PREPARATION AND CHARACTERISATION OF BRANCHED DECAORGANYLTETRATINS, A NEW CLASS OF ORGANOTIN COMPOUND

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(Received June 3rd, 1977)

Summary

The reaction of monoorganotin trihydrides with trimethyl(diethylamino)tin leads to the formation of branched decaorganyltetratins in good yield. These compounds have been characterized by spectroscopic methods, ^{119}Sn NMR spectroscopy offering the most conclusive proof of their structure. The thermal lability of the tetratins makes them difficult to obtain in a pure state: one main product of their thermolysis is hexamethylditin, suggesting that organotin-substituted stannylenes may be formed during the decomposition.

Introduction

As a continuation of our NMR studies of compounds containing tin—tin bonds [1,2], it appeared desirable to investigate the spectra of linear and branched tetratins $R_3Sn(SnR'_2)_2SnR_3$ and $RSn(SnR'_3)_3$. Though the former have earlier been described in the literature [3], the latter have not previously been characterized. We therefore decided to attempt to prepare these by the tin hydride/stannylamine condensation reaction previously used to prepare ditins [4], tritins [3] and linear tetratins [3].

Results and discussion

The preparative method used is described by equation 1. We found that,

$$RSnH_3 + 3\ Me_3SnNEt_2 \rightarrow RSn(SnMe_3)_3 + 3\ Et_2NH \tag{1}$$

when the trihydride was added to the stannylamine at room temperature an exothermic reaction occurred in which the required tetratins were readily formed; they could be obtained by careful but rapid vacuum distillation in good yields in a pure or almost pure state (see below) as colourless, high-boiling oils.

TABLE 1

BOILING POINTS AND ELEMENTAL ANALYSES FOR DECAORGANOTETRATINS
RSn(SnMe₃)₃

| R | B.p. (°C/mmHg) | Analysis (found (calcd.) (%)) | |
		C	H
Me	108—112/0.005	19.27 (19.21)	4.83 (4.75)
Et	120/0.005	20.90 (20.67)	5.06 (5.04)
Bu	140—145/0.005	23.75 (23.40)	5.41 (5.43)
i-Bu	147—150/0.005	22.45 (23.40)	5.45 (5.43)
n-Pentyl	135/0.005	25.15 (24.72)	5.69 (5.62)
Ph	166/0.01	24.87 (26.21)	5.24 (4.70)

The compounds so far prepared are listed in Table 1, together with their boiling points and elemental analyses *.

Though the elemental analyses were satisfactory, they are not on their own sufficient to establish the purity or the structure of the compounds. We therefore used a combination of spectroscopic methods to verify the structure and to investigate the purity of the compounds, and a discussion of the results of these investigations follows.

(a) ^{119}Sn NMR spectroscopy

It is known [2] that the trimethyltin resonances in hexaalkylditins, Me_3SnSnR_3, and octaalkyltritins, $Me_3SnSnR_2SnMe_3$, occur at ca. —100 ppm, while in the latter the R_2Sn resonance occurs at —200 to —270 ppm (depending on R); the branched tetratins show the expected two tin resonances (Table 2), one at ca. —90 ppm due to Sn in Me_3Sn and the other at —440 to —480 ppm due to Sn in RSn. In most cases a small signal at ca. —109 ppm is observed which can (by means of the satellites due to Sn—Sn coupling) readily be identified as hexamethylditin. Both tin signals of the tetratins exhibit satellites from which the

TABLE 2

TIN-119 AND CARBON-13 CHEMICAL SHIFT DATA FOR COMPOUNDS $(Me_3Sn^1)_3Sn^2R$ (in ppm: for ^{119}Sn δ(Me₄Sn) = 0, for ^{13}C δ(TMS) = 0)

R	δ(Sn¹)	δ(Sn²)	δ(C(Me))	δ(C(1R))	δ(C(2R))	δ(C(3R))	δ(C(4R))
Me	—89.5	—489.7	—7.84	—20.78	—	—	—
Et	—89.3	—440.9	—7.44	—3.18	17.03	—	—
Bu	—90.3	—459.9	—7.50	4.60	34.23	26.91	13.51
i-Bu	—90.8	—480.4	—7.44	16.86	30.32	26.29	—
n-Pentyl	—90.1	—460.5	—7.50	5.17	32.14	36.63	22.55 [a]
Ph	—83.2	—434.2	—7.55	135.82	138.82	127.98	127.08

[a] δ(C(5R)) 14.06. The carbon atoms in the group R are labelled 1 to 5 with increasing distance from the tin atom.

* Note added in proof: We have since prepared dodecamethylpentatin in a pure state starting from stannane (SnH₄) and Me₃SnNEt₂.

tin—tin coupling constants (Table 3) can be determined; the coupling constant values lie within the expected ranges. Extension of the method previously described [2] for the estimation of the Taft σ^* values for the Me_3Sn group (the tetratin is considered as a derivative of a ditin (Me_3SnSnR_3) in which two groups R have been replaced by Me_3Sn) gives values for σ^* (Me_3Sn) of ca. —0.53; this is in good agreement with the mean value of —0.57 found earlier [2].

(b) ^{13}C NMR spectroscopy

Chemical shift and coupling constant values are to be found in Tables 2 and 3. The feature which confirms the branched tetratin structure is that the trimethyltin carbons exhibit satellites due to coupling of carbon and tin over one, two and three bonds. Further support is provided by the low values of $^1J(Sn—C(1R))$ and the high-field shift of C(1R) compared with its values in the corresponding tritins $Me_3SnSnR_2SnMe_3$.

(c) ^1H NMR spectroscopy

While this technique is not suitable for establishing the structure of the tetratins, the observed values for the trimethyltin protons are given since they may be of use to other workers: $\delta(Me_3Sn)$ ca. 0.27 ppm, $^2J(Sn—H)$ ca. 48 Hz, $^3J(Sn—H)$ ca. 15 Hz. In $MeSn(SnMe_3)_3$ the methyltin signal occurs at 0.36 ppm; $^2J(Sn—H)$ could not be measured due to line overlapping.

(d) Raman spectroscopy

Although IR spectroscopy is rather uninformative, the Raman spectra of these compounds show two characteristic bands at very low frequencies, 106 ± 1 and 138 ± 2 cm^{-1}; these are the most intense bands in the spectra. It is known that $\nu(Sn—Sn)$ in ditins occurs at ca. 195 cm^{-1}, while cyclic polytins exhibit a strong band at 140—145 cm^{-1}, almost certainly due to a "ring breathing" mode [5]. Calculations show that the characteristic tetratin bands are combination bands involving both tin—tin stretching and tin—tin—carbon angle deformation *.

(e) Mass spectrometry

Molecular ions M^+ are visible, though only with low relative intensities. Computer analysis confirms that peak multiplets (several tin isotopes are present in relatively high abundance) due to species containing from one to four tin atoms are present, but that species with five and more tin atoms are absent. We plan to discuss the mass spectra in detail in a subsequent publication.

Thermal stability of branched tetratins

The repeated occurrence of signals due to Me_6Sn_2 in the ^{119}Sn and ^{13}C NMR spectra led us to consider whether this compound was obtained only during the formation of the tetratins or also as a product of their decomposition. It is clear that in a reaction involving the trifunctional $RSnH_3$, ligand exchange leading to the formation of Me_3SnH is conceivable; this could then condense with Me_3SnNEt_2 to give Me_6Sn_2. To check the possibility of formation of Me_6Sn_2 during thermolysis of the tetratins, we heated a benzene solution of a (spec-

TABLE 3

TIN-119 AND CARBON-13 COUPLING CONSTANT DATA FOR COMPOUNDS $(Me_3Sn^1)_3Sn^2R$ (in Hz)

R	$^1J(^{119}Sn^1-^{119}Sn^2)$	$^2J(^{119}Sn^1-^{117}Sn^1)$ [a]	$^1J(Sn-Me)$	$^2J(Sn-Me)$	$^3J(Sn-Me)$	$^1J(Sn-C(1R))$	$^2J(Sn-C(2R))$
Me	1733	287	236.9	66.3	11.5	131.1	0.2
Et	1538	259	234.6	37.8	10.3	b	10.3 [c]
Bu	1548	265	235.7	36.7	11.3	174.0	10.3 [d]
i-Bu	1546	262	235.8	36.7	10.3	175.1	11.4 [e]
n-Pentyl	1535	262	234.5	37.7	10.3	b	10.3 [f]
Ph	1570	271	244.2	41.6	7.8	b	b

[a] Calculated from $^2J(^{119}Sn-^{117}Sn)$. [b] Not measured. [c] $^2J(Sn-C(2R))$ 18.3 Hz. [d] $^2J(Sn-C(2R))$ 16.0, $^3J(Sn-C(3R))$ 51.5 Hz. [e] $^2J(Sn-C(2R))$ 12.6, $^3J(Sn-C(3R))$ 36.6 Hz. [f] $^2J(Sn-C(2R))$ 16.0, $^3J(Sn-C(3R))$ 45.8 Hz. Tin–tin coupling constants are accurate to ca. ± 3 Hz, tin–carbon to ca. ± 0.9 Hz.

troscopically) pure sample of $Me_{10}Sn_4$ at 80°C. The colourless solution slowly turned yellow, and ^{119}Sn spectra showed the formation of increasing amounts of Me_6Sn_2 with time; other as yet unidentified signals were also observed. This suggests the possibility of a decomposition of the following type:

$$MeSn(SnMe_3)_3 \rightarrow Me_6Sn_2 + MeSn(SnMe_3) \rightarrow products$$
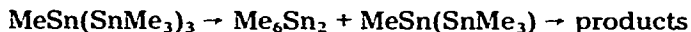
As far as we are aware the existence of methyl(trimethylstannyl)stannylene as an intermediate has not previously been postulated. It is clear that much work will be required to establish the mechanism and products of the thermolysis. Studies of the thermolysis and photolysis of these tetratins are under way.

Experimental

All manipulations were carried out under argon since the starting materials and the tetratins are extremely air-sensitive.

The tin trihydrides were prepared by reduction of $RSnCl_3$ by diisobutyl-aluminium hydride [6], the stannylamine according to the procedure of Jones and Lappert [7]. The tetratins were prepared by the following general procedure: Me_3SnNEt_2 (0.03 mol, 7.1 g) was placed in the flask of a distillation apparatus, and the trihydride (0.01 mol) was added with stirring from a dropping-funnel. After the exothermic reaction had subsided, the mixture was stirred for 30 min at room temperature. The tetratin was then distilled in vacuo as a colourless, air-sensitive oil.

The low boiling-point (0°C) of methyltin trihydride necessitated a modification of this procedure for the preparation of $Me_{10}Sn_4$. The trihydride was prepared at −30°C in dibutyl ether; on warming the ether solution the hydride distilled off and was allowed to bubble directly into the stannylamine, the mixture being kept at −10°C until the hydride had been consumed. The tetratin was vacuum-distilled as above.

Yields of the tetratins were good ($\geqslant 75\%$) except for $PhSn(SnMe_3)_3$, where it was only ca. 30%.

Spectroscopic data were obtained as follows: (a) ^{119}Sn NMR: Bruker HFX-90 spectrometer, 10 mm sample tubes, neat liquids containing 5% C_6D_6 as internal lock, 2% Me_4Sn as internal standard, 16K data points, spectral width 25000 Hz, frequency 33.546 MHz; (b) ^{13}C: Bruker WP-80 spectrometer, 10 mm sample tubes, neat liquids containing 5% C_6D_6 as internal lock, 2% Me_4Si as internal standard, 8K data points, spectral width 3750 Hz, frequency 20.155 MHz; (c) ^1H: Varian EM-360 spectrometer, neat liquids containing 2% Me_4Si as internal standard; (d) Raman: Coderg PHO spectrometer, Ar^+-laser (250 mW, 4880 Å); (e) Mass spectrometry: Varian MAT CH-5 spectrometer.

Acknowledgement

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