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THE SYNTHESIS OF SMALL-RING MONOSTANNACYCLOALKANES *

E.J. BULTEN and H.A. BUDDING
Institute for Organic Chemistry TNO, Utrecht (The Netherlands)

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Summary

The scope of a novel synthesis of small-ring monostannacycloalkanes, involving the disproportionation of α,ω-distannaalkanes, $\geqslant Sn(CH_2)_nSn \leqslant$, is discussed [2]. The reaction is best suited for the synthesis of 1,1-dialkyl-1-stannacyclopentanes and -hexanes.

A mechanism is proposed which involves an intramolecular electrophilic attack by tin at carbon.

Introduction

Cycloalkanes containing one heterocyclic silicon or germanium atom, i.e. monosila- and monogerma-cycloalkanes, have been extensively studied [3,4]. However, information on monostannacycloalkanes is remarkably scarce [5], and no monostannacyclobutane has been reported **.

The well-characterized monostannacyclo-pentanes, -hexanes and heptanes I—VI have been described.

The generally employed Grignard or organolithium procedures give rather poor yields (10—30%) of these ring compounds [7—11].

In the present paper we decribe studies of routes to monostannacycloalkanes. A new synthesis, based on the disproportionation of α,ω-distannaalkanes, is discussed in detail.

Investigations of the reactivity of monostannacycloalkanes will be discussed in a later paper.

Results and discussion

Grignard and alkali metal procedures

According to Bourhis [9] and to Topart [7] the Grignard reaction 1 gives about 25% of 1,1-dimethyl-1-stannacyclopentane, irrespective of the order of

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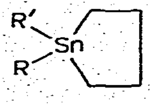
* A preliminary paper has appeared in print [1].

** Recently, Seyferth and Lefferts reported the first 1,3-distannacyclobutane [6].



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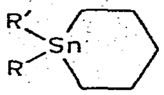

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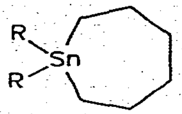

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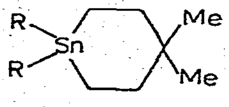

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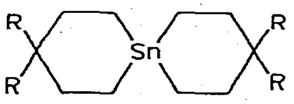

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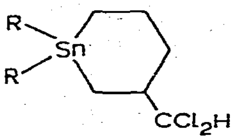
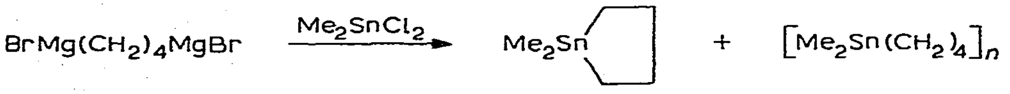


(VI)

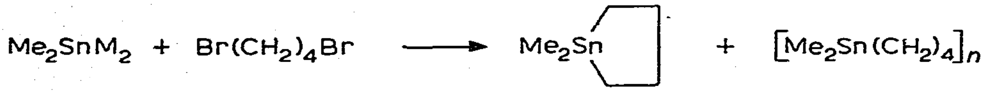
I, R = R′ = Me [1,7], Et [1], Bu, Neopentyl [8], Ph [7,9]; R = Me, R′ = Ph [7].
II, R = R′ = Me [1,7,10], Et [10], Bu, Neopentyl [8], Ph [7,8,9,11]; R = Ph, R′ = Me [7], R = Ph, R′ = Cl [7], Br [7,11], I [11]; R = R′ = Br [7,11], I [11].
III, R = R′ = Me [1,7,8], Et, Neopentyl [8], Ph [7–9], Br [7]; R = Me, R′ = Ph [7].
IV, R = Bu [12].
V, R = H [11], Me [12].
VI, R = Me [13].

addition of the reactants or the solvent used. Similarly, we observed that under various conditions always about 60% of pentane-soluble material is formed, and consists (^{1}H NMR) of approximately equal amounts of stannacyclopentane and its oligomers. Use of magnesiacyclopentane [14] did not improve the monomer/polymer ratio.



(1)

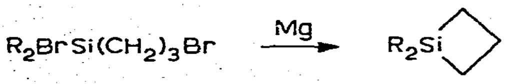
Reaction of 1,4-dibromobutane with dimethyltin disodium in liquid ammonia [15] or with dimethyltin dilithium in THF or HMPT [16] solution gave only traces of ring compound. However, reaction of the dimethyltin dialkali metal intermediates with butyl bromide followed by GLC analysis demonstrated that these compounds are formed in only poor yields, optimal results being obtained with the preparation of dimethyltin dilithium in THF (35%).



(2)

(M = Li, Na)

1,1-Disubstituted 1-silacycloalkanes are readily accessible by the intramolecular ring closure of (γ-haloalkyl)halosilanes with magnesium [3], e.g.:



(3)

(R = Me, Br)

Attempts to prepare in this way the unknown monostannacyclobutane ring were unsuccessful. In analogous experiments of the type indicated in equation

$$R_2BrSn(CH_2)_nBr \not\xrightarrow[\text{THF}]{\text{Mg}} R_2Sn(CH_2)_n \qquad (4)$$

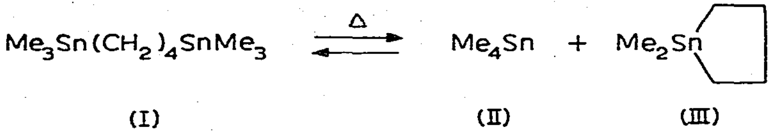
(R = Me, Br, n = 3; R = Br, n = 5)

4, (R = Br, n = 5) no formation of a six-membered ring was detected.

Disproportionation of α,ω-distannaalkanes, $\geqslant Sn(CH_2)_nSn \leqslant$

A new synthetic route to small-ring monostannacycloalkanes is based on the disproportionation of α,ω-distannaalkanes.

Analyses by ^{1}H NMR and GLC indicate that thermolysis of 1,4-bis(trimethylstannyl)butane (I) for 15 min at 256°C under reflux conditions gives a 44% conversion of I to give 90% of tetramethyltin (II) and 75% of 1,1-dimethyl-1-stannacyclopentane (III).



(5)

Under similar conditions, but in the presence of 20 mole percent of zinc chloride, 97% of I reacted, and gave 99% of II together with only 47% of III. Prolonged heating (90 min at 285°C) resulted in a further decrease of the amount of ring compound (12%). Apparently, zinc chloride catalysis enhances the rate of reaction 5, but also the degradation of the ring to give polymeric species. With aluminium trichloride as the catalyst reaction 5 is exothermic even at 160°C, but in addition to tetramethyltin only polymeric species are formed.

Optimal results are obtained when the reaction is carried out in a distillation apparatus with a pot temperature of 270—300°C and a column temperature well above the boiling points of II and III. In this way ring polymerization is kept at a minimum and the equilibrium is shifted to the right. That an equilibrium is indeed involved was demonstrated by the formation of I upon heating a 1:1 mixture of II and III in a sealed tube.

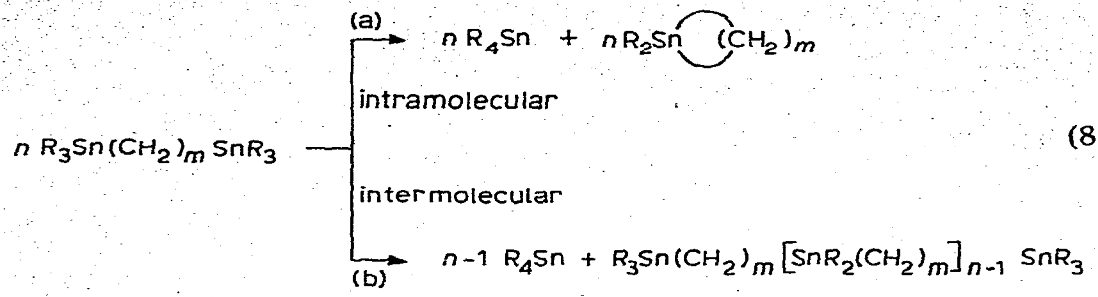
As regards the mechanism, reaction 5 is a special example of a disproportionation reaction between two tetraalkyltin species. Previously this type of reaction, which proceeds by electrophilic attack of tin at carbon, was observed only when Lewis acid catalysts were present, e.g. [17,18]:

$$Me_4Sn + Et_4Sn \xrightarrow[12\ \text{h},\ 120^\circ\text{C}]{AlCl_3} Me_4Sn + Me_3SnEt + Me_2SnEt_2 + MeSnEt_3 + Et_4Sn \quad (6)$$

We found that thermolysis of trimethyloctadecyltin for 1 h at 270°C in a distillation apparatus (without a catalyst) gives about 40% of tetramethyltin. In the presence of zinc chloride, a semi-quantitative yield of tetramethyltin was obtained after two hours.

$$2\ Me_3SnC_{18}H_{37} \xrightarrow{\Delta} Me_4Sn + Me_2Sn(C_{18}H_{37})_2 \qquad (7)$$

α,ω-Bis(trialkylstannyl)alkanes contain two identical tetraalkyltin species, linked together by a carbon—carbon bond. An intramolecular electrophilic substitution reaction results in the formation of the tetraalkyltin and the dialkyltin ring (Eq. 8a), whereas an intermolecular molecular reaction gives rise to the formation of polymeric species. Because of the much great volatility of the ring



(8)

compounds than of the polymers the conditions used will favour the ring formation. As reaction 8b is a bimolecular and 8a a unimolecular reaction, polymer formation can be further suppressed by carrying out the reaction at high dilution.

The reaction is generally applicable to the synthesis of 1,1-dialkyl-1-stannacyclo-pentanes and -hexanes in high yields (Table 1). Meinema et al. [19] have shown that stibacyclo-pentanes and -hexanes can be prepared analogously.

1,1-Dimethyl-1-stannacycloheptane is formed only when the reaction is carried out at high dilution using α-bromonaphthalene as the solvent (~40% yield). In the case of the corresponding stannacyclooctane only a trace of ring compound was detected.

Thermolysis of 1,3-bis(trimethylstannyl)propane gave tetramethyltin, but the formation of 1,1-dimethyl-1-stannacyclobutane could not be demonstrated.

TABLE 1.

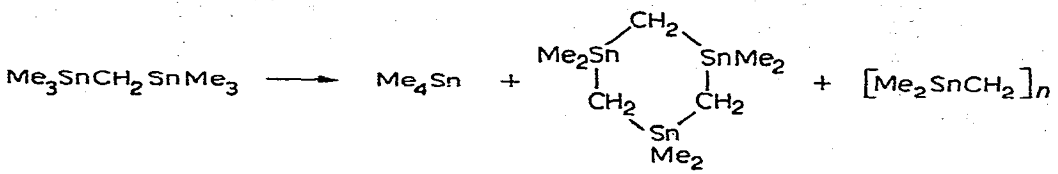
PHYSICAL CONSTANTS, YIELDS AND ^{1}H NMR DATA FOR α,ω-DISTANNAALKANES AND OF MONOSTANNACYCLOALKANES

Compound	B.p. (°C/mmHg)	n_D^{20}	Yield (%)	^{1}H NMR data in CCl_4 solution (TMS = 0)	
				δ(Me—Sn) (ppm)	$J(^{117/119}Sn—Me)$ (Hz)
$Me_3SnCH_2SnMe_3$	88—92/15	1.5056	48	0.075 [a]	50/52
$Me_3Sn(CH_2)_3SnMe_3$	60—64/0.1	1.5002	80	0.04	50/52
$Me_3Sn(CH_2)_4SnMe_3$	74—76/0.4	1.4980	90	0.03	49.5/51.5
$Me_3Sn(CH_2)_5SnMe_3$	87—90/0.6	1.4970	93	0.03	50/52
$Me_3Sn(CH_2)_6SnMe_3$	126—129/5	1.4945	77	0.02	50/52
$Me_3Sn(CH_2)_7SnMe_3$	112—115/0.4	1.4940	85	0.04	50/52
$Et_3Sn(CH_2)_4SnEt_3$	155—158/1.0	1.5050	84		
$Me_2BrSn(CH_2)_4SnBrMe_2$	(m.p. 74—76)		84	0.72	52/54
$Me_2ClSn(CH_2)_4SnClMe_2$	(m.p. 65—68)		58	0.63	52.5/54.5
$Me_2HSn(CH_2)_4SnHMe_2$	69—73/0.6	1.5110	60	0.11 [b]	54/56
$Me_2ClSn(CH_2)_4SnCl_3$	(m.p. 43—45)		90	0.66	53/55
$Me_2BrSn(CH_2)_5SnBrMe_2$	(m.p. 45—47)		88	0.69	51/53
$Me_2Sn(CH_2)_4$	47—48/20	1.5067	94 [c]	0.19 [d]	52/54
$Et_2Sn(CH_2)_4$	39—41/0.2	1.5095	80 [c] (48) [e]		
$Me_2Sn(CH_2)_5$	76—79/15	1.5027	90 [c]	0.10 [d]	51/53
$Me_2Sn(CH_2)_6$	82—84/15	1.5077	40 [c,f] (18) [e]	0.06 [d]	49.5/51.5

[a] δ(CH_2—Sn) —0.26 ppm; $J(^{117/119}Sn—CH_2)$ 58/60 Hz. [b] Doublet, J_{ab} 1.2 Hz; δ(Sn—H) 4.85 ppm. [c] Determined by GLC and ^{1}H NMR analysis, based on the amount of $R_3Sn(CH_2)_nSnR_3$ converted; isolated yields about 20% lower. [d] Cf. ref. 21. [e] Grignard procedure. [f] In α-bromonaphthalene solution.

$$Me_3Sn(CH_2)_3SnMe_3 \xrightarrow{\Delta} Me_4Sn + [Me_2Sn(CH_2)_3]_n \quad (9)$$

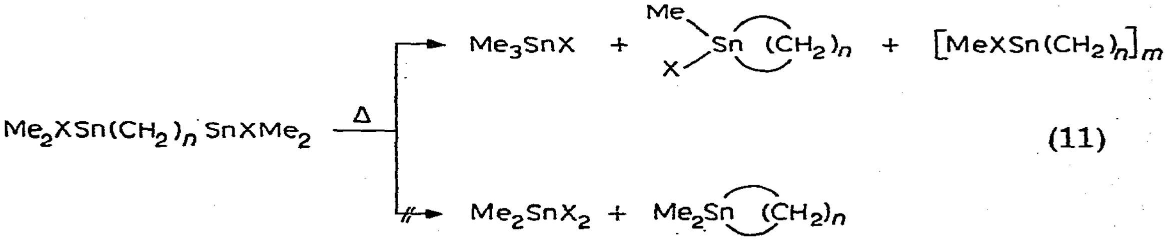
Likewise, thermolysis of 1,2-bis(trimethylstannyl)methane gave a semi-quantitative yield of tetramethyltin. However, in addition to polymeric species only minor amounts (~5%) of IV could be detected by ^1H NMR analysis [20].



(IV)

(10)

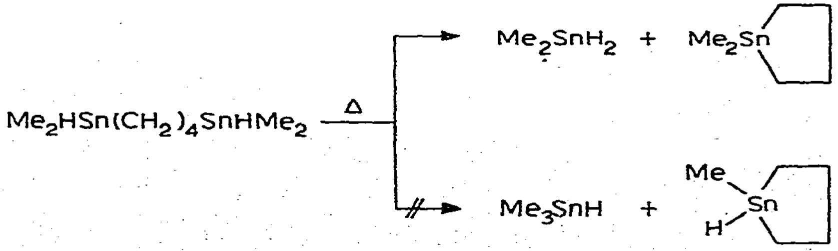
Several attempts were made to apply the disproportionation concept to the synthesis of metal-functionally substituted monostannacycloalkanes. Thermolysis of 1,4-bis(chlorodimethylstannyl)butane gave trimethyltin chloride together with insoluble polymeric $[MeClSn(CH_2)_4]_n$. Similar results were obtained with 1,4-bis(bromodimethylstannyl)butane and with 1,5-bis(bromodimethylstannyl)pentane. In both cases GLC analysis (after methylation) demonstrated the presence of small amounts of the corresponding ring compounds, the major products being polymeric species.



(11)

(X = Cl , Br ; n = 4,5)

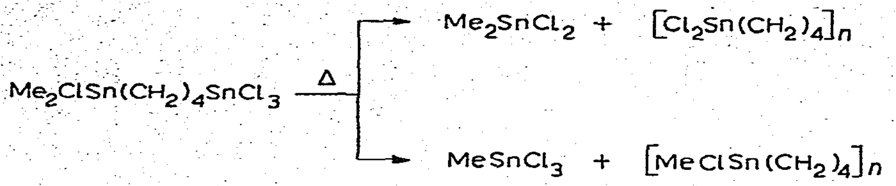
Unexpectedly, thermolysis of 1,4-bis(hydridodimethylstannyl)butane at 185°C resulted in the formation of 33% of 1,1-dimethyl-1-stannacyclopentane. whereas no trace of V was observed.



(12)

(V)

Disproportionation of 1-(chlorodimethylstannyl)-4-(trichlorostannyl)butane at 220—240°C gave exclusively dimethyltin dichloride together with a high-melting insoluble polymer.



(13)

In summary, it can be concluded that the disproportionation of α,ω-distannaalkanes is particularly suited for the synthesis of 1,1-dialkyl-1-stannacyclopentanes and -hexanes. The reaction is less attractive as a synthetic route to 1-halo-1-stannacycloalkanes in view of the formation of substantial amounts of polymeric species.

Table 1 lists the physical constants, yields and ^{1}H NMR data of the α,ω-distannaalkanes and monostannacycloalkanes prepared.

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 purified under nitrogen before use. Typical experiments are described below.

1,4-Bis(trimethylstannyl)butane

A solution of 38.7 g (0.18 mol) of 1,4-dibromobutane in 450 ml of tetrahydrofuran (THF) was added drop-wise during 5 h to 20.1 g (0.825 g-atom) of magnesium in 50 ml of THF. After standing overnight the resulting Grignard solution was separated from the excess of magnesium by decantation. A solution of 54.0 g (0.27 mol) of trimethyltin chloride in 75 ml of THF was added over a period of 1 h to the Grignard solution. The mixture was heated for 5 h at 60—65°C, cooled to 0°C and hydrolysed with 100 ml of a saturated aqueous solution of ammonium chloride. The organic phase was separated and the aqueous phase was extracted three times with 20 ml portions of diethyl ether. After drying with anhydrous magnesium sulphate the solvents were evaporated to give 52 g (100%) of crude product (n_D^{20} 1.4976). Distillation gave 46.9 g (90%) of pure 1,4-bis(trimethylstannyl)butane. $Me_3Sn(CH_2)_4SnMe_3$: b.p. 74—76°C/0.4 mmHg; n_D^{20} 1.4980. (Anal. Found: C, 31.7; H, 6.9. $C_{10}H_{26}Sn_2$ calcd.: C, 31.30; H, 6.83%).

In a similar way were prepared: $Me_3Sn(CH_2)_5SnMe_3$: b.p. 87—90°C/0.6 mmHg; n_D^{20} 1.4970; 93% yield. (Anal.: Found: C, 33.3; H, 7.3. $C_{11}H_{28}Sn_2$ calcd.: C, 33.22; H, 7.10%), $Me_3Sn(CH_2)_6SnMe_3$: b.p. 126—129°C/5 mmHg; n_D^{20} 1.4945; 77% yield. (Anal.: Found: C, 35.5; H, 7.5. $C_{12}H_{30}Sn_2$ calcd.: C, 35.00; H, 7.35%), $Me_3Sn(CH_2)_7SnMe_3$: b.p. 112—115°C/0.4 mmHg; n_D^{20} 1.4940; 85% yield. (Anal.: Found: C, 37.4; H, 7.2. $C_{13}H_{32}Sn_2$ calcd.: C, 36.67; H, 7.58%), $Et_3Sn(CH_2)_4SnEt_3$: b.p. 155—158°C/1.0 mmHg; n_D^{20} 1.5050; 84% yield. (Anal.: Found: C, 41.5; H, 8.1. $C_{16}H_{38}Sn_2$ calcd.: C, 41.08; H, 8.19%).

1,4-Bis(bromodimethylstannyl)butane

A solution of 10.2 g (0.05 mol) of 1,4-bis(trimethylstannyl)butane in 35 ml of carbon tetrachloride was cooled to 0°C. A solution of 16 g (0.10 mol) of bromide in 15 ml of carbon tetrachloride was added with cooling during 20 min. The slightly yellow solution was evaporated in vacuo to give 26.1 g of crude product, m.p. 68—73°C. Recrystallization from hexane gave 21.7 g (84%) of pure 1,4-bis(bromodimethylstannyl)butane. $Me_2BrSn(CH_2)_4SnBrMe_2$: m.p. 74—76°C. (Anal.: Found: C, 19.0; H, 4.0; Br, 31.1. $C_8H_{20}Br_2Sn_2$ calcd.: C, 18.71; H, 3.93; Br, 31.13%). In a similar way was obtained: $Me_2BrSn(CH_2)_5$-$SnBrMe_2$: m.p. 45—47°C; 88% yield. (Anal.: Found: C, 20.8; H, 4.4; Br, 29.8. $C_9H_{22}Br_2Sn_2$ calcd.: C, 20.49; H, 4.21; Br, 30.30%).

1,4-Bis(hydridodimethylstannyl)butane

A solution of 20.56 g (0.040 mol) of 1,4-bis(bromodimethylstannyl)butane in a mixture of 20 ml of diethyl ether and 30 ml of THF was added drop-wise to a suspension of 2.0 g (0.050 mol) of lithium aluminium hydride in 50 ml of diethyl ether. The resulting mixture was refluxed for 1 h and subsequently treated with 6 ml of water. After filtration the solvent was evaporated in vacuo. Distillation gave 8.4 g (60%) of pure 1,4-bis(hydridodimethylstannyl)butane. $Me_2HSn(CH_2)_4SnHMe_2$: b.p. 69—73°C/0.6 mmHg; n_D^{20} 1.5110. (Anal.: Found: C, 27.3; H, 6.4. $C_8H_{22}Sn_2$ calcd.: C, 27.02; H, 6.24%).

1-(Chlorodimethylstannyl)-4-(trichlorostannyl)butane

A solution of 1.32 g (0.005 mol) of tin tetrachloride in 3 ml of carbon tetrachloride was added slowly at 0°C to a solution of 1.03 g (0.005 mol) of 1,1-dimethyl-1-stannacyclopentane in 5 ml of carbon tetrachloride. The mixture was heated for 5 h at 80°C. Evaporation of the solvent in vacuo gave 2.05 g (90%) of pure 1-(chlorodimethylstannyl)-4-(trichlorostannyl)butane, m.p. 43—45°C. (Anal.: Found: C, 15.8; H, 3.1; Cl, 30.0. $C_6H_{14}Cl_4Sn_2$ calcd.: C, 15.49; H, 3.03; Cl, 30.47%).

In a similar way, 1,1-dimethyl-1-stannacyclopentane and dimethyltin dichloride gave 1,4-bis(chlorodimethylstannyl)butane, which was recrystallized from tetrachloroethylene. $Me_2ClSn(CH_2)_4SnClMe_2$: m.p. 65—68°C. (Anal.: Found: C, 22.9; H, 4.8; Cl, 17.0. $C_8H_{20}Cl_2Sn_2$ calcd.: C, 22.63; H, 4.75; Cl, 16.70%).

1,1-Dimethyl-1-stannacyclopentane

In a distillation apparatus a mixture of 18.4 g (0.048 mol) of 1,4-bis(trimethylstannyl)butane (I) and 1.36 g (0.010 mol) of zinc chloride was heated to 250—275°C by means of a Woods metal bath. The column temperature was kept at 170—180°C. In 1.5 h, 17.0 g of distillate (b.p. 60—170°C) was collected. ^{1}H NMR analysis, (with a weighed amount of methylnaphthalene as the internal standard) showed that 87.5% of I had reacted to give 94% of 1,1-dimethyl-1-stannacyclopentane (III) and 94% of tetramethyltin. Distillation gave 6.2 g of III (71% based on the amount of I converted) containing about 7% of tetramethyltin. Careful fractionation of a sample of this product gave pure 1,1-dimethyl-1-stannacyclopentane; b.p. 47—48°C/20 mmHg; n_D^{20} 1.5067. (Anal.: Found: C, 35.3; H, 7.0. $C_6H_{14}Sn$ calcd.: C, 35.18; H, 6.89%). In a similar way were prepared: $Et_2Sn(CH_2)_4$: b.p. 39—41°C/0.2 mmHg; n_D^{20} 1.5095; 80% yield. (Anal.: Found: C, 41.1; H, 7.9. $C_8H_{18}Sn$ calcd.: C, 41.25; H, 7.79%), Me_2Sn-$(CH_2)_5$: b.p. 76—79°C/15 mmHg; n_D^{20} 1.5027; 90% yield. (Anal.: Found: C, 38.3; H, 7.7. $C_7H_{16}Sn$ calcd.: C, 38.4; H, 7.4%).

Acknowledgements

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