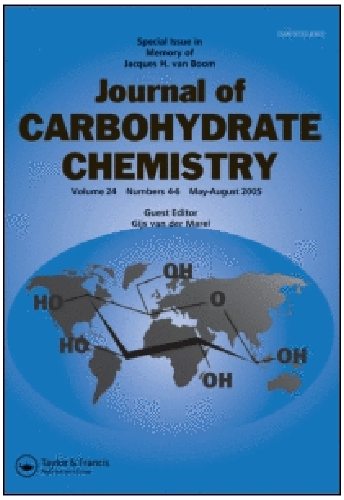

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^{119}Sn NMR SPECTRA OF SOME CARBOHYDRATE ORGANOTIN DERIVATIVES

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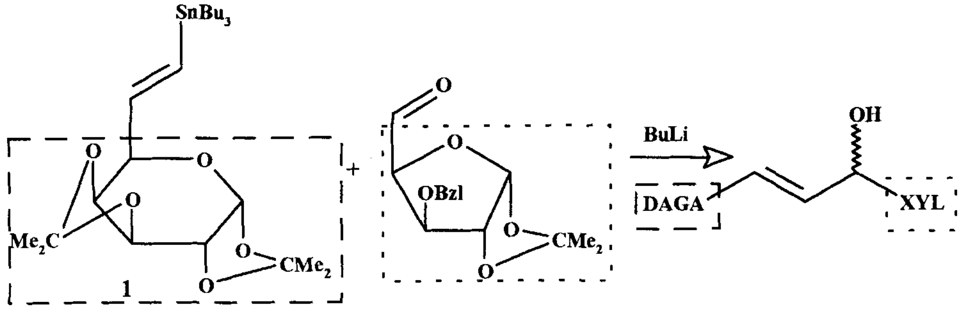
ABSTRACT

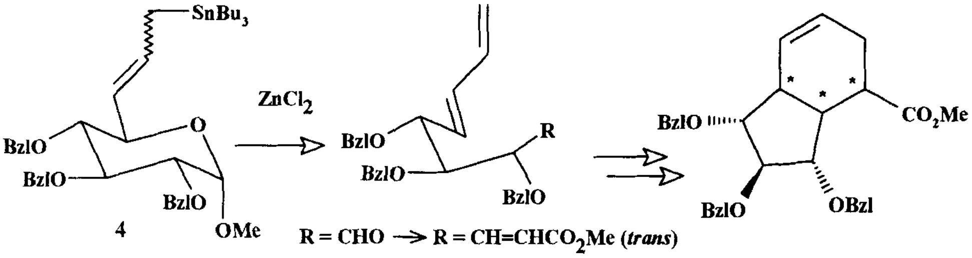
The ^{119}Sn NMR spectra of several sugar-tin derivatives were recorded. The geometric and steric isomers of all of the organotin derivatives studied were easily differentiated by ^{119}Sn NMR. The appropriate ^{119}Sn resonances are: ca -50 ppm for *trans* and -60 ppm for *cis* vinyltin derivatives (**1-3**), ca 16 ppm for allyltins **4-6**, and ca -32 ppm for tin-carbinols **9** and **11**. When the hydroxyl group in carbinol **9** was converted to an *O*-acetyl group, the chemical shift of ^{119}Sn was shifted to -22 ppm.

INTRODUCTION

Organostannanes are widely used as convenient intermediates in organic synthesis,[1] primarily for the creation of new carbon-carbon bonds. For example, allyltins are precursors of homoallylic alcohols[2] (reaction with aldehydes in the presence of Lewis acids), and vinyltins may serve as vinyl-anion equivalents.[3]



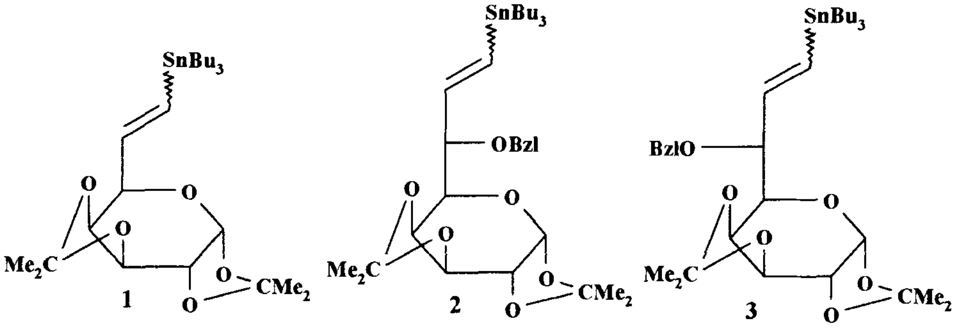
Scheme 1



Scheme 2

Usually, tri-*n*-butyltin hydride or tri-*n*-butyltin chloride are used for the preparation of organostannanes. The ^{1}H NMR spectra of such compounds (especially in the aliphatic region where Bu_3Sn-signals are located) are often difficult to interpret whereas their ^{13}C NMR spectra are much easier to interpret. However, while determination of the purity of organostannanes from these spectra is difficult, the ^{119}Sn NMR spectra of organostannanes should be useful for this purpose and allow correlation of compound structure with ^{119}Sn chemical shift. ^{119}Sn NMR spectra can be also used for studying the mechanisms of reactions catalyzed by tin species as ilustrated by a recently reported study on the formation of monoallyltin trihalides from allyl halides and tin dichloride[4].

The utility of carbohydrate tin compounds in synthesis is illustrated below. Several types of protected monosaccharide organostannanes prepared recently by us were used as convenient intermediates for the synthesis of higher carbon sugars[5] (e.g., precursor of a C_{12}-saccharide from **1**, Scheme 1) and highly oxygenated chiral dieno-aldehydes (from e.g, 4)[6] as suitable precursors of bicyclic products (Scheme 2).[7]



-48.8 (*trans*), -60.9 (*cis*) -48.4(*trans*), -61.2 (*cis*) -49.0 (*trans*), -62.9 (*cis*)

Fig. 1 ^{119}Sn chemical shifts (ppm) of compounds with tin bonded to an sp^2 carbon atom

This paper describes some results on correlation of ^{119}Sn chemical shift data with structures of some protected monosaccharide tin derivatives.

RESULTS AND DISCUSSION

Three classes of sugar derived organotins were prepared and their ^{119}Sn NMR spectra were recorded. These classes studied were with: (*i*) a Sn atom connected to an sp^2 carbon atom (Fig. 1 vinyltins: **1**[8], **2**[9], and **3**), (*ii*) a Sn atom connected to an sp^3 carbon atom (Fig. 2 allylltins: **4**, **5**, and **6**[7] and derivatives 7, **8**[10]), and (*iii*) a Sn atom connected to an sp^3 carbinol center (Fig. 3, compounds **9**, **10**, and **11**[10]).

Organotins **1-3** were prepared by the reaction of the appropriate sugar acetylenes with tri-*n*-butyltin hydride; the initially formed *cis*-vinyltin derivatives isomerised under the reaction conditions into the more thermodynamically stable *trans* isomers.[3,9] Usually ca 5:1 mixtures of *trans*:*cis* vinyltins were obtained and used directly for the preparation of higher carbon sugars (*cf.* Scheme 1).

The ^{119}Sn NMR spectra of such mixtures reveal two signals in the ratio 5-6:1. The *trans* isomer resonates at ca -49 ppm, while the *cis* is at -61 ppm. The large difference in the chemical shift between these geometric isomers is to be noted (12-14 ppm). The sugar substituent, however, has very little effect on these resonance positions (see Fig 1).

The ^{119}Sn signals of allyltins **4-6**[6] resonate at ca -15 ppm. Again, almost no difference in the chemical shift between different sugar derivatives (D-*gluco*- **4**, D-*galacto*- **5**, and D-*manno*- **6**) was observed. There are also very small differences between the chemical shifts of

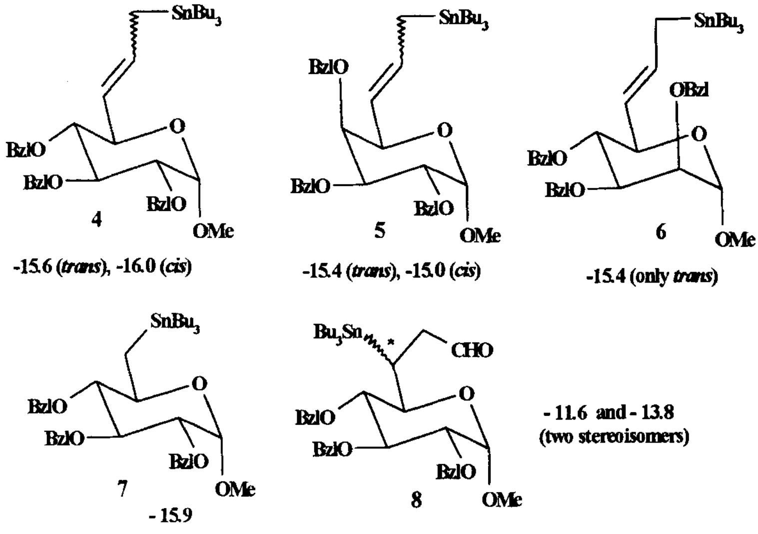


Fig. 2. ^{119}Sn chemical shifts (ppm) of compounds with tin bonded to an sp^3 carbon atom

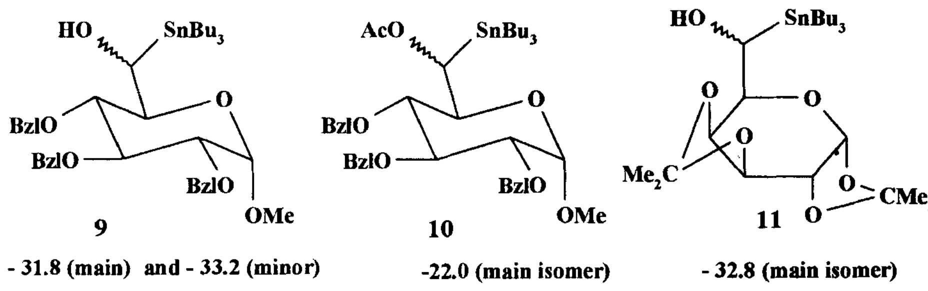


Fig. 3. ^{119}Sn chemical shift (ppm) of compounds with tin bonded to an sp^3 carbinol center

the geometric isomers. In the spectrum of a ca 5:1 mixture of *trans:cis* isomers[6] the appropriate resonances of the *trans* and *cis* isomers were separated.

^{119}Sn signals for **7**[10] and **8**[10] are similar to those for allyltins (see Fig. 2) and are indicative of a tin atom bonded to a CH_2R group.

In derivatives **9** - **11**[10] (Fig.3) the tin atom is also bonded to an sp^3 carbon, but this carbon atom is connected to a heteroatom and a significant difference of the tin chemical shift is observed. The ^{119}Sn resonance of carbinol **9** is deshielded by up to 16 ppm when compared to 7 (-31.8 *vs* -15.9 ppm). Acetylation of the carbinol **9** (to **10**) causes a tin shielding increase by about 10 ppm.

Two main conclusions can be drawn from this study. First, the $\delta(^{119}Sn)$ values are almost **independent** of the substituents which are **not connected** to the *C*-atom bonded to tin (e.g., *trans* vinyltins **1-3** resonate at δ - 49 ppm, *trans* allyltins **4-6** at - 15 ppm). Second, the differences between the geometric isomers are significant only for compounds in which the tin atom is located at the double bond (ca. -49 ppm for *trans* vinyltins versus ca. -61 ppm for *cis* isomers). For other types of compounds in which a Sn atom is located at the sp^3 carbon atom, the separate signals (although not very distinct from each other) can be seen in the ^{119}Sn spectra if both isomers are present in the mixture.

Such spectra provide information about the composition of the mixture of geometric isomers and may be used as a tool in studies such as selectivity of the addition of Bu_3SnH to acetylenes (in which the first step involves the preparation of the *cis* isomers which equilibrate to the more stable *trans* forms).

EXPERIMENTAL

Preparation of sugar organotin derivatives. Vinyltin derivatives (**1**, **2** and **3**) were prepared by semireduction of sugar acetylenes with tri-*n*-butyltin hydride according to references 5, 8 and 9. Allyltin derivatives (**4**, **5** and **6**) were prepared from allylxanthates according to reference 6. For the preparation of the remaining sugar tin derivatives (**7** - **11**) see reference 10.

NMR experiments. All ^{119}Sn NMR spectra were measured on approximately 0.5 M solutions in $CDCl_3$ at 300 °K, using a Bruker AM 500 spectrometer operating at 186.36 MHz frequency and equipped with a 5 mm inverse broad band probe. Experiments were conducted in a direct excitation mode. Typical experimental conditions were 31.25 kHz spectral width, 8 μs (45 ° flip angle) pulse width, 1.05 s acquisition time, 1s repetition delay, 1000 - 2000 transients and Waltz decoupling during acquisition. $SnCl_4$ (δ = -150 ppm from tetramethyltin) was used as spectral reference.

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