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Preliminary communication

SYNTHESIS OF TRIBUTYLSTANNYL ETHERS OF CARBOHYDRATES

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Summary

A series of new tributylstannyl ethers of simple sugars has been prepared by the reaction of bis(tributyltin) oxide with the appropriate mono- or disaccharide; chemical and spectroscopic evidence suggests that the 1-, 4- and 6-hydroxyl groups are the most reactive towards the trialkyltin compound.

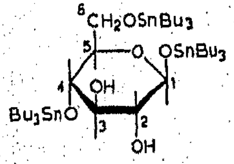
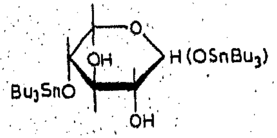
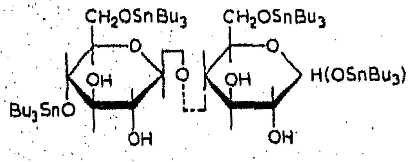
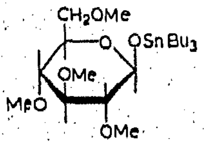
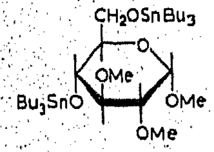
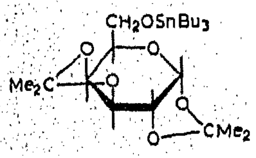
The reactions of organotin compounds with carbohydrates have, in general, remained largely unexplored [1-4]. Moffatt and his co-workers showed [1] that bis(tributyltin) oxide underwent an azeotropic dehydration reaction in refluxing benzene with the free (5′-) hydroxyl group of 4′-fluoro-2′,3′-*O*-isopropylideneadenosine, to form the 5′-*O*-tributylstannyl ether; bis(tributyltin) oxide was reported [2] to react with glucose under similar conditions, but the exact nature of the product was not fully described. As part of an investigation into the bonding of bis(tributyltin) oxide to wood cellulose [5,6] we have studied the reactions of this organotin compound with some mono- and di-saccharides, and now report our preliminary findings.

On azeotropic dehydration of bis(tributyltin) oxide (1 mol) and 1—2 mol of anhydrous D(+)-glucose in refluxing toluene beneath a Dean and Stark trap for 2 h, 2/3 mol of the sugar dissolved and 1 mol of water was liberated. Cooling of the solution, followed by filtration from unreacted sugar and removal of solvent at reduced pressure, gave a deep amber oil, which showed no absorption in the infrared spectrum due to ν_{as}(Sn—O—Sn) [7]. The appearance of a strong ν_{as}(Sn—O—C) band [7] at 1042 cm^{-1}, the elemental analysis and the integrated proton NMR spectrum all pointed to the formation of a tris(*O*-tributylstannyl) ether of glucose (I, eq. 1). D(+)-Xylose, which is

$$2\,\mathrm{Gluc(OH)_5} + 3(\mathrm{Bu_3Sn})_2\mathrm{O} \rightarrow 2\,\mathrm{Gluc(OH)_2(OSnBu_3)_3} + 3\,\mathrm{H_2O} \qquad (1)$$

structurally similar to D(+)-glucose, but lacks a 5-hydroxymethyl group, reacted with bis(tributyltin) oxide under identical conditions to incorporate only two tributylstannyloxy groups per mol, forming a bis(*O*-tributylstannyl)

TABLE 1. TRIBUTYLSTANNYL DERIVATIVES OF CARBOHYDRATES

Compound		Analytical Data: Found (Calcd.) (%)			B.P. (°C/mmHg)	Reflux Time[a] (hr)	ν_{max}(SnOC) (cm^{-1})	$^3J(CH_1-CH_2)$[b] (Hz)
		C	H	Sn				
	(I)	48.04 (48.13)	8.63 (8.59)	33.50 (34.10)	Oil	2	1042	8[c]
	(II)	48.05 (47.80)	8.50 (8.52)	31.80 (32.69)	Oil	2	1064	d
	(III)	48.14 (48.07)	8.70 (8.41)	32.70 (31.80)	Oil	16	1042	d
	(IV)	50.19 (50.28)	9.00 (8.76)	22.30 (22.67)	152-6°/0.15	2	1111	7[e]
	(V)	49.11 (49.50)	8.96 (8.75)	29.23 (29.75)	180°/0.05	8	1064	3
	(VI)	52.35 (52.46)	8.37 (8.38)	20.70 (21.70)	160-2°/0.06	6	1064	5

[a] In toluene. [b] In C_6D_6. [c] $\delta(C_1)$ 101.8 ppm downfield from TMS (in C_6D_6). [d] Signals broad, possibly due to exchange [4]. [e] $\delta(C_1)$ 101.9 ppm downfield from TMS (in C_6H_6).

ether (II, eq. 2). This suggested that, in I, the 6-carbon was carrying a tributylstannyloxy group.

$$\mathrm{Xyl(OH)_4 + (Bu_3Sn)_2O \rightarrow \underset{(II)}{Xyl(OH)_2(OSnBu_3)_2} + H_2O} \tag{2}$$

The β-1,4′-linked disaccharide, D(+)-cellobiose, was found to give the tetrakis(*O*-tributylstannyl) ether (III, eq. 3) and this may be taken to indicate

$$\mathrm{Cell(OH)_8 + 2(Bu_3Sn)_2O \rightarrow \underset{(III)}{Cell(OH)_4(OSnBu_3)_4} + 2\,H_2O} \tag{3}$$

that the other two tributylstannyloxy substituents in I, and also those in II, were attached to the 1- and 4-carbons.

In the ^{1}H NMR spectrum of I, the magnitude of the vicinal coupling constant ^3J(C(1)H—C(2)H), (8 Hz), is consistent with a stable chair conformation in which the three large tributylstannyloxy groups are occupying equatorial sites. On the basis of these data, the product I was concluded to be 1,4,6-tris(*O*-tributylstannyl)-β-D-glucose (Table 1).

Further confirmation of $\mathrm{Bu_3SnO}$-substitution at C(1) came from a comparison of the ^{13}C NMR spectrum of I with that of tributylstannyl-2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside (IV). In I and IV, the ^{13}C chemical shifts of C(1), the lowest field carbon, were identical within experimental error (Table 1).

The aprotic tributylstannyl ethers IV—VI (Table 1) could be distilled in vacuo as colourless liquids and resemble organotin alkoxides in that they are rapidly hydrolysed on exposure to the atmosphere. The compounds I—III, which contain free hydroxyl groups are, however, unusually stable in air (e.g. the infrared spectrum of I is unchanged after 2 days' exposure to atmospheric moisture) but undergo extensive decomposition on distillation at reduced pressure.

Further studies on these compounds are now in progress in order to gauge their synthetic utility in carbohydrate chemistry.

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