, 4H, *o*-H of Ph_2P), 7.54 (m, 8H, *m*-H + *o*-H of Ph_2P + *o*-H of Ph), 7.34 (m, 3H, *m*-H + *p*-H of Ph), 5.70 (s, 1H, PhC*H*), 4.83 (d, 1H, $J(^{31}P-^{1}H) = 8.5$ Hz, H-1), 4.35 (m, 4H, H-3 + H-4 + H-5 + H-6), 3.93 (m, 1H, H-6), 3.31 (s, 3H, OMe), 3.21 (d, 1H, $J(^{31}P-^{1}H) = 11.8$ Hz, H-2). ^1H NMR (DMSO). δ (ppm): 7.99 (m, 4H, *o*-H of Ph_2P), 7.57 (*m*, 6H, *m*-H + *p*-H of Ph_2P), 7.44 (m, 2H, *o*-H of Ph), 7.33 (m, 3H, *m*-H + *p*-H of Ph), 5.64 (s, 1H, PhC*H*), 5.19 (dd, 1H, $J = 1.20$ Hz, $J = 4.13$ Hz, OH), 4.55 (d, 1H, $J(^{31}P-^{1}H) = 9.7$ Hz, H-1), 4.10 (m, 3H, H-4 + H-5 + H-6), 4.05 (m, 1H, H-3), 3.67 (m, 1H, H-6), 3.40 (d, 1H, $J(^{31}P-^{1}H) = 13.4$ Hz, H-2), 3.37 (s, 3H, OMe). ^{13}C and ^{31}P NMR spectral data are displayed in Table 1. IR (cm^{-1}); 3400 (OH), 1220 (PO). MS EI m/z (%, fragment): 467 (5, MH^+), 449 (10, $M^+ - OH$), 435 (15, $M^+ - OMe$), 259 (20, $M^+ -$



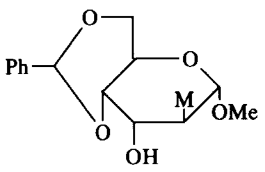
(2)

(3) (4: M = Ph_2P, Ph_2As or Ph_3Sn)

Table 1
^{13}C NMR spectral data ($\delta^{13}C$ (ppm), $J(^{119}Sn-^{13}C)$ (H_z); [$J(^{31}P-^{13}C)$] (H_z)) for compounds (**4**) [a]

M	C_1	C_2	C_3	C_4	C_5	C_6	C_7	OMe	PhCHO	Ph–M	$\delta^{13}P$ or $\delta^{119}Sn$
Ph_3Sn ($CDCl_3$ soln)	101.5 (14.5)	37.5 (327)	68.3 (9.6)	58.8	78.3	69.0	102.1	55.3	C_i 137.2 C_o 128.2 C_m 126.2 C_p 129.1	C_i 136.6 (519) C_o 137.2 (36.1 C_m 129.0 (50.1) C_p 129.6 (11.4)	−115.8
Ph_3Sn (solid state)	101.9	39.1	69.5	59.0	80.1	69.5	104.2	55.5	128.8 to 138.1 (broad signals)		−113.3 and −93.6
$Ph_2P(O)$-($CDCl_3$ soln)	97.0 [5.5]	46.6 [67.2]	64.9 [4.5]	57.7	77.0	69.0	101.9	55.4	C_i 137.2 C_o 128.2 C_m 126.2 C_p 129.0	C_i 131.0 [100.9]; 130.9 [99.9] C_o 130.7 [8.8]; 130.6 [8.8] C_m 129.0 [11.8] C_p 132.6 [–]	28.95
$Ph_2P(O)$ (DMSO soln.)	98.0 [6.3]	47.9 [66.0]	64.8 [4.3]	58.6	78.8	70.0	102.5	56.4	C_i 139.5 C_o 129.5 C_m 128.1 C_p 130.4	C_i 133.8 [98.5]; 133.4 [96.7] C_o 132.2$_3$ [8.8]; 132.18 [9.0] C_m 130.7 [11.4]; 130.6 [11.4] C_p 133.7 [2.1]; 133.1 [2.3]	29.14
Ph_2As ($CDCl_3$ soln.)	100.3	44.7	67.4	58.7	77.8	69.3	102.2	55.9	C_i 137.2 C_o 128.2 C_m 126.3 C_p 129.1	C_i 137.7; 137.3 C_o 133.3; 133.0 C_m 129.1; 129.1 C_p 129.3; 129.2	
Ph_2As (solid state)	102	45 (vbr)	68.9	60.8	78.0	70.6	102	55.5	128.5–138.4	128.5–138.4	

[a] Structure



PPh_2O, $-Me_2CO$), 203 (85, $Ph_2PO_2H_2^+$), 201 (100, Ph_2PO), 105 (39, $PhCO^+$), 91 (34, $C_7H_7^+$) MS CI(NH_3) m/z (%, fragment): 467 (100, MH^+), 449 (25, M^+–OH), 435 (30, M^+–MeO), 219 (10, $Ph_2PO_2H_2^+$), 203 (55, $Ph_2POH_2^+$), 106 (7, $PhCHO^+$).

2.5. Methyl 4,6-O-benzylidene-2-deoxy-2-C-diphenylarsino-α-D-altropyranoside (4, M = Ph_2As).

A stirred solution of lithium diphenylarsinide (22 mmol) in anhydrous THF (100 ml) [1] was cooled in an ice-bath and solution of compound (3) (5.3 g, 20 mmol) in anhydrous THF (50 ml) was added dropwise under dinitrogen. The reaction mixture became colourless on reaching room temperature. Stirring under dinitrogen was continued for 1 h. Water (100 ml) was added and the THF evaporated under reduced pressure. The aqueous solution was extracted with ethyl acetate (3 × 80 ml) and the combined extracts were washed with water, dried over anhydrous magnesium sulphate, and evaporated to give yellow solid (4, M = Ph_2As), which was recrystallised from ethyl acetate–hexane as yellow needles. Yield 7.9 g (79.5%); m.p. 185–187°C. Anal. Found: C, 63.2; H, 5.6%. $C_{26}H_{27}O_5As$ Calc.: C, 63.2; H, 5.5%.

^1H NMR ($CDCl_3$) δ (ppm): 7.58–7.27 [m, 15H, Ph_2As + Ph], 5.66[s, 1H, PhC*H*], 4.54 (s, 1H, H-1), 4.34 [m, 2H, J (H_5–H_6) = 5.0 Hz, J(H_6–H_6) = 11.8 Hz, H_5 + H_6], 4.12 [m, 2H, J(H_3–H_4) = 2.9 Hz, H-3 + H-4], 3.85 (m, 1H, H_6), 3.31 [s, 3H, OMe], 3.17 [d, 1H, J(H_2–H_3) = 1.89 Hz, H-2]. ^{13}C NMR spectral data are displayed in Table 1.

2.6. Methyl 4,6-O-benzylidene-2-deoxy-2-triphenylstannyl-α-D-altropyranoside (4, M = Ph_3Sn)

This was prepared by a modification of the procedure, published by Hall et al. [4]. A solution of triphenylstannyl-lithium [prepared from triphenyltin chloride (2.50 g, 6.50 mmol) and lithium (0.46 g, 0.065 mol) in anhydrous THF (20 ml) was added slowly under dinitrogen to a solution of (3) (1.00 g, 3.80 mmol) in anhydrous THF (25 ml). The green colour of the triphenylstannyl-lithium disappeared immediately on addition, to give a brown solution. The mixture was stirred for 1 h, hydrolysed with water (100 ml), neutralised with ammonium chloride, and extracted into chloroform (3 × 50 ml). The extract was dried over magnesium sulphate. The solvent was removed by rotary evaporation to leave a syrup, which was taken up in cold diethyl ether. Most of the hexaphenylditin byproduct was removed by filtration and the required product was isolated by thin layer chromatography (eluant: diethyl ether-hexane, 1:1) as a syrup, which gave a foam-like solid when all traces of solvent were removed. Yield 1.83 g, (78%). Anal. Found: C, 61.5; H, 5.1%. $C_{32}H_{32}O_5Sn$ Calc.: C, 62.5; H, 5.2%. ^1H NMR ($CDCl_3$)δ (ppm): 7.61–7.25 [m, 20H, J(^{119}Sn–^1H) = 50 Hz, Ph_3Sn + Ph], 5.05 [s, 1H, J(^{119}Sn–^1H) = 24 Hz, H-1], 5.04 (s, 1H, PhC*H*), 4.43 [dt, 1H, J (H_3–OH) = 7.84 Hz, J (H_2–H_3) = 2.52 Hz, J (H_3–H_4) = 2.80 Hz, H-3], 4.23 (m, 2H, H-5 + H-6), 3.65 (dd, 1H, J(H_3–H_4) = 2.80 Hz, J(H_4–H_5) = 9.36 Hz, H-4], 3.41 (m, 2H, OH + H-6), 3.34 (s, 3H, OMe), 2.81 [d, 1H, J(H_2–H_3) = 2.52 Hz, J(^{119}Sn–^1H) = 70 Hz, H-2]. MS (20 eV) m/z (%, fragment): 507(10, M^+ – Ph, –Me, –OH), 351 (48, Ph_3Sn^+), 291 (15, Ph_2SnOH^+), 274 (12, Ph_2Sn^+), 197 (34, $PhSn^+$), 154 (34), 149 (27), 120 (23, Sn^+), 105(100, $PhCO^+$). ^{13}C NMR and ^{119}Sn NMR spectral data of (4, M = Ph_3Sn) are displayed in Table 1.

Table 2
Crystal data and structure refinement

Empirical formula	$C_{26}H_{27}O_6P$
Formula weight	466.45
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 12.519(4) Å
	b = 5.815(2) Å
	c = 16.195(5) Å
	α = 90°
	β = 93.22(2)°
	γ = 90°
Volume	1177.1(7)$Å^3$
Z	2
Density (calculated)	1.316 Mg m^{-3}
Absorption coefficient	0.156 mm^{-1}
$F(000)$	492
Crystal size	0.60 × 0.40 × 0.14 mm
θ range for data collection	2.00 to 25.04°
Index ranges	$0 \leqslant h \leqslant 14$
	$0 \leqslant k \leqslant 6$
	$-19 \leqslant 1 \leqslant 19$
Reflections collected	2396
Independent reflections	2305 [R(int) = 0.0242]
Observed reflections ($I > 2\sigma(I)$)	1575
Refinement method	full-matrix l.s. on F^2
Number of parameters	302
Goodness-of-fit on F^2 (S)	0.906
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0576, $wR2$ = 0.1310
R indices (all data)	$R1$ = 0.0977, $wR2$ = 0.1447
Final weighting scheme	$w = 1/[\sigma^2(Fo^2)+(0.0871P)^2]$ where $P = (Fo^2 + 2Fc^2)/3$
Absolute structure parameter	0.0(3)
Residual diffraction max.	0.341 e $Å^{-3}$
Residual diffraction min.	−0.216 e $Å^{-3}$

2.7. X-ray structure determination for [4, M = $Ph_2P(O)$]

The X-ray data were collected on a Nicolet P3 automatic diffractometer with monochromatic Mo Kα

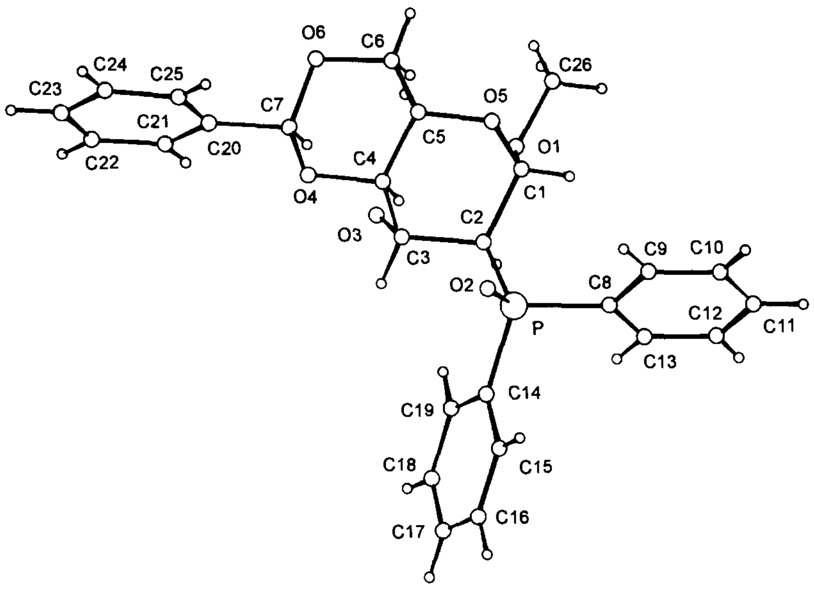


Fig. 1.

radiation; Table 2 lists details. Two standard reflexions monitored every 50 reflexions showed no significant variation in intensity.

The structure was determined by direct methods using SHELXL-86 [7], which revealed the approximate position of the phosphorus atom. The remaining nonhydrogen atoms were located from successive Fourier difference maps using SHELXL-93 [8]. All hydrogen atoms were placed in calculated positions with bond lengths of 1.0 Å, and during refinement were allowed to ride on their attached carbon atoms. Full matrix least-squares calculations with anisotropic temperature factors for the P, O and C and common isotropic temperature factors for the H atoms (methyl and nonmethyl) converged at $R1 = 0.0576$ $[I > 2\sigma(I)]$ and $wR2 = 0.1447$ (all data). The absolute configuration is based on the known stereochemistry of the carbohydrate moiety and gave a lower R value than that for obtained the inverted configuration. This stereochemistry was confirmed by the Flack x parameter = 0.0(3). The scattering factors were taken from SHELXL-93. Final $w = 1/(\sigma^2 Fo^2 + 0.0871P^2)$, where $P = (Fo^2 + 2Fc^2)/3$. All final $\Delta/\sigma = 0.02$, final $\Delta\rho_{min} = -0.216$ e Å^{-3}, final $\Delta\rho_{max} = 0.341$ e Å^{-3}. Molecular diagrams were obtained by the program SNOOPI [9].

Tables of hydrogen atom coordinates and anisotropic displacement parameters have been deposited at the Cambridge Crystallographic Centre.

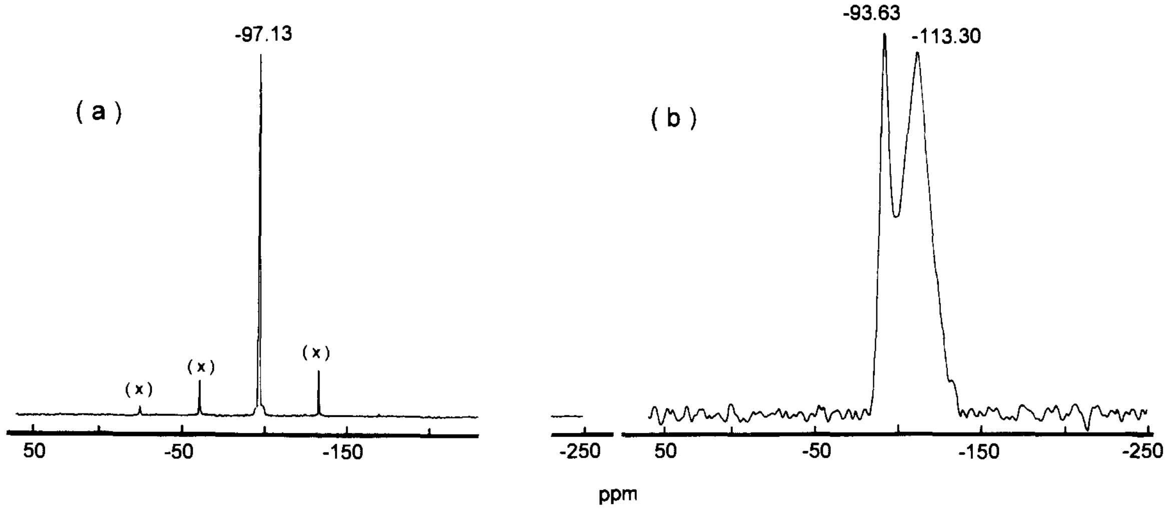


Fig. 2. Solid state ^{119}Sn NMR spectra of (a) (**1**, M = Ph_3Sn), relaxation delay 30 s and (b) (**4**, M = Ph_3Sn); relaxation delay 2.0 s. In both cases cross polarization with flip-back contact time of 1.0 ms was used. x = spinning side bands.

3. Results and discussion

The opening of the epoxide ring in methyl 2,3-anhydro-4,6-O-benzylidene-α-D-allopyranoside (**3**) has been reported by Hall et al. [4] to occur regio- and stereo-specifically on reaction with Ph_3SnLi to give methyl 4,6-O-benzylidene-2-deoxy-2-M-α-D-altropyranoside (**4**, M = Ph_3Sn), (Eq. (2)). As reported in this study, similar reactions occur between (**3**) and either Ph_2AsLi or Ph_2P, the products being (**4**, M = Ph_2As or Ph_2P). Whereas (**4**, M = Ph_2As) is stable in air, (**4**, M = Ph_2P) undergoes ready oxidation, and was indeed characterised as its oxidation product, [**4**, M = $Ph_2P(O)$]. A similar facile oxidation was observed for the isomer of (**4**, M = Ph_2P), namely methyl 4,6-O-benzylidene-3-deoxy-3-M-α-D-altropyranoside (**1**, M = Ph_2P) [2].

Of the three compounds (**4**, M = Ph_3Sn), (**4**, M = Ph_2As) and [**4**, M = $Ph_2P(O)$] prepared in this study, only [**4**, M = $Ph_2P(O)$] gave crystals suitable for X-ray crystallography.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq} [a]
P	7774(1)	1774(3)	6381(1)	33(1)
O(1)	7558(3)	−2747(8)	8203(2)	49(1)
O(2)	8246(3)	4064(8)	6589(2)	45(1)
O(3)	9672(3)	−2996(8)	7502(2)	44(1)
O(4)	10873(3)	860(8)	8018(2)	46(1)
O(5)	8072(3)	1044(7)	8524(2)	41(1)
O(6)	10779(3)	2193(10)	9365(2)	60(1)
C(1)	7573(5)	−450(11)	7933(3)	38(2)
C(2)	8135(4)	−538(10)	7109(3)	32(1)
C(3)	9369(4)	−762(10)	7231(4)	34(1)
C(4)	9739(4)	969(10)	7881(3)	35(1)
C(5)	9189(4)	641(12)	8673(3)	40(2)
C(6)	9628(5)	2408(12)	9300(4)	54(2)
C(7)	11205(5)	2580(12)	8590(4)	51(2)
C(8)	6328(4)	1889(15)	6314(3)	43(1)
C(9)	5813(5)	3680(14)	6671(4)	63(2)
C(10)	4716(7)	3783(20)	6618(6)	89(3)
C(11)	4136(6)	2062(24)	6230(6)	91(3)
C(12)	4638(6)	263(20)	5884(6)	86(3)
C(13)	5738(5)	165(14)	5927(5)	65(2)
C(14)	8154(4)	768(11)	5377(3)	37(1)
C(15)	8030(5)	2346(12)	4744(4)	50(2)
C(16)	8334(5)	1739(18)	3958(4)	59(2)
C(17)	8770(6)	−347(15)	3806(4)	59(2)
C(18)	8890(6)	−1876(13)	4435(4)	59(2)
C(19)	8589(5)	−1388(12)	5219(4)	46(2)
C(20)	12418(6)	2506(15)	8699(4)	62(2)
C(21)	12989(7)	664(22)	8473(8)	129(5)
C(22)	14093(8)	638(25)	8583(8)	153(6)
C(23)	14618(8)	2478(27)	8917(7)	113(5)
C(24)	14060(9)	4305(29)	9148(6)	113(5)
C(25)	12944(8)	4346(22)	9022(6)	102(3)
C(26)	7004(6)	−3064(18)	8929(4)	72(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Bond lengths (Å) and angles (°)

P–O(2)	1.488(5)
P–C(8)	1.808(5)
P–C(14)	1.815(6)
P–C(2)	1.829(6)
O(1)–C(1)	1.406(8)
O(1)–C(26)	1.410(7)
O(3)–C(3)	1.417(7)
O(4)–C(7)	1.410(7)
O(4)–C(4)	1.426(6)
O(5)–C(1)	1.412(7)
O(5)–C(5)	1.425(6)
O(6)–C(7)	1.408(7)
O(6)–C(6)	1.444(7)
C(1)–C(2)	1.544(8)
C(2)–C(3)	1.552(7)
C(3)–C(4)	1.511(8)
C(4)–C(5)	1.502(7)
C(5)–C(6)	1.525(8)
C(7)–C(20)	1.520(9)
C(8)–C(9)	1.369(10)
C(8)–C(13)	1.376(10)
C(9)–C(10)	1.372(10)
C(10)–C(11)	1.369(14)
C(11)–C(12)	1.358(14)
C(12)–C(13)	1.376(9)
C(14)–C(15)	1.378(8)
C(14)–C(19)	1.397(9)
C(15)–C(16)	1.395(9)
C(16)–C(17)	1.358(12)
C(17)–C(18)	1.354(9)
C(18)–C(19)	1.375(8)
C(20)–C(21)	1.350(13)
C(20)–C(25)	1.346(12)
C(21)–C(22)	1.384(12)
C(22)–C(23)	1.35(2)
C(23)–C(24)	1.34(2)
C(24)–C(25)	1.401(13)
O(2)–P–C(8)	111.3(3)
O(2)–P–C(14)	111.7(3)
C(8)–P–C(14)	105.7(3)
O(2)–P–C(2)	115.6(2)
C(8)–P–C(2)	106.0(3)
C(14)–P–C(2)	105.8(3)
C(1)–O(1)–C(26)	113.5(6)
C(7)–O(4)–C(4)	108.9(5)
C(1)–O(5)–C(5)	114.0(4)
C(7)–O(6)–C(6)	110.4(4)
O(1)–C(1)–O(5)	112.8(4)
O(1)–C(1)–C(2)	104.6(5)
O(5)–C(1)–C(2)	113.6(5)
C(1)–C(2)–C(3)	113.1(4)
C(1)–C(2)–P	115.2(4)
C(3)–C(2)–P	110.6(4)
O(3)–C(3)–C(4)	109.2(4)
O(3)–C(3)–C(2)	111.3(5)
C(4)–C(3)–C(2)	107.3(5)
O(4)–C(4)–C(5)	111.3(4)
O(4)–C(4)–C(3)	110.0(5)
C(5)–C(4)–C(3)	111.9(5)
O(5)–C(5)–C(4)	109.1(4)
O(5)–C(5)–C(6)	108.4(5)
C(4)–C(5)–C(6)	108.5(5)
O(6)–C(6)–C(5)	108.1(5)

Table 4 (continued)

O(6)–C(7)–O(4)	111.1(5)
O(6)–C(7)–C(20)	108.6(5)
O(4)–C(7)–C(20)	108.2(6)
C(9)–C(8)–C(13)	119.6(6)
C(9)–C(8)–P	119.8(6)
C(13)–C(8)–P	120.7(6)
C(10)–C(9)–C(8)	120.0(8)
C(11)–C(10)–C(9)	120.0(9)
C(12)–C(11)–C(10)	120.4(7)
C(11)–C(12)–C(13)	119.8(9)
C(8)–C(13)–C(12)	120.2(8)
C(15)–C(14)–C(19)	119.3(6)
C(15)–C(14)–P	115.3(5)
C(19)–C(14)–P	125.3(5)
C(14)–C(15)–C(16)	119.0(7)
C(17)–C(16)–C(15)	121.7(7)
C(18)–C(17)–C(16)	118.6(6)
C(17)–C(18)–C(19)	122.3(7)
C(18)–C(19)–C(14)	119.0(6)
C(21)–C(20)–C(25)	118.7(9)
C(21)–C(20)–C(7)	122.1(7)
C(25)–C(20)–C(7)	119.1(9)
C(20)–C(21)–C(22)	121.0(10)
C(23)–C(22)–C(21)	120.1(13)
C(24)–C(23)–C(22)	119.4(11)
C(23)–C(24)–C(25)	120.4(12)
C(20)–C(25)–C(24)	120.4(12)

3.1. Crystal structure of [4, $M = Ph_2P(O)$]

The atomic arrangement of [**4**, $M = Ph_2P(O)$] and the numbering system used in the crystallographic study are shown in Fig. 1. Atomic coordinates are listed in Table 3, bond lengths and valency angles are shown in Table 4. The pentavalent phosphorus atom has a distorted tetrahedral geometry with C–P–C valency angles in the very narrow range from 105.7(3) to 106.0(3)°; the C–P–O valency angles range from 111.3(3) to 115.6(2)°. The P–C(aryl) bond lengths [1.808(5) and 1.815(6) Å] and the P–C(alkyl) bond length [1.829(6) Å] in [**4**, $M = Ph_2P(O)$] can be compared to the corresponding values in [**1**, $M = Ph_2P(O)$], i.e. [1.823(8) and 1.819(8) Å] and 1.851(8) Å, respectively [2]. The P=O bond length [1.488(5) Å] is similar to those found for other phosphorus carbohydrates, e.g. 1.490(5) Å in [**1**, $M = Ph_2P(O)$] [2], 1.480(5) Å in 1,2,3,5-tetra-O-acetyl-4-deoxy-4-C-[(*S*)-ethylphosphinyl]-α-D-ribofuranose [10] and 1.492(4) Å in 2,3,4-tri-O-acetyl-1,5-anhydro-5,6-dideoxy-5-C-[(*S*)-phenylphosphinyl]-L-iditol [11].

Both the benzylidene and pyranose rings adopt chair conformations in [**4**, $M = Ph_2(O)$]; the pyranose ring conformation is $^4C_1$. The pyranose ring is slightly more distorted from an ideal chair conformation than the benzylidene ring. (See Table 5 for appropriate torsional angles.)

Molecules are linked via intermolecular H-bonds involving P=O(2) and HO(3); O(3)–H(3) = 0.82 Å, O(3) ··· O(2)* = 2.829 Å, O(2)* – H(3) = 2.022 Å and O(2)*–H(3)O(3) = 168.3°. [(2)* indicates the coordinates of O(2) transposed by x, $y-1$, z.]

Table 5
Selected torsional angles (°) [a] determined for [**4**, $M = Ph_2P(O)$] in the solid state

(i) Pyranose ring	
O(5)–C(1)–C(2)–C(3)	45.5(7)
C(1)–C(2)–C(3)–C(4)	46.6(6)
C(2)–C(3)–C(4)–C(5)	56.2(6)
C(3)–C(4)–C(5)–O(5)	−63.5(6)
C(4)–C(5)–O(5)–C(1)	60.4(6)
C(5)–O(5)–C(1)–C(2)	−52.3(6)
(ii) Benzylidene ring	
O(4)–C(4)–C(5)–C(6)	55.0(6)
C(7)–O(4)–C(4)–C(5)	−58.8(6)
C(4)–O(4)–C(7)–O(6)	63.4(6)
C(6)–O(6)–C(7)–O(4)	−65.2(7)
C(7)–O(6)–C(6)–C(5)	59.4(7)
C(4)–C(5)–C(6)–O(6)	−54.0(6)

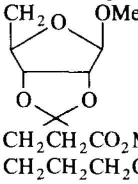
[a] Torsional angles for ideal chair conformations = ±60°.

The exocyclic angles phosphorus makes with one of the phenyl rings (involving C(14) to C(19)) are quite different; C(15)–C(14)–P = 115.3(5)° and C(19)–C(14)–P = 125.3(5)°. The exocyclic angles to the other phenyl ring are essentially the same.

3.2. NMR spectra

The solid state ^{13}C NMR spectra of (**4**, $M = Ph_2As$) and (**4**, $M = Ph_3Sn$) and the solid state ^{119}Sn spectrum of (**4**, $M = Ph_3Sn$) have been obtained (Table 1). No significant differences were observed between the solution (in $CDCl_3$) and solid state ^{13}C NMR spectra of either (**4**, $M = Ph_2As$) or (**4**, $M = Ph_3Sn$), although the solid state spectra were considerably broader, especially in the case of the tin compound; the values of $\delta\,^{13}C$ for particular carbon atoms are similar in all three com-

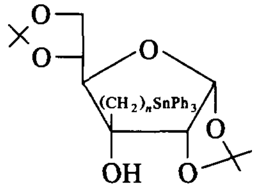
Table 6
$^1J(^{119}Sn-^{13}C)$ coupling constants [a] and $\delta\,^{119}Sn$ values for selected alkyltriphenyltin compounds (Ph_3SnR) in $CDCl_3$ solution

R	$J(^{119}Sn-^{13}C\alpha)$	$J(^{119}Sn-^{13}C_i)$	$\delta\,^{119}Sn$	Ref.
Me	377	510	−92.5	[13]
Et	405	481	−97.3	[13]
Pr	398	480	−101.0	[13]
$CH_2OC_6H_4Me$-p	467	515	−140.8	[14]
(**7**, $n=0$)	484	495	−143.6	[12]
(**7**, $n=1$)	377	518	−111.3	[12]
(**1**, $M = Ph_3Sn$)	379	519	−118.4	[3]
(**4**, $M = Ph_3Sn$)	327	517	−115.8	[b]
	361	509	−109.6	[13]
$CH_2CH_2CO_2Me$	396	504	−99.6	[15]
$CH_2CH_2CH_2OH$	398	491	−100.0	[16]

[a] α-carbon atom is the aliphatic carbon; C_i = *ipso* (aromatic) carbon atom.
[b] This study.

pounds (**4**, M = Ph_2As), (**4**, M = Ph_3Sn) and [**4**, M = $Ph_2P(O)$], except for the values for C-2, the bonding atom of the sugar moiety to the Ph_nM units. The solid state ^{119}Sn spectrum of (**4**, M = Ph_3Sn) gave essentially an envelope of δ ^{119}Sn values (see Fig. 2), from which two maxima at −113.3 and −93.6 ppm could be designated. One of these values corresponds to the single solution $\delta^{119}Sn$ value (−115.8 ppm). The solid state ^{119}Sn NMR spectrum of (**1**, M = Ph_3Sn), an isomer of (**4**, M = Ph_3Sn), was sharp and gave a single $\delta^{119}Sn$ value (−97.1 ppm, Fig. 2); the solution value for (**1**, M = Ph_3Sn), in $CDCl_3$, was determined to be −118.4 ppm [3]. The shift of ca. 20 ppm in going from the solid state to the solution phase merely reflects the phase change and not a conformational or structural change.

The sample of (**4**, M = Ph_3Sn), used to obtain the solid state NMR spectra, was subsequently used for a repeat solution NMR study which gave the spectra the same as those previously recorded. This clearly indicates that in the pure solid sample of (**4**, M = Ph_3Sn), obtained as described in Section 2, tin is present in more than one environment, one of which is similar to that found in solution. As deduced by Hall et al. from the ^1H NMR spectra in benzene, (**4**, M = Ph_3Sn) exists mainly in the $^4C_1$ conformation [4]. The $\delta^{119}Sn$ solution value for another (*β*-hydroxyl-alkyl)triphenyltin compound, (**7**, *n* = 1), is −111.3 ppm [12] and is very close to the values recorded for (**1**, M = Ph_3Sn) and (**4**, M = Ph_3Sn) in solution.



(7)

The value of the coupling constant involving tin and the alpha (aliphatic) carbon, $^1J(^{119}Sn-^{13}C\alpha)$, of 327 Hz for (**4**, M = Ph_3Sn) is markedly lower than the values determined for various other alkyltriphenyltin compounds, including (*β*-hydroxyalkyl)tins (see Table 6). The value of $^1J(^{119}Sn-^{13}C_i)$ (C_i = *ipso* aryl carbon) for (**4**, M = Ph_3Sn) is, on the other hand, comparable with the values for related compounds.

The resolution obtained in the ^1H NMR spectra of (**4**, M = Ph_2As) and [**4**, M = $Ph_2P(O)$] in chlorocarbon solvents at 250 MHz was not sufficient to obtain reliable J(H–H) values for hydrogen atoms in the pyranose ring and hence it was not possible to deduce a conformation of this ring solution for either compound. The two aryl groups in each of (**4**, M = Ph_2As) and [**4**, M = $Ph_2P(O)$] are diastereotopic, as shown by the two sets of signals for the carbon atoms in the aryl rings in each of the metallated sugars (see Table 1).

Acknowledgements

The authors wish to thank the SERC for support to MAB and OJT and the SERC services at Durham (solid state NMR) and at Swansea (mass spectrometry).

References

[1] M.A. Brown, R.A. Howie, J.L. Wardell, P.J. Cox and O.A. Melvin, *J. Organomet. Chem.*, in press.
[2] P.J. Cox, O.A. Melvin, M.A. Brown, R.A. Howie and J.L. Wardell, *J. Chem. Crystallogr., 24,* (1994) 105.
[3] S.M.S.V. Doidge-Harrison, I.W. Nowell, P.J. Cox, R.A. Howie, O.J. Taylor and J.L. Wardell, *J. Organomet. Chem., 401* (1991) 273.
[4] L.D. Hall, P.R. Steiner and D.C. Miller, *Can. J. Chem., 57* (1979) 38.
[5] R. Whistler, *Methods in Carbohydrate Chemistry*, Vol. 1, Academic Press, New York, 1962, pp. 308, 351.
[6] R. Whistler, *Methods in Carbohydrate Chemistry,* Vol. II, Academic Press, New York, 1963, p. 189.
[7] G.M. Sheldrick, *Acta Crystallogr., A46* (1990), 467.
[8] G.M. Sheldrick, SHELXL-93, Program for the Refinement of Crystal Structures from Diffraction Data. Universitat Gottingen, Germany.
[9] K. Davies, SNOOPI, Chemical Crystallography Laboratory University, 1980.
[10] P. Luger, E. Muller, H. Yamamoto and S. Inokawa, *Carbohydrate Res., 145* (1985) 25.
[11] H. Yamamoto, K. Yamamoto, S. Inokawa and P. Luger, *Carbohydrate Res., 113* (1983) 31.
[12] L.A. Burnett, S.M.S.V. Doidge-Harrison, S.J. Garden, R.A. Howie, O.J. Taylor and J.L. Wardell, *J. Chem. Soc. Perkins Trans. 1* (1993) 1621.
[13] R.A. Howie and J.L. Wardell, *Main Group Metal Chem., 17* (1994) 571.
[14] P.J. Cox, S.M.S.V. Doidge-Harrison, R.A. Howie and J.L. Wardell, *J. Crystallog. Spect. Chem., 21* (1991) 735.
[15] P. Harston, R.A. Howie, G.P. McQuillan, J.L. Wardell, E. Zanetti, S.M.S.V. Doidge-Harrison, N.S. Stewart and P.J. Cox, *Polyhedron,* (1991) 1085.
[16] A.R. Forrester, S.J. Garden, R.A. Howie and J.L. Wardell, *J. Chem. Soc. Dalton Trans,* (1992) 2615.