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Structure elucidation of the dibutylchlorostannyl intermediate during dibutyltin oxide-mediated acylation of sugars

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Abstract

^{119}Sn NMR and APcI-MS indicate the presence of a dimeric species as the dibutylchlorostannyl intermediate after dibutyltin oxide-mediated bezoylation of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside. The stannyl groups in the dimer dismutate to form a dialkoxystannyl species loosely complexed to dibutyltin dichloride. This species and its isomer were also prepared by treating the benzoylated sugar with bis(dibutylchlorotin) oxide. The dialkoxytin complex and isomer was also prepared by treating the benzoylated sugar with dibutyltin oxide.

Keywords: carbohydrates; mass spectrometry; NMR; tin compounds.

The discrete regioselectivities dialkyltin species induce in the derivatisation of diols and polyols is ascribed to the propensity of stannylene complexes to dimerise.[1] The driving force behind the dimerisation and oligomerisation of tetravalent tin species is the need of the central tin atom to expand its coordination number to 5 and 6.[2] During acylation, addition of two mole equivalents of acylating reagent leads to selective diacylation of polyols.[3] The reactivity of the first acylating step is necessarily greater than that of the second step.[4] This is due to the transformation of the activating tin species from dibutylstannylene in the first step to dibutylchlorostannyl in the second (Scheme 1). Dibutylchlorostannyl complexes, with the help of dibutylstannylene complexes, catalyse very rapid intramolecular transesterification, amounting to an equilibrium process that is faster than the ^{1}H NMR relaxation time scale on non-cyclic diols.[5] The analogous intermolecular transesterification is slow, but when such dismutation of the chlorostannyl-acyl compound occurs, the bis(dibutylchlorostannyl) species that forms is rapidly converted to a dimer of dibutylstannylene dichloride and the original 1,3,2-dioxastannolane (Scheme 2).[6] It has been observed that dibutyltin dichloride is always present when dibutylchlorostannyl species develop during the derivatisation of dioxastannolane species.[7] Chlorostannyl-mediated intramolecular transesterification, however, occurs only at above 85°C for methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-

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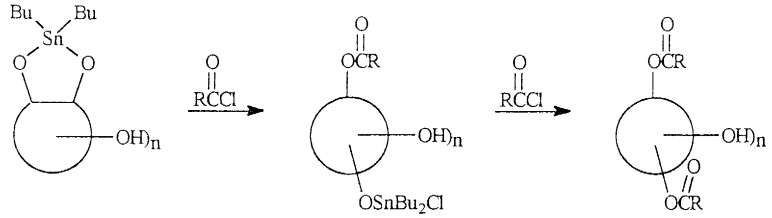
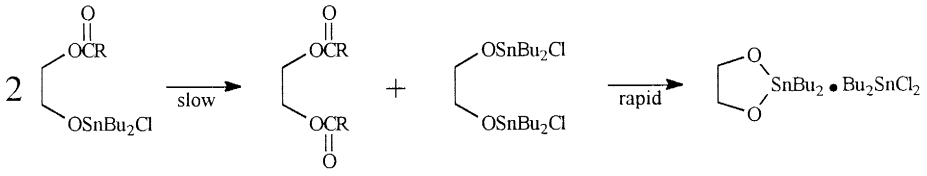
D-glucopyranoside (**1**).[8] We herein propose a structure for the dibutylchlorostannyl complex of **1** and related species on the grounds of NMR and APcI-MS.



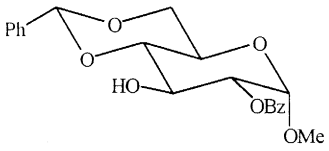
Scheme 1.



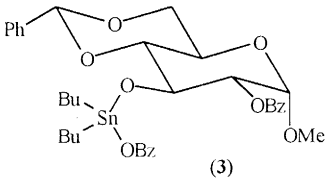
Scheme 2.

Even though dibutyltin complexes occur predominantly as dimers, it has been generally accepted that the dibutylchlorostannyl group, like the tributylstannyl group, is monomeric since it can expand its coordination number to 5 intramolecularly, including the complexes of cyclic sugar derivatives. If this is so, the stannylene dimer is disrupted when both components are derivatised. The ^{1}H and ^{13}C NMR spectra of the dibutylchlorostannyl complex of **1** obtained at 25°C in $CDCl_3$ indicate single sets of signals that are similar to the spectra of **1** (unstannylated), barring the butyl signals which are double sets.[8] The ^{119}Sn spectrum of the dibutylchlorostannyl complex of **1**, however, reveals two signals of equal integral at δ −89.41 ($Bu_2SnCl_2\cdot$) and δ −136.75 [$Bu_2Sn(OR)_2\cdot$] relative to tetramethylstannane (δ 0) as an external reference. These ^{119}Sn signals both have satellites due to ^{119}Sn-^{119}Sn- and ^{119}Sn-^{117}Sn-coupling, indicating dimeric structure. This suggests that two dibutylchlorotin groups have dismutated to yield a dimer in which one tin bears the chloro groups and the other the alkoxy groups. It would seem that the tin complexes maintain a primarily dimeric structure from the start, yielding the mixed stannylene dimer **2** after the addition of one mole equivalent of benzoyl chloride. The dibutyltin dichloride also seems to be loosely bound to the dialkoxytin complex allowing for rapid exchange of the tin chloride intra- and possibly intermolecularly. The existence of intramolecular exchange may be justified by the fact that the signal at δ −89.41 is broader and of smaller amplitude than the other tin signal and also the singularity of the sugar ^{1}H and ^{13}C NMR signals. Structure **2** corroborates the presence of dibutyltin dichloride always observed in conjuction with dibutylchlorostannyl intermediates.[7] Structure **2** also incorporates pentavalent tin complexes as indicated by the ^{119}Sn chemical shifts.[9]

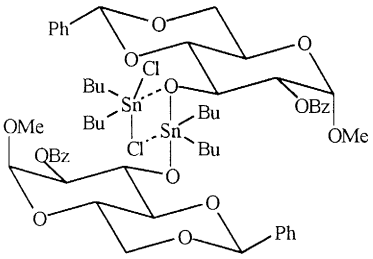
In order to confirm the dimeric nature of **2**, APcI-MS was utilised as a means of soft ionisation in an effort to preserve the complex in its dimeric state. Polar aqueous/organic solvents are usually used to transport the compound in APcI-MS experiments in order to be able to ionise the compound. Tin complexes, however, are unstable in water and alcohols. The inherent instability of the tin complex allows for ionisation using dichloromethane as solvent. Besides several other clusters of isotopic peaks, two clusters, indicative of the dimeric structure, are prominent in the spectra that were taken under a variety of conditions, including different acceleration energies. The main peak of a cluster at *m/z* 1003 may be assigned to $(\mathbf{2} - Bu_2SnCl_2)^+$. Similarly *m/z* 737 may be assigned to $(\mathbf{3})^+$. Small peak clusters at *m/z* above 1307.5, the average molecular mass of **2**, suggest greater oligomers than dimers. These may be natural or produced by the ionisation process.



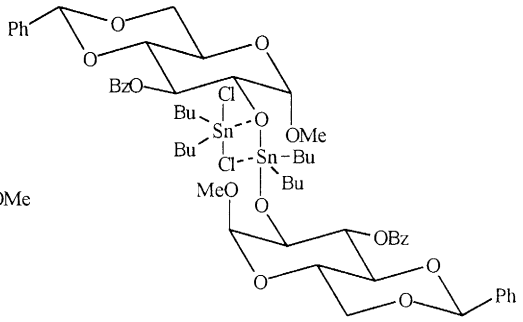
(1)



(3)



(2)



(4)

Alternate preparation of **2** by the respective complexing 2-*O*- and 3-*O*-benzoylated methyl 4,6-*O*-benzylidene-α-D-glucpyranoside with bis(dibutylchlorotin) in refluxing toluene in both cases yielded an equilibrated mixture of **2** and its isomer **4** (45:55).[8] The Bu_2Sn signals in the ^1H, ^{13}C and ^{119}Sn NMR spectra of both **2** and **4** are identical to those of **2** prepared above. The ESMS-APcI spectrum of the compounds prepared in this way is very similar to the previous spectra.

The main signals (δ −89.59 and δ −142.58) in the ^{119}Sn NMR characterisation of the equilibrated mixture (**2** and **4**) obtained by heating **2** at 108°C does not differ from that of **2** before its heating in toluene-d_8. Two other signals, each integrating as a third of either of the main signals, at δ 123.02 and δ −24.38 are tetracoordinate[9] and may be correlated with the process of partial debenzoylation of the glucopyranoside.[8]

Finally, efforts to stannylate **1** with Bu_2SnO in refluxing toluene produced a mixture of the complex with **1** (2-*O*-Bz, 3-*O*-Sn) and its isomer (2-*O*-Sn, 3-*O*-Bz) in a ratio of 4:5 with a small amount of debenzoylated product. The ^{119}Sn spectrum consists of a major signal at δ −135.66 [$Bu_2Sn(OR)_2\cdot$] and two small signals at δ −168.73 and δ −212.01. The chemical shifts indicate pentacoordinate tin complexed to oxygen atoms.[9] The ^1H and ^{13}C signals for the Bu_2Sn components are complex. These complexes are likely to consist of two sugars bridged by a stannylene that then expands its coordination state intramolecularly.

Acknowledgements

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