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Preliminary communication

A NEW PREPARATION OF HEXAALKYLDITINS. ^{119}Sn NMR AND CHROMATOGRAPHIC DATA ON LINEAR POLYTINS

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Summary

The reaction of triorganotin oxides and formic acid provides a good route to ditin derivatives. Several new linear polytin compounds have been isolated, and the vicinal and long range ^{119}Sn—^{119}Sn coupling constants determined. A linear relationship has been demonstrated between the logarithm of the HPLC retention time and the number of tin atoms in the compounds.

Hexa-n-butylditin is of value for synthetic and industrial applications. In recent years it has found increasing use in the generation of organic radicals [1] in reduction reactions. It also shows bactericidal and fungicidal activity [2, 3] and it is an efficient wood preservative because of its good penetrating properties [4].

The preparation of ditin compounds usually involves reactions of the corresponding halides with metals (which can be accelerated by ultrasound [5]) or condensation of tin hydrides with tin oxides, alkoxides, or amines [1]. Electrolytic methods from various precursors have also been developed [6].

We report here our investigations of the preparation of hexaalkylditin compounds from triorganotin oxides and formic acid, as well as some physicochemical data on the linear polytins which are formed as by-products in this process.

Thermal decarboxylation of tributyltin formate has been used as route to tributyltin hydride [7], and it is known that triorganotin oxides can react with triorganotin hydrides to give hexaorganoditins [8]. Although the thermal decomposition of tributyltin formate can be directed in part to the production of

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hexabutylditin [9], we thought that the combination of "in situ"-generated triorganotin hydride and triorganotin oxide might provide a convenient preparation of hexaalkylditins. The following sequence describes the reactions probably involved in the production of hexaalkylditin:

$$(R_3Sn)_2O + HCO_2H \rightarrow R_3SnO_2CH + 1/2\ (R_3Sn)_2O + 1/2\ H_2O$$

$$R_3SnO_2CH \rightarrow R_3SnH + CO_2$$

$$R_3SnH + 1/2\ (R_3Sn)_2O \rightarrow R_6Sn_2 + 1/2\ H_2O$$

The overall stoechiometry of the process represents a very simple one-pot reduction of the triorganotin oxide by formic acid:

$$(R_3Sn)_2O + HCO_2H \rightarrow R_6Sn_2 + CO_2 + H_2O$$

In a typical procedure, formic acid and the triorganotin oxide were mixed and heated at 100°C for 4 h, then at 200°C for a further 4 h at a pressure of 200 mmHg. After cooling to room temperature, a small amount of metallic tin was removed by filtration and the mixture was examined by ^{119}Sn NMR spectroscopy and HPLC. The results presented in Table 1 show that ditins are obtained in good yields, although rather complex mixtures are sometimes initially obtained. The oxygen-containing compounds can be easily removed after rapid treatment with formic acid, thus converting the remaining oxides into formates. The latter are very soluble in methanol whereas ditins are not. Thus a simple reaction and decantation give ditins with less than 1% triorganotin oxide. After the evaporation of methanol, pure formates can be recovered and recycled.

As shown in Table 1, tetraalkyltins and octaalkyltritins were formed in small amounts along with hexaalkylditins in the investigated reactions. These compounds probably come from the slow decomposition of hexaalkylditins in the reaction mixture, involving stannylene intermediates [10]. In an attempt to lower the reaction temperature, and thus reduce the amounts of by-products we examined the effect of adding decarboxylation catalysts ($Pb(OAc)_4$, Pt/C, . . .) to the reaction mixture. In all cases, the rate of the reaction was little affected but the quantity of oligomeric by-product was increased.

In the case of n-butyl compounds, reversed-phase HPLC analysis revealed the presence of traces of higher oligomers. We suspected that these were linear

TABLE 1

COMPOSITION OF REACTION MIXTURES (BY WEIGHT)

R	R_6Sn_2	R_4Sn	R_8Sn_3	$R_{10}Sn_4$	$R_{12}Sn_5$	R_6Sn_2O	$R_3SnOCHO$
n-Bu	47(65[a])	7	14	1	1	17	13
i-Bu	40(66[a])	10	4	—	—	—	46
n-Oct	71[b]	15	14	—	—	—	—

[a] Yield after addition of methanol. [b] Addition of methanol is not necessary in this case.

deca-n-butyltetratin and dodeca-n-butylpentatin since the thermal decomposition of ditins is known to give linear oligomers, branched derivatives being formed are only obtained under forcing conditions [10]. We obtained these compounds by preparative reversed-phase HPLC from a mixture obtained from the reaction of tributyltin hydride and dibutyltin oxide [11] and confirmed their ties by mass and ^{119}Sn NMR spectroscopy. (Preparation involving from the coupling of tin hydrides and tributyl(*N*-phenylformamido)tins [12] gives a mixture of products as revealed by modern methods of analysis.) The parent ion for each compound was seen in the mass spectrum, which demonstrates their good stability under electron impact conditions (70 eV).

We report here the first ^{119}Sn NMR data for n-Bu_8Sn_3, n-$Bu_{10}Sn_4$ and n-$Bu_{12}Sn_5$, which provide proof of the structure of these products (Table 2) (Some ^{119}Sn NMR data were previously available for some tritins [13] and branched tetratins [14].) The products gave spectra characterized by a large number of satellites due to vicinal and long-range ^{117}Sn—^{119}Sn and ^{119}Sn—^{119}Sn coupling, from which the coupling constants were determined. The tritin compound shows two tin resonances in the expected region, with values of ^1J and ^2J(Sn—Sn) close to those reported for $Et_3SnEt_2SnSnEt_3$ [13]. The tin chemical shifts of the triorganotin and diorganotin moieties in the tetra- and penta-tin derivatives correspond to those for these groups in the tritin compound. Although long range Sn—Sn coupling constants through 5 carbon bonds are known [15], only ^2J couplings through tin—tin bonds have been reported [13]. For the tetratin compound we were able to determine the Sn—Sn coupling constant ^3J between 3 tin—tin bonds, and the value of 233 Hz is not very different from that of ^2J.

Linear relationships between the logarithm of the retention factor (log k') and the number of backbone atoms are important both from theoretical and analytical points of view in explaining retention mechanisms and in helping to identify unknown compounds. Extensive studies have been conducted on this subject with organic compounds and, with few exceptions [16] these relationships are well-accepted [17]. They have been established for linear derivatives, with or without functional groups, with chain lengths up to about 30 carbon atoms [18]. Little work has been done on branched long chain compounds except for some substituted aromatic systems [19]. To our knowledge, only

TABLE 2

^{119}Sn NMR DATA OF ORGANOPOLYTINS

	n-Bu_8Sn_3	n-$Bu_{10}Sn_4$	n-$Bu_{12}Sn_5$
$\delta(SnR_3)$[a]	−75.6	−74.3	−73.8
$\delta(Sn(2)R_2)$	−226.6	−212.6	−199
$\delta(Sn(3)R_2)$			−210
$^1J(1—2)$[b]	1596	1426	1368
$^2J(1—3)$	417[c]	295	261
$^3J(1—4)$		233[c]	220
$^1J(2—3)$		601[c]	[d]

[a] δ in ppm from external Me_4Sn. [b] $J(^{119}Sn—^{119}Sn)$ in Hz. [c] Calculated value from $J(^{119}Sn—^{117}Sn)$. [d] The others tin—tin coupling constants cannot be attributed because of the proximity of Sn(2) and Sn(3) chemical shifts.

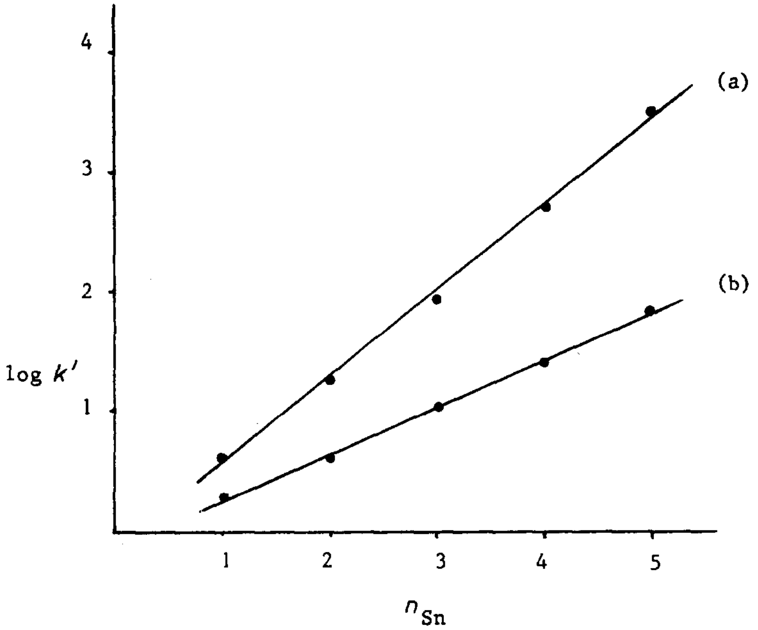

Fig. 1. Log k' vs. number of tin atoms (n_{Sn}) plots on C_{18} bonded phase for linear polytins in methanol (a) or methanol isopropanol (70/30) (b) mixture.

one study of this type has been conducted with organotin compounds which can be regarded as branched derivatives [20] and these results reveal a linear correlation of the logarithm of the chromatographic capacity factor with the calculated solvophobic parameter [21] for compounds $R_2R'_2Sn$ where $R \neq R'$ or $R = R'$. Our HPLC investigations involved the polytin derivatives $Bu_3Sn(Bu_2Sn)_nSnBu_3$ using a C_{18} packing with two different mobile phase compositions. In each case, a straight line was obtained (Fig. 1), showing that this kind of relationship applies to branched long chain compounds.

Preparation of hexaalkylditins. A mixture of 0.08 mol (48 g) of trialkyltin oxide and 0.10 mol (4.6 g) of formic acid was stirred together at 100°C for 4 h. The mixture was then heated at 200°C for 4 h at a pressure of 200 mmHg. The pressure was raised to that of the room, 0.028 mol (1.3 g) of formic acid was introduced, and the mixture was heated at 100°C for 30 min. After cooling to room temperature, methanol (50 ml) was added with vigorous stirring and the resulting solution was decanted. The lower layer was diluted with 200 ml of petroleum ether, and the solution was filtered. The solvent was evaporated off and the residue distilled to give the ditin compound. The upper methanolic layer was evaporated to dryness, giving pure triorganotin formate.

In some cases the product mixture before the addition of methanol was examined by ^{119}Sn NMR spectroscopy and HPLC, with the results shown in Table 1 and 2.

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