

THE REACTIVITY OF SMALL-RING MONOSTANNACYCLOALKANES

III *. RING-EXPANSION REACTIONS OF 1,1-DIMETHYL-1-STANNACYCLOPENTANE

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(Received August 21st, 1978)

Summary

As a result of the enhanced reactivity of the *endo*-cyclic tin–carbon bond 1,1-dimethyl-1-stannacyclopentane readily undergoes ring-expansion reactions with a variety of substrates to produce new organotin heterocycles. Illustrative examples include ring-expansion reactions with oxygen, sulphur, sulphur dioxide, diiron nonacarbonyl, dichlorocarbene and diethyl azodicarboxylate.

Introduction

Since the discovery of the first organotin compound over a century ago considerable knowledge has been gathered concerning the reactivity of the tin–carbon bond of non-cyclic organotin compounds [2]. In contrast, little information is available concerning the reactivity of the tin–carbon bond in organotin heterocycles such as stannacycloalkanes [3].

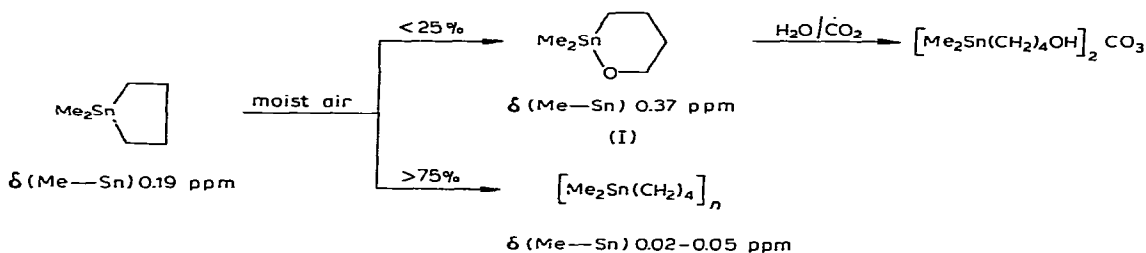
During recent years we have made a systematic study of the synthesis and reactivity of 1,1-dialkyl-1-stannacycloalkanes [4]. The first paper in this series dealt with the synthesis of stannacycloalkanes [5]. Subsequent studies into the chemistry of stannacycloalkanes have shown that the small-ring compounds, especially stannacyclopentanes, display unusual reactivity of the *endo*-cyclic tin–carbon bond [1,6]. Illustrative examples of ring-expansion reactions of 1,1-dimethyl-1-stannacyclopentane are discussed below.

Results and discussion

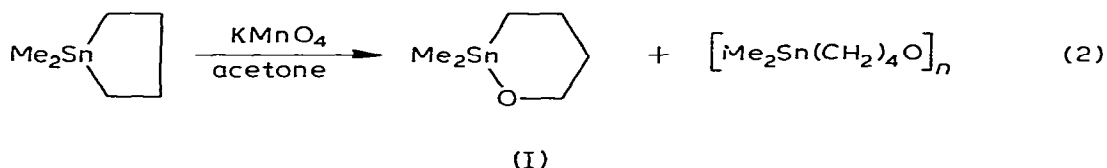
As reported previously [1] 1,1-dimethyl-1-stannacyclopentane (DMSC-5) slowly deteriorates on exposure to the atmosphere to give a viscous oil and

* For Part II, see ref. 1.

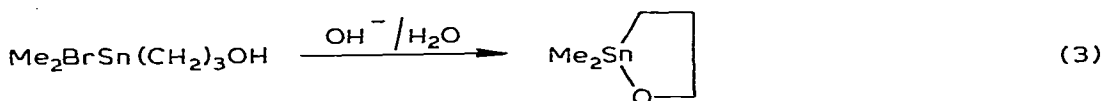
finally a vitreous product. From spectroscopic evidence it was concluded that two different reactions are involved, viz. oligomerization of DMSC-5 and, to a minor extent ($\leq 25\%$), ring-expansion as a result of oxygen insertion into the *endo*-cyclic tin-carbon bond. The identity of I was confirmed by the reaction of



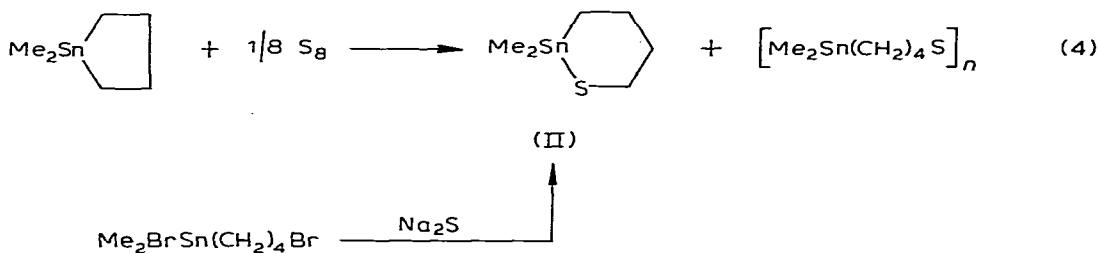
DMSC-5 with potassium permanganate in acetone solution, which gave a 66% yield of the same new compound 1,1-dimethyl-1-stanna-2-oxacyclohexane (I), together with a small amount of oligomeric material, $[Me_2Sn(CH_2)_4O]_n$. Vapour pressure osmometry indicates that compound I is monomeric in benzene solution.



As monostannacyclobutanes are still unknown the five-membered ring homologue 1,1-dimethyl-1-stanna-2-oxacyclopentane cannot be synthesized by ring expansion. Interestingly, however, we observed that the latter compound is formed quantitatively upon alkaline hydrolysis of (3-hydroxypropyl)dimethyltin bromide in aqueous solution [7].



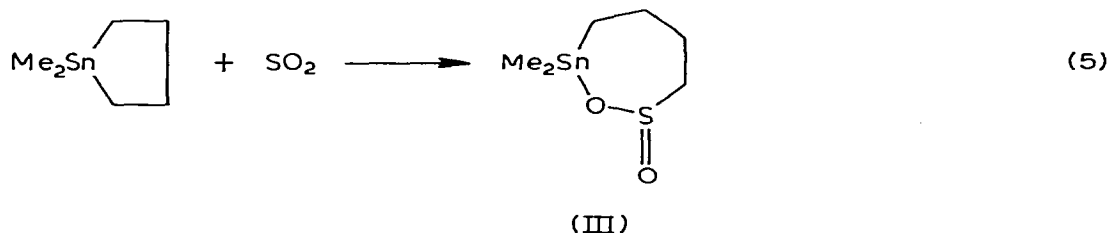
Reaction of DMSC-5 with sulphur at 200°C proceeds in a similar way to give the monomeric ring expansion product 1,1-dimethyl-1-stanna-2-thiacyclohexane (II), together with oligomeric material. An alternative route to II involves cycli-



zation of (4-bromobutyl)dimethyltin bromide [8] with sodium sulphide [7].

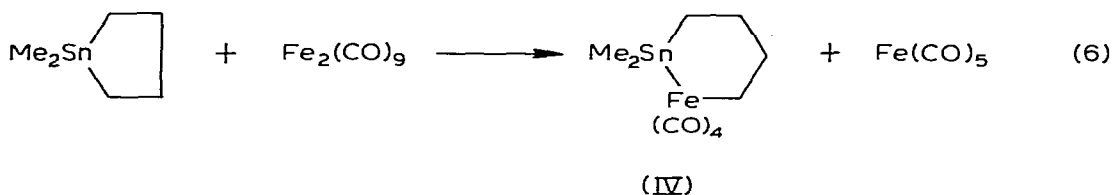
In contrast with the results obtained by Odenhausen [9], we observed that reaction of DMSC-5 with sulphur dioxide proceeds by a 1,2-dipolar addition of

the *endo*-cyclic tin—carbon bond to a sulphur—oxygen double bond to give the high-melting (m.p. 238–242°C) crystalline product 1,1-dimethyl-1-stanna-2-oxa-3-thiacycloheptane-3-oxide (III). The crystals tenaciously retain residual solvent (CCl₄ or cyclohexane), which could be removed only by prolonged heating in high vacuo. Reaction is accompanied by the formation of a small amount of oligomeric [Me₂Sn(CH₂)₄]_n side-product. Compound III is only sparingly soluble



in apolar hydrocarbon solvents, but is quite soluble in complexing solvents such as dimethyl sulphoxide. Probably intermolecular coordinative bonding between tin and oxygen gives rise to the formation of coordination polymers. Mass spectrometry showed the expected molecular ion at *m/e* 270.

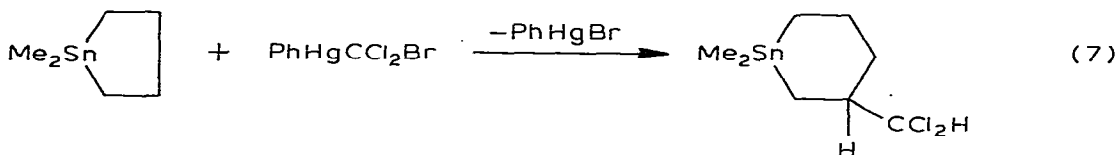
Reaction of DMSC-5 with diiron nonacarbonyl likewise proceeds by ring-expansion yielding the new binuclear complex IV and iron pentacarbonyl. Cundy and Lappert reported a similar reaction with silacyclobutanes [10]. Compound IV is extremely air-sensitive and tends to decompose slowly already at room temperature. Although an analytically pure sample of IV could not be obtained, the



molecular ion as well as the fragmentation pattern observed in the mass spectrum (cf. Experimental section) are in complete agreement with the proposed structure.

No reaction was observed between DMSC-5 and dicobalt octacarbonyl.

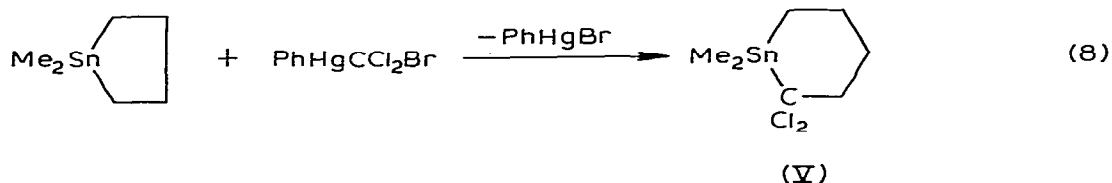
According to Seyferth and Washburn [11] reaction of phenyl(bromodichloromethyl)mercury with DMSC-5 proceeds by insertion of dichlorocarbene into the β-C—H bond.



This result was confirmed by the presence of a doublet at 5.57 ppm (²*J* ≈ 3 Hz) in the ¹H NMR spectrum of the product obtained by reaction 7, which is assigned to the CCl₂H proton.

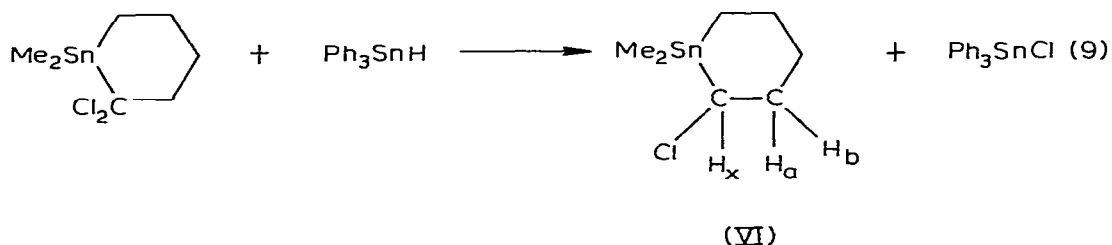
In contrast, reaction of DMSC-5 with phenyl(bromodichloromethyl)mercury was found to proceed exclusively by insertion of dichlorocarbene into the *endo*-

cyclic tin-carbon as in eq. 8 Insertion of dichlorocarbene into the β -C-H bond



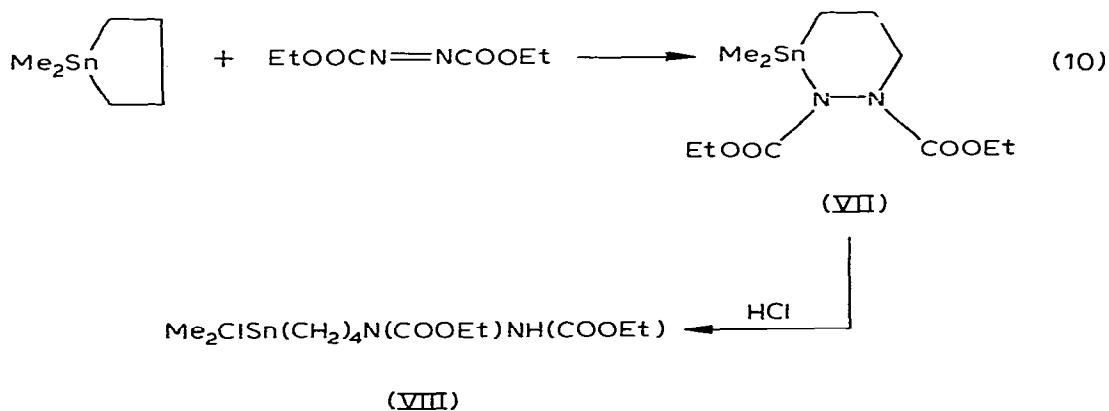
was not observed. Attempts to achieve a similar reaction of DMSC-5 with the carbene generator sodium trichloroacetate in dimethoxyethane solution failed.

Reaction of V with triphenyltin hydride in the presence of azobisisobutyronitrile gave 1,1-dimethyl-2-chloro-1-stannacyclohexane (VI). Mass spectro-



metry showed the expected molecular ion at m/e 254. The ^1H NMR spectrum showed two methyltin resonances of equal intensities at $\delta(\text{Me}-\text{Sn})$ 0.05 ppm, $J(^{111/119}\text{Sn}-\text{Me})$ 53/55 Hz and at $\delta(\text{Me}-\text{Sn})$ 0.22 ppm, $J(^{117/119}\text{Sn}-\text{Me})$ 54/56 Hz. The hydrogen bound to the chiral α -carbon atom showed an ABX resonance pattern at 3.49 ppm (distorted triplet, $J \approx 6.5$ Hz) and at 3.25 ppm (quartet, $J \approx 6.5$ Hz), approximate ratio 3/2. Possibly the compound consists of a mixture of two conformers, one with an axial and one with an equatorial chlorine atom. These observations warrant more detailed spectroscopic studies into the structure of this interesting new organotin heterocycle.

DMSC-5 did not react with diazomethane, iodomethylzinc iodide or ethyl(iodomethyl)zinc.



Reaction of DMSC-5 with diethyl azodicarboxylate also proceeds by ring-expansion to give the first example of a diazastannacycloalkane (VII). This compound, which is monomeric in benzene solution, is quite susceptible to proto-

TABLE 1
 PHYSICAL CONSTANTS, YIELDS AND ^1H NMR DATA FOR SOME NEW HETEROCYCLIC ORGANOTIN COMPOUNDS

Compound	B.p. ($^{\circ}\text{C}/\text{mmHg}$) (m.p. ($^{\circ}\text{C}$))	n_{D}^{20}	Yield (%)	^1H NMR data in CCl_4 solution (TMS 0 ppm)	
				δ (Me—Sn) (ppm)	$J(^{117}\text{Sn—Me})$ (Hz)
I	(m.p. 135—138)		66	0.38	56.5
II	87—90/0.3	1.5940	34	0.46	53.5
III	(m.p. 238—242)		45	0.48 ^a	65 ^a
IV				0.44	45
V	67—70/0.5	1.5370	43	0.38	54
VI				0.05	53
				0.22	54
VII	150—152/0.3	1.5135	53	0.49	56
VIII	185—190/0.4	1.5050	38	0.63	56

^a In $\text{DMSO}-d_6$ solution.

lysis. Treatment of VII with aqueous hydrochloric acid gave the novel functionally substituted organotin compound VIII.

DMSC-5 did not react with unsaturated systems such as phenyl acetylene, chloral and phenyl isocyanate.

According to Hänssgen and Odenhausen [12] DMSC-5 reacts readily with the nitrogen—sulphur double bond of sulphur diimide systems to give the corresponding seven-membered ring-expansion product.

In Table 1 physical constants, yields and ^1H NMR data of a series of new heterocyclic organotin compounds are listed.

The results discussed above together with those reported in preceding publications [1,4—6] illustrate clearly the enhanced reactivity of the *endo*-cyclic tin—carbon bond in stannacyclopentanes as compared with that of the six-membered homolog. Apparently ring-strain effects are of prime importance. Exact information about the bond angles in stannacyclopentanes, such as might be obtained from X-ray studies, is not yet available. However, calculations based on ^1H NMR data [13] indicate that the cyclic C—Sn—C bond angle in DMSC-5 is only slightly smaller than that in DMSC-6 or in linear tetraorganotins. In cyclopentane, ring strain effects are largely due to eclipsing strain rather than bond-angle strain [14]. Similarly, the enhanced reactivity of stannacyclopentane as compared with the larger heterocycles will primarily be the result of eclipsing strain effects.

Experimental

All reactions were performed under dry oxygen-free nitrogen. Liquids were handled by the syringe technique. Unless otherwise indicated the starting materials were prepared by published procedures or purchased. All materials were redistilled under nitrogen before use. ^1H NMR spectra were recorded using Varian Associates HA 60 and HA 100 spectrometers. IR spectra were recorded on a Perkin—Elmer model 577 instrument. Elemental analyses were carried out by the Elemental Analysis Section of this Institute.

Typical experiments are described below.

1,1-Dimethyl-1-stanna-2-oxacyclohexane (I)

A solution of 2.09 g (0.0102 mol) of DMSC-5 and 1.08 g (0.0068 mol) of KMnO_4 in 320 ml of dry, oxygen-free, redistilled acetone was stirred for 1 h at room temperature. Decoloration was complete within 15 minutes. The MnO_2 precipitate was removed by filtration, and the filtrate was evaporated to give a partly-liquid partly-crystalline residue. Filtration gave 1.5 g (66%) of crude I. An analytically pure sample was obtained by recrystallization from acetone, m.p. 135–138°C.

Anal.: found: C, 32.5; H, 6.5; Sn, 53.6; mol. wt. found (vapor pressure osmometry in benzene); 242. $\text{CH}_{14}\text{SnO}_6$ calcd.: C, 32.63; H, 6.39; Sn, 53.74%; mol. wt. calcd.: 220.868. $^1\text{H NMR}$: $\delta(\text{Me-Sn})$ 0.38 ppm; $J(^{117}\text{Sn-Me})$ 56.5 Hz. IR characteristic absorptions suitable for identification of tin containing six-membered ring systems were observed at ν 917 and 970 cm^{-1} (for comparison in DMSC-6, ν 907 and 970 cm^{-1}) [3,13].

Evaporation of the filtrate gave an oily liquid consisting ($^1\text{H NMR}$) of a mixture of I and an unidentified product of a composition fairly similar to I, possibly oligomeric $[\text{Me}_2\text{Sn}(\text{CH}_2)_4\text{O}]_n$, $\delta(\text{Me-Sn})$ 0.33 ppm.

1,1-Dimethyl-1-stanna-2-thiacyclohexane (II)

A mixture of 1.06 g (0.005 mol) of DMSC-5 and 0.160 g (0.005 mol) of sulfur was heated for 3 h at 200°C in a sealed tube to give a yellowish oily liquid. Distillation gave 0.4 g (34%) of pure II, b.p. 87–90°C/0.3 mmHg; n_D^{20} 1.5940.

Anal.: found: C, 30.2; H, 5.9; mol. wt. (vapor pressure osmometry in benzene), 260. $\text{C}_6\text{H}_{14}\text{SnS}$ calcd.: C, 30.42; H, 5.96%; mol. wt., 236.933. $^1\text{H NMR}$: $\delta(\text{Me-Sn})$ 0.46 ppm; $J(^{117}\text{Sn-Me})$ 53.5 Hz.

In addition 0.2 g of yellow oil was obtained (b.p. 116–130°C/0.3 mmHg; n_D^{20} 1.5842), consisting ($^1\text{H NMR}$) largely of II together with a mixture of $[\text{Me}_2\text{Sn}(\text{CH}_2)_4\text{S}]_n$ oligomers, $\delta(\text{Me-Sn})$ 0.38, 0.39, 0.43, 0.48 ppm. Characteristic IR absorptions were observed at ν 900 and 950 cm^{-1} .

1,1-Dimethyl-1-stanna-2-oxa-3-thiacycloheptane-3-oxide (III)

A slow stream of dry sulphur dioxide gas was passed for 0.5 h through a solution of 2.0 g (0.009 mol) of DMSC-5 in 7 ml of CCl_4 at room temperature. A white solid separated. After standing overnight, filtration gave 1.1 g (45%) of crude III. According to $^1\text{H NMR}$ spectrometry the filtrate consisted largely of unreacted DMSC-5, together with a small amount of polymerized DMSC-5 ($^1\text{H NMR}$, $\delta(\text{Me-Sn})$ 0.03–0.05 ppm) [6]. Analytical data indicated the presence of residual CCl_4 in the crystals: Found: C, 24.5; H, 4.8; O, 10.9; S, 10.2; Sn, 39.8; Cl, 8.9%. For a mixture containing 90.4% of III and 9.6% of CCl_4 the analysis data were calculated to be: C, 24.96; H, 4.74; O, 10.75; S, 10.77; Sn, 39.88; Cl, 8.88%.

Only after prolonged heating (7 h) in high-vacuo at 160°C could a solvent-free sample of III be obtained, m.p. 238–242°C. Found: C, 26.5; H, 5.2; mol. wt. 268.932. $\text{C}_6\text{H}_{14}\text{SnO}_2\text{S}$ calcd.: C, 26.80; H, 5.25%. GC-MS analysis showed the product to be >90% pure, the parent peak being observed at m/e 270.

Reaction of DMSC-5 with diiron nonacarbonyl (IV)

A mixture of 0.89 g (2.45 mmol) of $\text{Fe}_2(\text{CO})_9$, 0.50 g (2.45 mmol) of DMSC-5

and 6 ml of dry benzene was stirred for 6 days at room temperature. The benzene-insoluble $\text{Fe}_2(\text{CO})_9$, gradually dissolved to give a clear brown solution. According to ^1H NMR spectrometry $> 80\%$ of DMSC-5 ($\delta(\text{Me}-\text{Sn})$ 0.19 ppm) had been converted into a new product having $\delta(\text{Me}-\text{Sn})$ 0.44 ppm, $J(^{117}\text{Sn}-\text{Me})$ 45 Hz.

Distillation gave a small amount of $\text{Fe}(\text{CO})_5$ (b.p. $103^\circ\text{C}/750$ mmHg) leaving a green partly solid residue. Pentane (6 ml) was added. Filtration and subsequent evaporation of the pentane gave 0.75 g (82%) of crude IV. The product appeared to be rather unstable thereby preventing the isolation of an analytically pure sample. However, the structure proposed, $\text{Me}_2\text{Sn}(\text{CH}_2)_4\text{Fe}(\text{CO})_4$, was confirmed by mass spectrometry.

In addition to the molecular ion, m/e 374, the following fragments were observed: m/e 359 ($\text{MeSn}(\text{CH}_2)_4\text{Fe}(\text{CO})_4$), 346 ($\text{Me}_2\text{Sn}(\text{CH}_2)_4\text{Fe}(\text{CO})_3$), 344 ($\text{Sn}(\text{CH}_2)_4\text{Fe}(\text{CO})_4$), 318 ($\text{Me}_2\text{Sn}(\text{CH}_2)_4\text{Fe}(\text{CO})_2$), 316 ($\text{Sn}(\text{CH}_2)_4\text{Fe}(\text{CO})_3$), 290 ($\text{Me}_2\text{Sn}(\text{CH}_2)_4\text{Fe}(\text{CO})$), 288 ($\text{Sn}(\text{CH}_2)_4\text{Fe}(\text{CO})_2$), 262 ($\text{Me}_2\text{Sn}(\text{CH}_2)_4\text{Fe}$), 260 ($\text{Sn}(\text{CH}_2)_4\text{FeCO}$), 232 ($\text{Sn}(\text{CH}_2)_4\text{Fe}$), 204 ($\text{Sn}(\text{CH}_2)_2\text{Fe}$), 198 ($\text{Sn}(\text{CH}_2)_4$), 168 ($\text{Fe}(\text{CO})_4$), 140 ($\text{Fe}(\text{CO})_3$), 135 (MeSn), 120 (Sn), 112 ($\text{Fe}(\text{CO})_2$), 84 (FeCO), 56 (Fe), 28 (CO).

1,1-Dimethyl-2,2-dichloro-1-stannacyclohexane (V)

By means of a syringe 4.34 g (0.02) mol of DMSC-5 was added to a solution of 3.5 g (0.008 mol) of $\text{PhHgCCl}_2\text{Br}$ in 20 ml of benzene kept at 80°C . After 4 h the precipitated PhHgBr was filtered off.

Distillation gave 1.0 g (43% based on $\text{PhHgCCl}_2\text{Br}$) of crude V containing (^1H NMR) a small amount of Me_2SnCl_2 . An analytically pure sample was obtained by column chromatography over neutral silica gel (eluent, light-petroleum, b.p. $40-60^\circ\text{C}$) followed by redistillation; b.p. $67-70^\circ\text{C}/0.5$ mmHg; n_D^{20} 1.5370. Found: C, 29.8; H, 5.0; Cl, 24.8; Sn, 40.6; mol. wt. 287.786. $\text{C}_7\text{H}_{14}\text{SnCl}_2$ calcd.: C, 29.22; H, 4.90; Cl, 24.64; Sn, 41.24%. GC-MS analysis showed the product to be $>95\%$ pure. In addition to the molecular ion at m/e 288, tin-containing mass fragments were observed at m/e 273 ($\text{MeSnCCl}_2(\text{CH}_2)_4$), 245 ($\text{MeSnCCl}_2(\text{CH}_2)_2$), 237 ($\text{MeSnCClCH}(\text{CH}_2)_3$), 205 ($\text{Me}_2\text{Sn}(\text{CH}_2)_2\text{CHCH}_2$), 185 (Me_2ClSn), 155 (SnCl), 135 (MeSn), 120 (Sn).

1,1-Dimethyl-2-chloro-1-stannacyclohexane (VI)

A mixture of 53.4 mg (0.19 mmol) of V, 63.5 mg (0.18 mmol) of Ph_3SnH and 5-mol-percent of azobisisobutyronitrile (AIBN) in 0.4 ml of benzene was heated for 24 h at 60°C . The ^1H NMR spectrum indicated that V had been completely converted into a product to which structure VI was tentatively assigned. Mass spectrometry showed the expected molecular ion at m/e 254.

1,1-Dimethyl-2,3-bis(carboethoxy)-1-stanna-2,3-diazacycloheptane (VII)

A mixture of 4.15 g (0.020 mol) of DMSC-5 and 3.6 g (0.021 mol) of diethyl azodicarboxylate was kept for 4 weeks at room temperature. The ^1H NMR spectrum indicated that the starting material had been almost completely consumed. Distillation gave 4.1 g (53%) of VII, b.p. $150-152^\circ\text{C}/0.3$ mmHg; n_D^{20} 1.5135. Found: C, 38.0; H, 6.4; N, 7.6; Sn, 30.7; mol. wt., 379 (vapour pressure osmometry in benzene). $\text{C}_{12}\text{H}_{24}\text{SnN}_2\text{O}_4$ calcd.: C, 38.03; H, 6.38; N, 7.39; Sn, 31.31%, mol. wt. 379.027.

1-[4-(Dimethylchlorostannyl)butyl]-1,2-bis(carboethoxy)hydrazine (VIII)

A mixture of 1.07 g (0.005 mol) of DMSC-5 and 0.9 g (0.005 mol) of diethyl azodicarboxylate was kept at room temperature for 4 weeks. The viscous yellowish mixture was dissolved in 5 ml diethyl ether and treated with 5 ml of 1 N aqueous HCl. The organic phase was separated, dried over MgSO₄ and distilled to give 0.7 g (34%) of VIII. The ¹H NMR spectrum indicated that the product was contaminated with some 10% of oligomeric [Me₂Sn(CH₂)₄]_n [6]. VIII, b.p. 185–190°C/0.4 mmHg; *n*_D²⁰ 1.5050. Found: C, 34.0; H, 6.0; N, 6.8; Cl, 7.9%; mol. wt. 415.488. C₁₂H₁₅SnN₂O₄Cl calcd: C, 35.69; H, 6.07; N, 6.74; Cl, 8.53%. ¹H NMR: δ(Me–Sn) 0.63 ppm; *J*(^{117/119}Sn–Me) 56/58.5 Hz; δ(NH) 6.80 ppm; δ(CH₂O) 4.20 ppm; δ(CH₂N) 3.50 ppm; δ(CH₃–C) 1.28 ppm.

Acknowledgements

Financial support by the International Tin Research Institute, London, is gratefully acknowledged.

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