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α-Tributylstannylacetals: preparation via transacetalisation of diethoxymethyltributyltin, and use for the synthesis of new α-stannylated ethers

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Abstract

The transacetalisation of readily available diethoxymethyltributyltin affords a large variety of new α-stannylacetals, which are expected to have a high potential for selective organic synthesis when they contain labile or chiral alkoxy groups. The α-stannylacetals can be converted into the corresponding substituted α-stannylethers by treatment with organoaluminium halides or by use of an acetyl chloride/Grignard reagent sequence. The study has concentrated on allylic, homoallylic, and homopropargylic derivatives, which offer the best potential for organic synthesis.

Introduction

Diethoxymethyltributyltin (**1**) and dimethoxymethyltributyltin (**2**) have been obtained previously in only low yields through reaction of tributylstannylmagnesium chloride with the corresponding trialkylorthoformates [1] but use of diethylphenylorthoformate has provided a valuable procedure for large scale preparation of **1** [1,2,3] , according to:

$$PhOCH(OEt)_2 + Bu_3SnMgCl \xrightarrow[(>80\%)]{\text{ether, r.t.}} Bu_3SnCH(OEt)_2 + PhOMgCl$$

This result is interesting, but the method has some limitations as it cannot be generalized owing to the difficulty of preparing the required mixed orthoformates in

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a pure state [4]. New approaches involving use of tributylstannylmagnesium chloride in the presence of galvinoxyl have been recently suggested by Shiner et al. [3] to make **1** and **2** from triethyl- or trimethyl-orthoformate. (For compound **2**, trimethyl-orthoformate must be used as a complex $[(MeO)_2CH]^+[BF_3OMe]^-$ if satisfactory yields are to be obtained [3].)

These α-stannylacetals can be regarded as masked formylanion equivalents and their possible applications [1,3] appear to offer effective competition to those of other synthons of this type [5,6] when the conditions used for generation of dialkoxymethyllithiums via transmetallation with butyllithium at low temperature are carefully controlled. Shiner et al. have recently recommended the use of cyclic acetals for the generation and trapping of organolithium reagents such as 2-lithio-1,3-dioxolane or 2-lithio-1,3-dioxane at −78°C. In contrast with our earlier report, he reports that there is a fast decomposition of organolithium species, even at −95°C, when diethoxy- or dimethoxy-methyllithium is used [3]. The differences in structure of the acetal moiety cannot account for the dependence of the stability of the diethoxymethyllithium upon the source or purity of its precursor [7]. By use of a new method of making of **1**, involving reaction of tributylstannylmagnesium chloride with diethoxymethyl acetate, we have been able to generate and trap diethoxymethyllithium at −78°C with reasonable yields and this aspect will be discussed in detail in the near future [8].

In addition to the use of the acetals as masked formylanions, it is noteworthy that the reactions of the acetal function of diethoxymethyltributyltin afford a large variety of useful α-ethoxy substituted organotin derivatives that can act as d^1 or d^3 "umpolung" reagents [9–12]; for example:

$$Bu_3SnCH(OEt)_2 \xrightarrow[\text{or } R_nAlX_{3-n}]{\text{(1) AcCl, (2) RMgX}} Bu_3SnCH(OEt)R$$

(1)

(R = alkyl, phenyl, allyl, vinyl, $SnBu_3$)

Thus extension of the range of available α-stannylacetals in order to widen their scope is of much interest. The α-stannylacetals containing more labile alkoxy groups (such as allyloxy or benzyloxy) are expected to be useful in the field of polyol and carbohydrate chemistry, and chiral acetals could be efficient tools for asymmetrical formylations.

Results

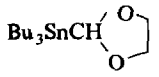
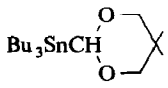
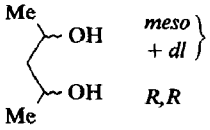
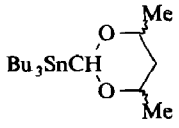
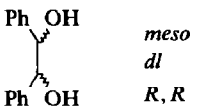
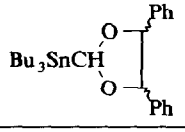
Owing to the ease of its preparation on a large scale [2], diethoxymethyltributyltin is an attractive starting point in making the required α-stannylacetals if the conditions necessary for the transacetalisation reaction, usually involving acid catalysis in the case of organic acetals [13] are compatible with the presence of an α-stannyl group. In practice exchange of the alkoxy groups of diethoxymethyltributyltin has proved to be possible when appropriate alcohols are used and when benzene or cyclohexane is used as the solvent and *para*-toluenesulfonic acid (PTSA) as the catalyst [14]:

$$Bu_3SnCH(OEt)_2 \underset{(-EtOH)}{\overset{ROH/PTSA}{\rightleftharpoons}} Bu_3SnCH(OEt)(OR) \underset{(-EtOH)}{\overset{ROH/PTSA}{\rightleftharpoons}} Bu_3SnCH(OR)_2$$

(1) **(3)** **(4)**

Table 1

Transacetalisation of diethoxymethyltributyltin **1** catalyzed by para-toluenesulfonic acid

Starting ROH	Exp. [c]	New α-stannylacetals	No.	Yield (%)	^{119}Sn NMR δ, ppm/Me_4Sn
PhOH	A	$Bu_3SnCH(OEt)OPh$	**3a**	82 [b]	−47.8
PhOH	B	$Bu_3SnCH(OPh)_2$	**4a**	82 [b]	−25.1
$PhCH_2OH$	A	$Bu_3SnCH(OEt)OCH_2Ph$	**3b**	72 [b]	−55.5
$PhCH_2OH$	B	$Bu_3SnCH(OCH_2Ph)_2$	**4b**	74 [a]	−53.9
$CH_2{=}CHCH_2OH$	C	$Bu_3SnCH(OCH_2CH{=}CH_2)_2$	**4c**	78 [a]	−54.6
$HC{\equiv}CCH_2OH$	C	$Bu_3SnCH(OCH_2CH{\equiv}CH)_2$	**4d**	80 [b]	−51.4
$HOCH_2CH_2OH$	D		**4e**	72 [a]	−56.4
$Me_2C(CH_2OH)_2$	E		**4f**	96 [a]	−55.6
 *meso* + *dl*	E		**4g** + **4h**	95 [a,d]	−58.3 / −56.3
R,R	E		**4h***	96 [a]	−56.3
 *meso*	E		**4i**	58 [a,e]	−47.2
dl	E		**4j**	82 [a,f]	−49.3
R,R	E		**4j***	76 [a,f]	−49.3

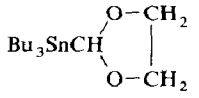
[a] Isolated yields; [b] Conversion rate (NMR evaluation). [c] Experimental conditions: A = ROH (1 equiv.), B = ROH (~ 2.4 equiv.), C = ROH (20 equiv.), D = (ROH, 1 equiv. in benzene), E = (ROH, 1 equiv. in cyclohexane). In every case *para* toluenesulfonic acid was added as catalyst. [d] Only two diastereomers were observed. Only one of the two possible *meso* isomers was obtained with three equatorial substituants. [e] Only one of the two possible *meso* diastereomers. The moderate yields are due to the obtention of a monoexchanged acetal $Bu_3SnCH(OEt)OCHPhCHPhOH$ (**4k**) (δ(^{119}Sn) −52.6 ppm). [f] A minute amount of monoexchanged acetal is obtained as a mixture of diastereomers (**4l**/**4l'** 83/17).

The new α-stannylacetals have been obtained in good yields by removal of the ethanol by distillation in order to shift the equilibrium in the appropriate direction (cf. Table 1). However, while pure dibenzyloxymethyltributyltin is readily obtained by exchange with the theoretical amount of benzyl alcohol, the isolation of satisfactorily pure diallyloxymethyltributyltin requires use of a large excess of allylic alcohol for the transacetalisation, its boiling point being close to that of ethanol. The preparation of mixed acetals **3** has been attempted only with heavy alcohols (or phenol) for the same reason.

In the case of diols, it must be noted that the transacetalisation must be carried out in a solvent (benzene or cyclohexane, cf. Table I) to ensure miscibility. Use of the appropriate solvent allows ready azeotropic elimination of ethanol, and possibly of water (in cases where dehydration of the diol might occur), so avoiding possible destruction of the α-stannylacetals via the unstable formyltributyltin [2]. In practice, if dehydration does occur it is only to a minute extent, as demonstrated by reactions involving 2,4-pentanediols and hydrobenzoins in which no isomerization is observed and good yields of the expected acetals are obtained after transacetalisation. It

Table 2

Reaction of organoaluminium halides with α-tributylstannylacetals

α-Stannylacetals	R′ in $R'Al_{2/3}Br$ solvent, T (°C)	α-Stannylethers		Yields (%)
$Bu_3SnCH(OEt)OPh$	$H_2C{=}C{=}CH$ Ether, 35	$Bu_3SnCH(OEt)CH_2C{\equiv}CH$	(5)	65 [a]
$Bu_3SnCH(OCH_2Ph)_2$	$H_2C{=}C{=}CH$ Ether, 35	$Bu_3SnCH(OCH_2Ph)CH_2C{\equiv}CH$	(6)	70 [a]
$Bu_3SnCH(OCH_2Ph)_2$	$H_2C{=}CHCH_2$ Ether, 35	$Bu_3SnCH(OCH_2Ph)CH_2CH{=}CH_2$	(7)	75 [a]
$Bu_3SnCH(OCH_2C{\equiv}CH)_2$	$CH_2{=}CHCH_2$ Ether, 35	$Bu_3SnCH(OCH_2C{\equiv}CH)CH_2CH{=}CH_2$	(8)	70 [b]
	$H_2C{=}C{=}CH$ Ether, 35	$Bu_3SnCH(OCH_2CH_2OH)CH_2C{\equiv}CH$	(9)	65 [b]

[a] Isolated yields. [b] Conversion rates (NMR after elimination of solvents).

should be emphasized that 2*R*-,4*R*-pentanediol and *R*,*R*-hydrobenzoin give the optically active α-stannylacetals ($[\alpha]_D^{22}$ +15.9° (*c* 1.35, $CHCl_3$) for **4h*** and $[\alpha]_D^{24}$ +19.1° (*c* 1.5, $CHCl_3$) for **4j***). Chiral α-stannylacetals (expected to be of considerable interest for carrying out formylation reactions with chirality transfer) can thus be regarded as readily available precursors.

Since a large variety of α-stannylacetals are now readily accessible, we thought it appropriate to examine the reactions of useful α-stannyl ethers of the $Bu_3SnCHROR'$ type for a range of alkoxy groups. The results summarized in Table 2 show that organoaluminium halides react in the expected way with the acetal function [11] at least in the case of allylic or propargylic reagents:

$$Bu_3SnCH(OR')_2 \xrightarrow[\text{ether, } 35\,^\circ C]{RAl_{2/3}Br} Bu_3SnCHROR' + R'OAl_{2/3}Br$$

(1) **(5–9)** (R = C_3H_5 or C_3H_3)

However, α-stannyl ethers containing prenyl skeleton cannot be made in this way from **4b** and **4c**, a two step method (reaction with acetyl chloride followed by reaction with isobutenylmagnesium bromide) [12] had to be used to obtain compound **11**:

$$Bu_3SnCH(OAll)_2 \xrightarrow[(-AcOAll)]{AcCl} Bu_3SnCH(Cl)OAll \xrightarrow{Me_2C{=}CHMgBr} Bu_3SnCH(OAll)CH{=}CMe_2$$

(4c) **(10)** **(11)**

It should be noted then that the acetate formed (in this case an allylacetate) must be sufficiently volatile to be readily removed under vacuum after the first step. It is

apparent from the above examples that α-stannyl ethers containing a labile alkoxy-group and an allylic, homoallylic, or homopropargylic skeleton are now readily available. Organotin reagents with such structures are known to be efficient tools in organic synthesis [7,12,15,16,17], and the new organotin reagents described herein can be expected to increase their scope considerably.

Conclusion

α-Tributylstannylacetals can now be readily made, whatever the nature of the alkoxy groups, by transacetalisation catalysed by *para*-toluenesulfonic acid. The method is effective even in the case of optically active diols, which give α-stannyl-acetals likely to be able to induce chirality transfer [18,19]. The new acetals can undergo reactions at the acetal group to give new α-stannylethers of potential interest in organic synthesis.

Experimental

1. General

Infrared spectra were recorded on a Beckman Acculab 2 spectrometer and GLC analyses were performed with an Intersmat IGC 120MB (TC detector), a Girdel 300C (FID detector) or a Carlo-Erba 4200 (FID detector, fitted with a 25 m × 0.32 mm SE 52 capillary column) instrument.

The ^{1}H NMR spectra were recorded on a Varian EM 360 spectrometer (60 MHz) or a Jeol FX 90Q spectrometer (89.55 MHz). The latter was also used for the ^{13}C NMR spectra (22.49 MHz) and ^{119}Sn NMR spectra (33.35 MHz). The chemical shifts are relative to (internal) Me_4Si for ^{1}H and ^{13}C and to (internal) Me_4Sn for ^{119}Sn NMR spectra.

The mass spectra were obtained with a Finnigan-Mat 112 apparatus and the peaks are given for ^{120}Sn (isotopic abundance 33%). This means that the reported abundances (values in brackets) for organotin fragments are only roughly one third of the correct value taking account of the 10 isotopes of tin compared with those of organic fragments.

2. Starting materials

Diethoxymethyltributyltin (**1**), the key starting point for the syntheses, was obtained by treating tributylstannylmagnesium chloride (made from tributyltin hydride and isopropylmagnesium chloride) with diethylphenylorthoformate in ether. The reaction was conducted, as previously described [2] on a 0.5 molar scale and gave **1** in good yields (always > 75%).

The alcohols and diols used in this work were commercial samples, except for chiral hydrobenzoin which was kindly provided by Dr A. Alexakis (Paris) *.

3. Transacetalisation reactions

(a) Experimental procedure

*Acetals **4a–4d.*** Diethoxymethyltributyltin (**1**, 0.05 mol) was treated with the relevant alcohol in the presence of *para*-toluenesulfonic acid (50 mg). In the case of

* The *R,R*-hydrobenzoin was made by the Sharpless method [21].

benzyl alcohol or phenol the equilibrium was shifted by use of a slight excess (2.4 equiv.) of the alcohol or phenol derivatives and continuous distillation of the ethanol, and compounds **4a** and **4b** were readily obtained as crude products *. When 1 equiv. was used the mixed acetals **3a** and **3b** were mainly obtained. For the preparation of **4c** and **4d**, a large excess of alcohol was used (20 equiv.) in order to effect complete displacement of the ethanol by distillation. After removal of ethanol, in cases where the acetals were needed pure, the reaction mixture was shaken with a sodium hydroxide solution (0.1 *N*) then dried over potassium carbonate before distillation or column chromatography.

*Acetals **4e–4j**.* Diethoxymethyltributyltin (0.01 mol) was allowed to react with the appropriate diol (0.015 mol) in 100 ml of solvent (benzene for synthesis of **4e**; cyclohexane in the other cases) in the presence of *para*-toluenesulfonic acid (20 mg) during 24 h in a Dean–Stark apparatus (bath temperature 100 °C). The mixture was subsequently shaken with 10 ml of 0.1 *M* aqueous sodium hydroxide and extracted with diethyl ether. The organic layer was dried over potassium carbonate, concentrated, and chromatographed on silica gel (70–230 mesh) with hexane/triethylamine (99/1) as eluent. The yields are reported in Table 1.

(b) Characterization of the obtained α-stannylacetals

Compounds **1** and **2** have been described previously [1,2,3]. In the case of the other acetals, the IR spectra are consistent with the α-stannylacetal structure (strong absorption in the range 1050–1200 cm^{-1} depending on the structure of the alkoxy group), as are the ^{119}Sn NMR shifts, which are listed in Table 1. Details of only significant ^{1}H and ^{13}C NMR and mass spectral data are reported below, e.g. butyl absorptions are not reported in detail).

3a: ^{1}H NMR ($CDCl_3$): 0.7–1.9 (30H, m), 3.56 (1H, $^{2}J_{1H}$ −9.3 Hz, $^{3}J_{3H}$ 7 Hz), 3.76 (1H, $^{2}J_{1H}$ −9.3 Hz, $^{3}J_{3H}$ 7 Hz), 5.80 (1H, s, ^{2}J(SnH) 29.2 Hz), 6.5 to 7.3 ppm (5H, m). Mass spectrum **: organotin fragments: m/z = 385 (3), 327 (3), 291 (61), 279 (14), 235 (78), 179 (100), 177 (48), 121 (78); organic fragments: m/z = 151 (100), 123 (52), 95 (52), 94 (43).

3b: ^{1}H NMR ($CDCl_3$): 0.7–1.9 (27H, butyl absorptions superimposed with 3H, t, at 1.15), 3.43 (2H, $^{3}J_{3H}$ = 7 Hz), 4.50 (1H, $^{2}J_{1H}$ −11.8 Hz), 4.57 (1H, $^{2}J_{1H}$ −11.8Hz), 5.30 (1H, s, ^{2}J(SnH) = 30.4Hz), 7.3 ppm (5H, bs). Mass spectrum: organotin fragments: m/z = 399 (0.5), 365 (1.5), 291 (17), 235 (20), 179 (30), 177 (10), 121 (14); organic fragments: m/z = 165 (15), 91 (100).

4a: ^{1}H NMR ($CDCl_3$): 0.7 to 2 (27H, m), 6.6 to 7.3 ppm (m, 11H: aromatic absorption + acetal hydrogen). Mass spectrum: organotin fragments: m/z = 291 (40), 235 (67), 179 (100), 177 (62), 121 (57); significative organic fragment: m/z = 199 (41).

4b: ^{1}H NMR ($CDCl_3$): 0.7 to 1.9 (27H, m), 4.60 (4H, s), 5.43 (1H, s, ^{2}J(SnH) 33.6Hz), 7.35 ppm (10H, bs). Mass spectrum: organotin fragments: m/z = 291 (48), 235 (59), 179 (50), 177 (45), 121 (41); significative organic fragments: m/z = 227 (4), 91 (100), 57 (25).

* These reactions can be also carried out in toluene (50 ml).

** The relative abundancies are given for the crude product on the basis of a spectrum recorded by the direct introduction mode.

4c: ^{1}H NMR ($CDCl_3$): 0.7 to 1.9 (27H, m), 4.02 (4H, $^3J_{1H}$ 5.3 Hz, $^4J_{2H}$ 1 Hz), 5.14 (2 × 1H, $^3J_{1H}$ 10.2 Hz, $^4J_{1H}$ 1 Hz, $^2J_{1H}$ 2 Hz), 5.28 (2 × 1H, $^3J_{1H}$ 17.3 Hz, $^4J_{1H}$ 1 Hz, $^2J_{1H}$ 2 Hz), 5.29 (1H, s, ^2J(SnH) = 30.5 Hz), 5.90 ppm (2 × 1H, $^3J_{1H}$ 17.3 Hz, $^3J_{1H}$ 10.2 Hz, $^3J_{2H}$ 5.3 Hz). Mass spectrum: organotin fragments: m/z = 305 (1), 291 (6), 235 (42), 179 (55), 177 (30), 121 (27); organic fragments: m/z = 127 (67), 85 (3), 81 (100), 57 (12).

4d: ^{1}H NMR ($CDCl_3$): 0.7 to 1.9 (27H, m), 2.40 (2 × 1H, $^4J_{2H}$ 2.1 Hz), 4.12 (2 × 1H, $^4J_{1H}$ 2.1 Hz, $^2J_{1H}$ −15.5 Hz), 4.23 (2 × 1H, $^2J_{1H}$ −15.5 Hz, $^4J_{1H}$ 2.1 Hz), 5.46 ppm (1H, s, ^2J(SnH) = 26 Hz). Mass spectrum: organotin fragments: m/z = 291 (41), 235 (47), 179 (80), 177 (37), 121 (57); significative organic fragments: m/z = 123.04_4 (30), 57 (70), 55 (36), 39 (100). IR: ν(C–H) 3290 cm^{-1}, ν(C–O) 1060 cm^{-1}.

4e: ^{1}H NMR (CCl_4): 0.7 to 1.9 (27H, m), 3.40 to 4.0 (4H, AA′BB′ system), 4.90 ppm (1H, s, ^2J(SnH) 101/106 Hz). Mass spectrum: organotin fragments: m/z = 291 (6), 235 (10), 179 (15), 177 (22), 121(21); organic fragments: m/z = 73 (100), 57 (50). These physicochemical data are in good agreement with those recently reported for this compound [3], including the high value of ^2J(Sn–H) (≈ 100 Hz) observed for the signal near 5 ppm.

4f: ^{1}H NMR ($CDCl_3$): 0.6 to 1.9 (27H, m), butyl absorptions superimposed with 2 × 3H (s) at 0.69 and 1.18, 3.22 (2 × 1H, $^2J_{1H}$ −10.5 Hz), 3.59 (2 × 1H, $^2J_{1H}$ −10.5 Hz), 5.03 ppm (1H, s, ^2J(SnH) 39.2 Hz). ^{13}C NMR (C_6D_6): 9.6 (3C, ^2J(SnC) = 312/327 Hz), 14.4 (3C), 23.1 (1C), 23.5 (1C), 28.0 (3C, ^3J(SnC) 60 Hz), 29.7 (3C, ^2J(SnC) 21 Hz), 31.5 (1C), 79.6 (2C, ^2J(SnC) 39 Hz), 107.5 ppm (1C, ^1J(SnC) 491/514 Hz). Mass spectrum: organotin fragments m/z = 349 (0.1), 291 (8), 235 (9), 179 (11), 177 (5), 121 (13); organic fragments m/z = 115 (100), 69 (40), 45 (10), 41 (8).

4g: (isomer *meso*): 0.7 to 2.1 (35H, m), 3.45 (2 × 1H, $^3J_{1H}$ ≈ 13 Hz, $^3J_{3H}$ ≈ 6.6 Hz, $^3J_{1H}$ ≈ 3.4 Hz), 5.18 ppm (1H, s, ^2J(SnH) 39.4 Hz).

4h and **4h***: ^{1}H NMR ($CDCl_3$): 0.7 to 2.1 (35H, m), 3.74 (1H, $^3J_{1H}$ 8.6 Hz, $^3J_{3H}$ 6 Hz, $^3J_{1H}$ 2.7 Hz), 4.18 (1H, $^3J_{4H}$ ≈ 6.7 Hz, $^3J_{1H}$ ≤ 1.2 Hz broad quintet), 5.57 ppm (1H, s, ^2J(SnH) 39.4 Hz). ^{13}C NMR (C_6D_6): 9.2 (3C, ^1J(SnC) 313/328 Hz), 14.0 (3C), 16.3 (1C), 22.5 (1C), 27.4 (3C, ^3J(SnC) 53 Hz), 29.4 (3C, ^2J(SnC) 22 Hz), 38.5 (1C), 67.6 (1C, ^3J(SnC) 36.6 Hz), 69.0 (1C, ^3J(SnC) 38.1 Hz), 98.1 ppm (1C, ^1J(SnC) 513/536 Hz). Mass spectrum: (for **4g** and **4h**) organotin fragments: m/z = 349 (0.2), 291 (1.5), 235 (3), 179 (9), 177 (8), 121 (14); organic fragments m/z = 115 (100), 69 (87), 57 (3), 45 (43), 41 (17).

4i: ^{1}H NMR ($CDCl_3$): 0.7 to 2 ppm (27H, m), 5.10 (2 × 1H, s), 5.50 (1H, s, ^2J(SnH) 89/93 Hz), 7.00 ppm (10H, bs). ^{13}C NMR (C_6D_6): 8.7, 12.6, 26.2 and 28.1 (butyl absorptions) 82.5 (2C), 105.7 (1C), 123–126 (10C, superimposed with C_6D_6), 136.4 ppm (1C).

4j and **4j***: ^{1}H NMR ($CDCl_3$): 0.6 to 1.9 (27H, m), 4.54 (1H, $^3J_{1H}$ 8.2 Hz), 4.57 (1H, $^3J_{1H}$ 8.2 Hz), 5.80 (1H, s, ^2J(SnH) 97/102 Hz), 7.15–7.40 ppm (10H, m). ^{13}C NMR (C_6D_6): 8.08, 12.7, 26.2 and 28.1 (butyl absorptions), 83.8 and 86.8 (2C), 107.0 (1C), 123.8 (2C), 124.6 (4C), 126.3 (4C), 136.3 (1C), 138.3 ppm (1C). Mass spectrum: **4j** is fairly unstable, and although the expected organic fragments were observed in the mass spectrum at m/z = 225 and 197 and organotin fragments at m/z = 291, 235, 179, 177 and 121, the spectrum also showed peaks from heavy organotin fragments (polytin species), and a signal at m/z = 180 assigned to stilbene. This behaviour may be due to decomposition of **4j** into stilbene and tributyltinformate, which is known to give polytin derivatives when heated [23].

4k: ^{1}H NMR ($CDCl_3$): 0.6 to 1.8 (27H, m, superimposed with 3H, t at 1.02, $^3J_{2H}$ 7 Hz), 2.45 (1H, hydroxyl group), 2.95 (2H, $^3J_{3H}$ 7 Hz), 4.73 (2 × 1H, s), 4.99 (1H, s, ^2J(SnH) 29.3Hz), 7.25 ppm (10H, bs).

4l: (major isomer ~ 83%)^{1}H NMR ($CDCl_3$): 0.6 to 1.8 (30H, m), 3.1 to 3.7 (2H, m), 3.62 (1H, hydroxyl group, $^3J_{1H}$ 1.7 Hz), 4.60 (1H, $^3J_{1H}$ 8.5 Hz), 4.71 (1H, $^3J_{1H}$ 8.5 Hz, $^3J_{1H}$ 1.7 Hz), 5.10 (1H, s, ^2J(SnH) 31Hz), 6.9–7.25 ppm (10H, m).

4l': (minor isomer ~ 17%), similar spectrum, excepted 4.32 (1H, $^3J_{1H}$ 8.4 Hz), 4.68 (1H, $^3J_{1H}$ 8.4 Hz), 5.36 ppm (1H, s, ^2J(SnH) 33 Hz).

From the above data it appears that the $^2J(^{117,119}SnH)$ value is close to 100 Hz in the case of five-membered ring cyclic acetals, whereas a value of ca. 30 Hz is observed in other cases (absence of strain in the cycle). This observation is consistent with earlier data [1–3].

4. Preparation of α-tributylstannylethers 5–9

The organoaluminium bromides were made in ether at 35 °C by reaction of aluminium turnings with allyl bromide or propargyl bromide in the presence of a catalytic amount of mercuric chloride as previously described [21]. The appropriate α-stannylacetal (0.008 mol) in ether (10 ml) was then added dropwise to the solution of the organoaluminium bromide (0.01 mol in 25 ml of ether) at 35 °C, and the mixture was stirred for 3 h then treated with 5*M* aqueous sodium hydroxide (10 ml). After extraction with ether (3 × 25 ml), the extract was dried over magnesium sulfate, the solvent removed under vacuum and the product distilled or chromatographed on silica gel.

Characterization of the obtained α-stannylethers

5: ^{1}H NMR ($CDCl_3$): 0.6–1 ppm (15H) and 1.15–1.7 (12H): butyl groups absorptions, 1.15 (3H, $^3J_{2H}$ 6.9 Hz), 1.96 (1H, $^4J_{2H}$ 2.6 Hz), 2.64 (1H, $^2J_{1H}$ −16.6 Hz, $^3J_{1H}$ 7.7 Hz, $^4J_{1H}$ 2.6 Hz, ^3J(SnH) 49 Hz), 2.72 (1H, $^2J_{1H}$ −16.6 Hz, $^3J_{1H}$ 6.6 Hz, $^4J_{1H}$ 2.6 Hz, ^3J(SnH) 49 Hz), 3.36 (1H, $^2J_{1H}$ −9.1 Hz, $^3J_{3H}$ 6.9 Hz), 3.52 (1H, $^2J_{1H}$ −9.1 Hz, $^3J_{3H}$ 6.9 Hz), 3.79 ppm (1H, $^3J_{1H}$ 7.7 Hz, $^3J_{1H}$ 6.6 Hz, ^2J(SnH) 4.4 Hz). ^{119}Sn NMR (C_6D_6): −31.2 ppm. IR: 3320, 1080 cm^{-1}. Mass spectrum: organotin fragments: $m/z = 388$ ($0.1 = M^+$), 359 (1), 331 (18), 291 (58), 279 (3), 275 (5), 235 (100), 179 (97), 177 (37), 121 (40); organic fragments: $m/z = 97$ (28), 69 (58), 57 (10).

6: ^{1}H NMR ($CDCl_3$): 0.7 to 1.6 ppm (27H, m); 1.86 (1H, $^4J_{2H}$ 1.7 Hz), 2.75 (1H, $^3J_{1H}$ 6.3 Hz, $^4J_{1H}$ 1.7 Hz) and 2.75 (1H, $^3J_{1H}$ 8 Hz, $^4J_{1H}$ 1.7 Hz): the slight inequivalence between these two protons is too small to permit determination of the ^2J value; 3.90 ppm (1H, $^3J_{1H}$ 6.3 Hz, $^3J_{1H}$ 8 Hz), 4.41 and 4.62 (2H, $^2J_{1H}$ −12Hz), 7.35 ppm (5H, bs). IR: 3280, 1050 cm^{-1}.

7: ^{1}H NMR (CCl_4): 0.6 to 1.6 ppm (27H, m); 2.63 (2H, bt, $^3J_{2H}$ 6.6 Hz), 3.93 (1H, $^3J_{2H}$ 6.6 Hz, ^2J(SnH) 6.5 Hz), 4.38 and 4.57 ($^2J_{1H}$ −11.7 Hz), 5.05 (1H, $^3J_{1H}$ 9.8 Hz, $^2J_{1H}$ 2.1 Hz, $^4J_{2H}$ ~ 1.2 Hz), 5.10 (1H, $^3J_{1H}$ 17.2 Hz, $^2J_{1H}$ 2.1 Hz, $^4J_{2H}$ ~ 1.2 Hz), 5.88 (1H, $^3J_{2H}$ 6.6 Hz, $^3J_{1H}$ 17.2 Hz, $^3J_{1H}$ 9.8 Hz), 7.40 ppm (5H, bs). IR: 1640, 1060 cm^{-1}.

8: ^{1}H NMR (CCl_4): 0.6 to 2 (27H, m); 2.26 (2H, $^4J_{2H}$ 2.4 Hz), 2.55 (2H, bt, $^3J_{2H}$ ~ 7 Hz), 3.64 (1H, $^3J_{1H}$ 7 Hz), 4.08 (2H, $^4J_{1H}$ 2.4 Hz); 5.00 (1H, $^3J_{1H}$ 10 Hz) and 5.03 (1H, $^3J_{1H}$ 17 Hz), ^2J and ^4J n.d.; 5.84 ppm (1H, $^3J_{1H}$ 17 Hz, $^3J_{1H}$ 10 Hz, $^3J_{3H}$ 6.8 Hz).

9: ^{1}H NMR (CCl_4): 0.7 to 1.7 (27H, m); 1.93 (1H, $^4J_{2H}$ 1.7 Hz), 2.20 (1H, hydroxyl), 2.73 (2H, $^3J_{1H}$ 6.7 Hz, $^4J_{1H}$ 1.7 Hz), 3.20 to 3.40 (4H, m), 3.84 ppm (1H, $^3J_{2H}$ 6.7 Hz). IR: 3500, 3270, 1070 cm^{-1}.

5. Preparation of α-allyloxyprenyltributyltin (11)

The α-stannylacetal **4c** (0.005 mol) was treated at room temperature with a large excess of acetyl chloride (0.02 mol) and the progress of the reaction was monitored by ^{1}H NMR spectroscopy (comparison of the signals at 5.29 and 5.94 ppm). When **4c** had been almost fully comverted into **10**, the volatile products (acetyl chloride and allyl acetate) were eliminated under vacuum without warming, and the residual crude product **10** was dissolved in THF (10 ml). The solution was dropwise added under nitrogen to a chilled solution (0 °C) of 2-methylpropenylmagnesium bromide in THF [22] (0.007 mol in 7 ml THF), and the mixture was stirred for 2 h at 0 °C before hydrolysis and the usual work-up. The crude product was chromatographed on silica gel (eluent hexane/triethylamine 99/1) to afford 0.94g of **11** (45% overall yield).

10: ^{1}H NMR ($CDCl_3$): 0.7 to 1.8 (27H, m); 4.53 (2H, $^3J_{1H}$ 5.3 Hz, $^4J_{2H}$ ~ 1.3 Hz), 5.19 (1H, $^3J_{1H}$ 10.4 Hz, $^2J_{1H}$ ~ 1.7 Hz, $^4J_{2H}$ ~ 1.3 Hz), 5.26 (1H, $^3J_{1H}$ 17.2 Hz, $^2J_{1H}$ ~ 1.7 Hz, $^4J_{2H}$ 1.3 Hz), 5.85 (1H, $^3J_{1H}$ 17.2 Hz, $^3J_{1H}$ 10.4 Hz, $^3J_{3H}$ 5.3 Hz), 5.94 ppm (1H, s, ^2J(SnH) 30 Hz).

11: ^{1}H NMR ($CDCl_3$): 0.6–1.8 (27H, m) superimposed with 3H, bs at 1.58 ppm and 3H, bs at 1.72), 3.5 to 4.2 (2 inequivalent H, $^2J_{1H}$ −13.6 Hz, $^3J_{1H}$ 5 Hz, ^4J n.d), 4.52 (1H, $^3J_{1H}$ 10.4 Hz), 5.10 (1H, $^3J_{1H}$ 10.3 Hz, ^2J and ^4J n.d.), 5.17 (1H, $^3J_{1H}$ 17.5 Hz, ^2J and ^4J n.d.), 5.40 (1H, bd, $^3J_{1H}$ 10.4 Hz), 5.89 ppm (1H, $^3J_{1H}$ 17.5 Hz, $^3J_{1H}$ 10.3 Hz, $^3J_{2H}$ 5 Hz).

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