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THE REACTIVITY OF SMALL-RING MONOSTANNACYCLOALKANES

II *. TRANSALKYLATION REACTIONS OF 1,1-DIALKYL-1-STANNACYCLOALKANES. SYNTHESIS OF NEW METAL-FUNCTIONALLY SUBSTITUTED STANNACYCLOALKANES

E.J. BULTEN and H.A. BUDDING
Institute for Organic Chemistry T.N.O., Utrecht (The Netherlands)
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Summary

Comparative studies of halodemetallation (Cl_2, Br_2, I_2) and trans-alkylation ($Me_{4-n}SnCl_n$, $GeCl_4$, $HgCl_2$) reactions of 1,1-dimethyl-1-stannacyclo-pentane, -hexane and -heptane are described. In the case of the five-membered ring compounds, both halodemetallation and transalkylation reactions proceed exclusively by ring cleavage, rather than by demethylation, which points to substantial strain. These transalkylation reactions proved to be most valuable for the synthesis of new types of unsymmetric organotin compounds, such as $Me_2ClSn(CH_2)_4SnCl_nMe_{3-n}$ (n = 1—3), $Me_2ClSn(CH_2)_4GeCl_3$, $Me_2ClSn(CH_2)_4HgCl$.

Reactions of the six- and seven-membered ring systems with iodine likewise proceed by preferential cleavage of the *endo*-cyclic tin—carbon bond, the order of cleavage being: $(CH_2)_4Sn > (CH_2)_5Sn > (CH_2)_6Sn >$ MeSn. However, possibly as a result of steric effects, a rather different reactivity order is observed in transalkylation reactions with tin and mercury halides: $(CH_2)_4Sn >$ MeSn > $(CH_2)_5Sn > (CH_2)_6Sn$.

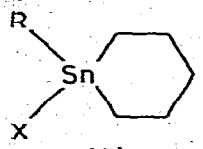
On the basis of the latter observations a new synthesis for 1-chloro-1-methyl-1-stannacyclo-hexane and -heptane was developed. These compounds are shown to be useful starting materials for the synthesis of a variety of new metal-functionally substituted stannacycloalkanes.

Introduction

While heterocycloalkanes containing silicon and germanium have attracted considerable attention [2,3], information on stannacycloalkanes is still scarce

* For Part I, see ref. 1.

[4]. The synthesis of 1,1-dialkyl-1-stannacyclo-pentanes, -hexanes and -heptanes has been discussed in several recent papers [4—6]. As regards monostannacycloalkanes with functionality of the metal, structures A and B are the only well-characterized representatives reported to date.

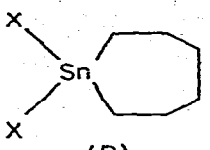


(A)

R = Me, X = Cl, Br [5]

R = Ph, X = I [7]

R = X = Br, I [5, 7]



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X = Br [5]

Studies of the reactivity of stannacycloalkanes are limited to some halo- and protodemetallation reactions [5,8—10].

During recent years we have made a systematic study of the synthesis and reactivity of small-ring 1,1-dialkyl-1-stannacycloalkanes [11]. As discussed in a previous paper [1], stannacyclopentanes are very susceptible to ring-opening polymerization under polar conditions. Other examples of the unusual reactivity of the *endo*-cyclic tin—carbon bond of stannacyclopentanes in halodemetallation and transalkylation reactions are presented in the present paper. Furthermore, the synthesis and properties of a variety of new metal-functionally substituted stannacyclo-hexanes and -heptanes are reported.

Ring-expansion reactions will be discussed in a separate paper [12].

Results and discussion

Halodemetallation and transalkylation reactions

In accord with observations by Grüttner et al. [8] and by Hänssgen et al. [10], we found that bromodemetallation of 1,1-dimethyl-1-stannacyclo-pentane (DMSC-5) and -hexane (DMSC-6) in carbon tetrachloride proceeds exclusively by cleavage of the *endo*-cyclic tin—carbon bond (eq. 1).

$$Me_2Sn(CH_2)_n \xrightarrow[CCl_4]{Br_2} Me_2BrSn(CH_2)_nBr \qquad (1)$$

$(n = 4, 5)$

Halodestannylation reactions are known to proceed more selectively in nucleophilic than in apolar solvents [13]. Therefore, some iododestannylations were carried out in methanol at —70°C. Reactions were monitored by ^1H NMR spectrometry.

With DMSC-5 and DMSC-6, ring cleavage takes place almost exclusively, where-

$$Me_2Sn(CH_2)_n + I_2 \xrightarrow[-70°C]{MeOH} Me_2ISn(CH_2)_nI + MeISn(CH_2)_n + MeI \qquad (2)$$

$n = 4$	100%	—
$n = 5$	≈98%	trace
$n = 6$	65%	35%

as with DMSC-7 about 35% of demethylation also occurs (eq. 2).

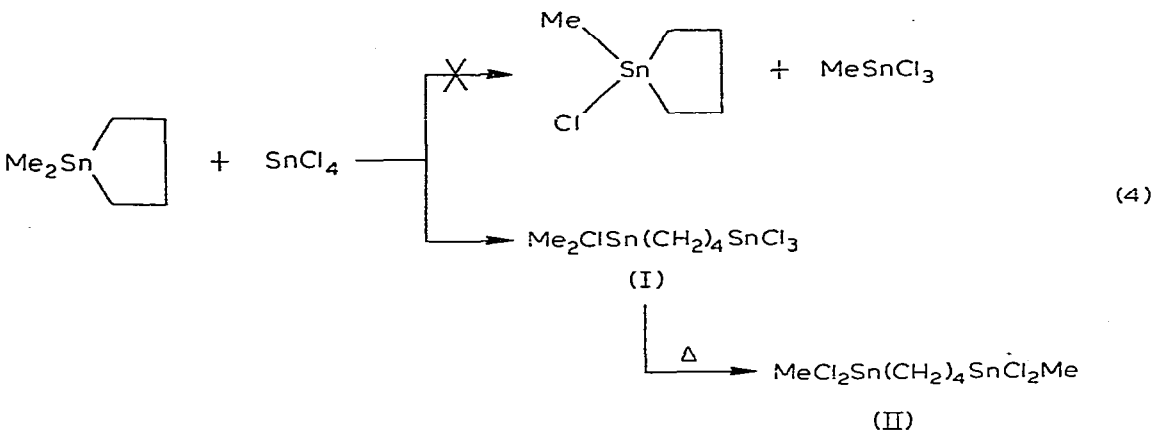
Chlorodestannylation of DMSC-5 and DMSC-6 proceeds by cleavage of both *endo*-cyclic and *exo*-cyclic tin—carbon bonds, to give a complex mixture of all conceivable tin halides (cf. ref. 10). The expected cleavage products $Me_2ClSn(CH_2)_nCl$ (n = 4, 5) were prepared for the first time by a different route, viz. by treating DMSC-5 or DMSC-6, with sulphuryl chloride under free-radical conditions (eq. 3).

$$Me_2Sn(CH_2)_n + SO_2Cl_2 \xrightarrow{(PhCOO)_2} Me_2ClSn(CH_2)_nCl + SO_2 \qquad (3)$$

(n = 4, 5)

A very satisfactory route to organotin halides is the so-called transalkylation reaction of tetraorganotins with tin tetrahalides or with other metal halides [14]. Previous studies into transalkylation reactions of organogermanium compounds with tin tetrachloride have shown that in polar solvents reactions can be very selective, the reactivity order being Me >> Et > Pr ≥ Bu [15].

Reaction of DMSC-5 with tin tetrachloride in carbon tetrachloride gave exclusive cleavage of the *endo*-cyclic tin—carbon bond (eq. 4), with formation of

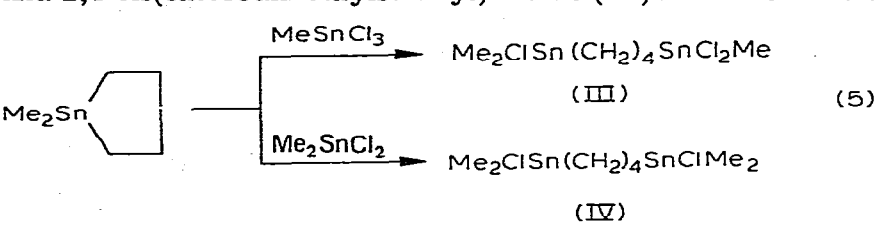


(4)

the new product 1-(chlorodimethylstannyl)-4-(trichlorostannyl)butane (I). Similar results were obtained in nitromethane, only a trace of methyltin trichloride being detectable by ^1H NMR analysis.

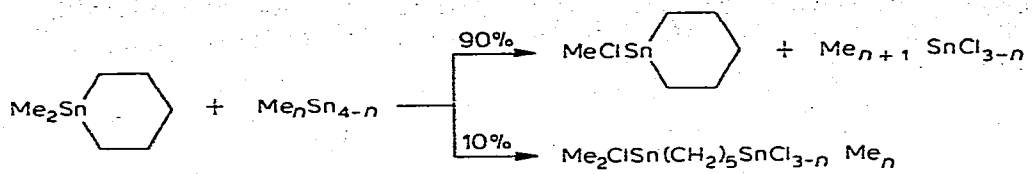
Interestingly, in the solid compound I (m.p. 44—46°C) slowly undergoes an intramolecular redistribution reaction to give the symmetrical 1,4-bis(dichloromethylstannyl)bútane (II), m.p. 206—210°C.

The reactions of DMSC-5 with methyltin trichloride and with dimethyltin dichloride likewise involve exclusive ring-cleavage and high yields of the new compounds 1-(chlorodimethylstannyl)-4-(dichloromethylstannyl)butane (III) and 1,4-bis(chlorodimethylstannyl)butane (IV) have been obtained (eq. 5).



(5)

In contrast, reaction of DMSC-6 with tin tetrachloride in CCl_4 gives about 70% cleavage of the *exo*-cyclic tin—carbon bond. In polar solvents such as nitromethane and acetonitrile, and at low temperatures (—30°C), reaction proceeds more selectively, yielding 85—90% (^{1}H NMR) of 1-chloro-1-methyl-

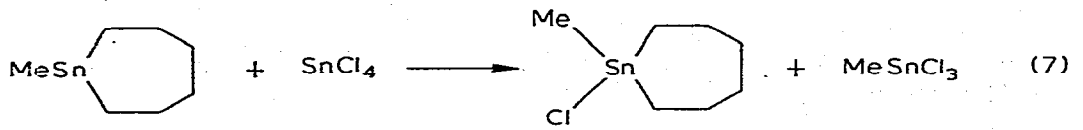


(6)

($n = 0,1$)

1-stannacyclohexane (eq. 6). Similar results are obtained with methyltin trichloride.

DMSC-7 and tin tetrachloride react exclusively by demethylation (eq. 7).



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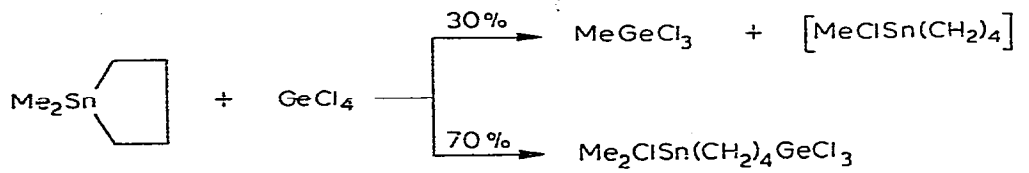
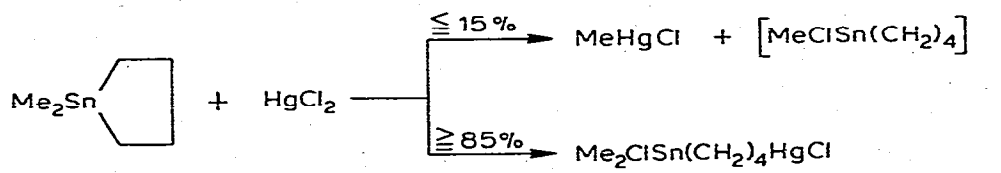
Germanium tetrachloride does not react with DMSC-5 at room temperature. Reaction at 60°C in nitromethane (cf. ref. [15]) gave the new compound 1-(chlorodimethylstannyl)-4-(trichlorogermyl)butane (V) (eq. 8). A substantial amount of methylgermanium trichloride was also formed, but (^{1}H NMR; ≈30%); GLC-MS (gas chromatography-mass spectrometry) analysis did not provide conclusive evidence for the formation of 1-chloro-1-methyl-1-stannacyclopentane.



(8)

(V)

Likewise, reaction of DMSC-5 with mercury dichloride in nitromethane largely involved cleavage of the *endo*-cyclic tin—carbon bond (eq. 9). In con-



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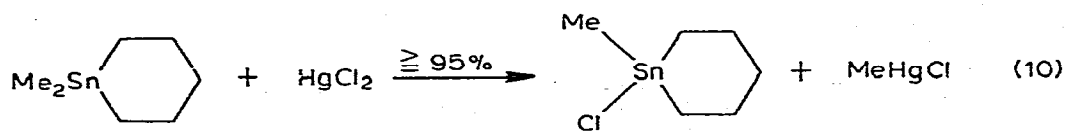
trast, the analogous reaction with DMSC-6 gave almost excusive cleavage of the *exo*-cyclic tin—carbon bond (eq. 10).



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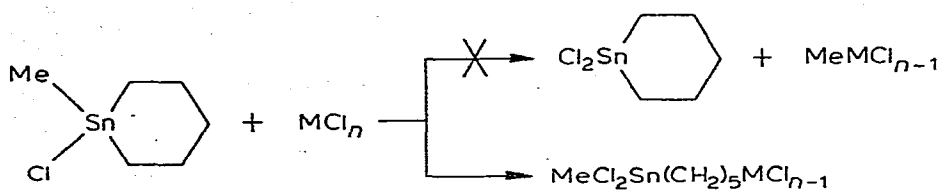
Attempts to replace the second methyl group by chlorine failed because of ring-cleavage (eq. 11).



(11)

(M = Sn, n = 4 ; M = Hg, n = 2)

These results demonstrate once more (cf. ref. 1) the high reactivity of the *endo*-cyclic tin—carbon bonds of the stannacyclopentane ring towards electrophilic reagents. With iodine as well as with tin and mercury halides, ring cleavage largely predominates over demethylation. The same is true for reactions of the six- and seven-membered ring systems with iodine, the order of cleavage being: $(CH_2)_4Sn > (CH_2)_5Sn > (CH_2)_6Sn >$ MeSn.

With mercury dihalides, however, and with tin tetrachloride or methyltin trichloride, the reactivity order changes significantly, possibly as a result of steric effects, and is: $(CH_2)_4Sn >$ MeSn $> (CH_2)_5Sn > (CH_2)_6Sn$.

The enhanced reactivity of the *endo*-cyclic tin—carbon bond in DMSC-5 as compared with that of DMSC-6 and DMSC-7 is probably due to ring-strain effects, both angle strain and eclipsing strain [16]. The cyclic C—Sn—C bond angle in DMSC-5 will be smaller than that in DMSC-6 and DMSC-7. As a result the *endo*-cyclic tin carbon bonds will have more *p*-character and accordingly the *exo*-cyclic tin—carbon bonds will have more *s*-character. This trend is reflected in the chemical shifts and coupling constants of the ^{1}H NMR methyltin resonances (Table 1). Calculations by Gielen and Topart based on these ^{1}H NMR data show that the C—Sn—C bond angle β in DMSC-5 is only slightly smaller than that in linear tetraorganotins, viz. β(DMSC-5) 109.0°, β(DMSC-6) 109.7°, β(DMSC-7) 111°, β(Me_2SnEt_2) 111.2° [17]. The much greater reactivity of the five-membered ring as compared with the larger cycles suggests that eclipsing strain effects are of prime importance.

New metal-functionally substituted stannacycloalkanes

As discussed above the transalkylation reactions of DMSC-6 and DMSC-7 with tin tetrachloride or mercury dichloride provide a satisfactory new method

TABLE 1

^{1}H NMR DATA FOR SOME STANNACYCLOALKANES

Compound	δ(Me—Sn) (ppm)	J($^{117/119}$SnMe) (Hz)
$Me_2Sn(CH_2)_4$	0.19	52/54
$Me_2Sn(CH_2)_5$	0.10	51/53
$Me_2Sn(CH_2)_6$	0.06	50/52
$[Me_2Sn(CH_2)_4]_n$ [a]	0.00—0.05	48/50

[a] Oligomer mixture obtained by polymerization of DMSC-5.

TABLE 2

PHYSICAL CONSTANTS, YIELDS AND ^{1}H NMR DATA FOR SOME NEW LINEAR AND CYCLIC ORGANOTIN COMPOUNDS

Compound	B.p. (°C/mmHg)	n_D^{20}	Yield (%)	^{1}H NMR data in CCl_4 solution (TMS = 0)		
				δ(Me—Sn) (ppm)	$J(^{117}Sn—Me)$ (Hz)	Other data
$Me_2ClSn(CH_2)_4SnCl_3$	(m.p. 44—46)		88	0.66	53	
$MeCl_2Sn(CH_2)_4SnCl_2Me$	(m.p. 206—210)		73	1.08 [a]	62 [a]	
$Me_2ClSn(CH_2)_4SnCl_2Me$	(m.p. 110—112)		78	0.68 [b, c]	53 [b, c]	δ($MeCl_2Sn$) [b] 1.21 ppm; $J(^{117}Sn—Me)$ [b] 60 Hz
$Me_2ClSn(CH_2)_4SnClMe_2$	(m.p. 65—68)		87	0.64	53	
$Me_2ClSn(CH_2)_4GeCl_3$	128—131/1.0	1.5390	30	0.63	53	
$Me_2ClSn(CH_2)_4Cl$	98—100/0.7	1.5208	54	0.63	54	δ(CH_2Cl) 3.57 ppm (t)
$Me_2ClSn(CH_2)_5Cl$	117—120/0.8	1.5172	45	0.60	53	δ(CH_2—Cl) 3.52 ppm (t)
$MeClSn(CH_2)_5$	61—62/0.8 [d]	1.5465	60	0.69	56	
$MeClSn(CH_2)_6$	80—81/0.6	1.5472	65	0.62	52	
$[Me(CH_2)_5Sn]_2O$	106—107/0.2	1.5480	76	0.33	54	
$[Me(CH_2)_5SnO]_2CO$	(m.p. 92—94)		100	0.59	56	
$Me(ICH_2)Sn(CH_2)_5$	70—71/0.2	1.5879	70	0.25	53	δ(CH_2—I) 1.97 ppm; $J(^{117}Sn—H)$ 20 Hz
$MeHSn(CH_2)_5$	65—66/24.0	1.5165	65	0.11 [e]	54 [e]	δ(H—Sn) 4.78 ppm; $J(^{117}Sn—H)$ 1649 Hz
$Me(CH_2)_5SnCH=CHPh$	108—110/0.3	1.5844	53	[f]	[f]	
$[Me(CH_2)_5Sn]_2$	115—119/0.5	1.5896	42	0.25	46	$J(^{117}Sn—SnMe)$ 15 Hz

[a] In DMSO-d_6 solution. [b] In $CDCl_3$ solution. [c] Me_2Sn moiety. [d] Solidified on standing (m.p. 27—28°C). [e] In C_6D_6 solution. [f] See Experimental Part.

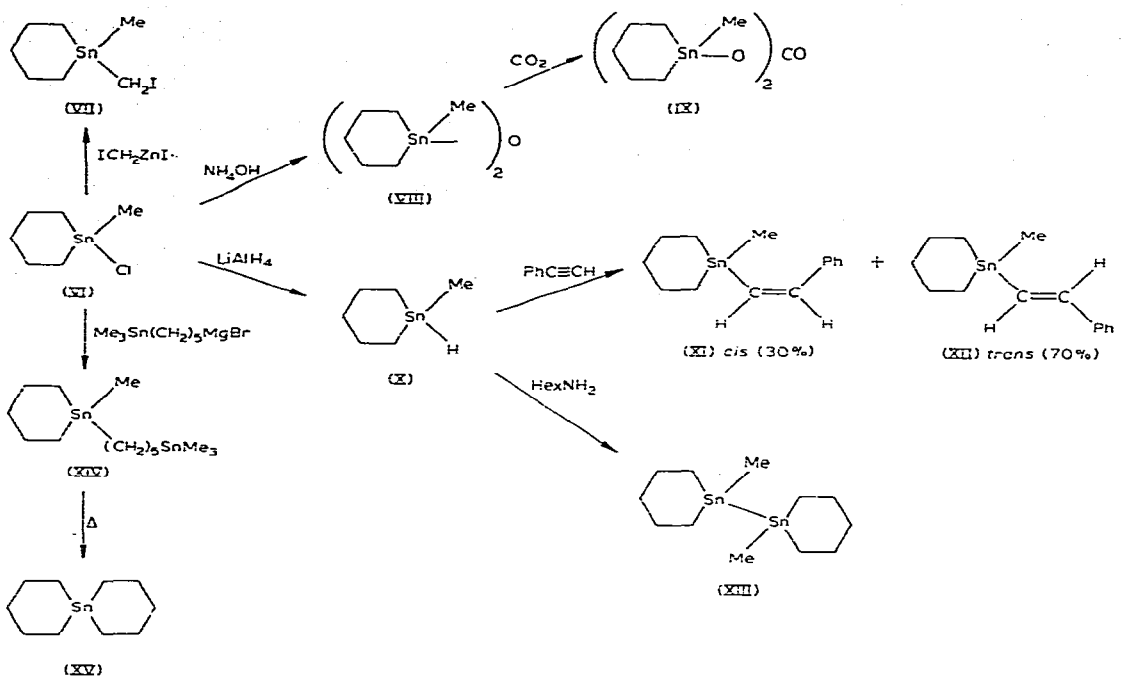


Fig. 1. Some reactions of 1-chloro-1-methyl-1-stannacyclohexane (VI).

for the synthesis of 1-chloro-1-methyl-1-stannacyclo-hexane and -heptane, respectively (eq. 6 and 7). The latter compounds are useful starting materials for the synthesis of a variety of new metal-functionally substituted stannacycloalkanes (Fig. 1). In Table 2 the physical constants, yields and ^{1}H NMR data for a series of such compounds are listed.

Reaction of 1-chloro-1-methyl-1-stannacyclohexane (VI) with iodomethylzinc iodide [18] gave the expected substitution product 1-methyl-1-(iodomethyl)-1-stannacyclohexane (VII) in high yield. Hydrolysis of VI with aqueous ammonium hydroxide gave the corresponding oxide, 1,1'-oxybis(1-methyl-1-stannacyclohexane) (VIII). On standing in the atmosphere the latter rapidly absorbs carbon dioxide to give the carbonate IX.

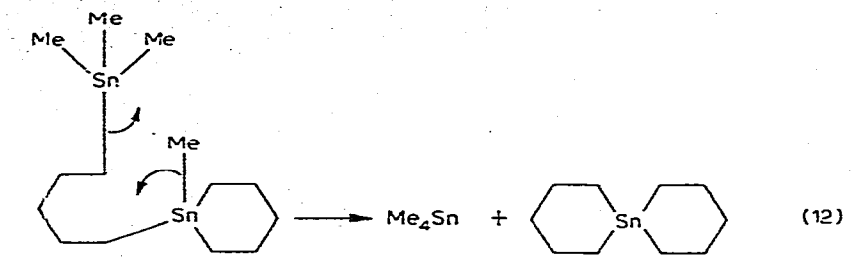
Reaction of VI with lithium aluminium hydride provided the first example of a hydridostannacyclohexane, X. Addition of this cyclic organotin hydride to phenylacetylene under free radical conditions gave a mixture of the expected *cis/trans* adducts in the ratio 3/7. Conclusive evidence for the structure of the adducts XI and XII was derived from the ^{1}H NMR spectra characteristics (see Experimental). Both the chemical shifts and the coupling constants of the olefinic protons are in line with previous results [19].

In accord with the well-known catalysed decomposition of linear organotin hydrides [20], reactions of X with a catalytic amount of hexylamine at 90°C resulted in the formation of the first tin—tin bonded heterocycle 1,1-bis(1-methyl-1-stannacyclohexane) (XIII).

Alkylation of VI by means of Grignard or organolithium reagents proceeds smoothly and without appreciable ring cleavage. Thus, reaction of VI with

ω-(trimethylstannyl)pentylmagnesium bromide, prepared according to ref. [21], gave 1-methyl-1-[ω-(trimethylstannyl)pentyl]-1-stannacyclohexane (XIV), identified by GLC-MS.

Thermolysis of the latter compound following the previously reported procedure for the preparation of stannacycloalkanes could be [6] expected to give a range of products, including the tin spirocycle 6-stannaspiro[5.5]undecane (XV). Equations 12 and 13 illustrate the two possible routes for intramolecular attack of tin at carbon. Equation 14 shows one of the intermolecular electrophilic substitution reactions which may lead to polymeric species.



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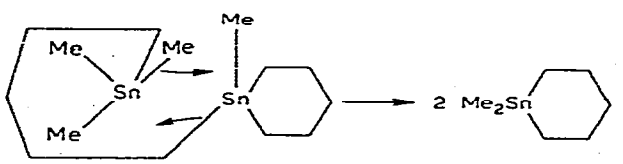

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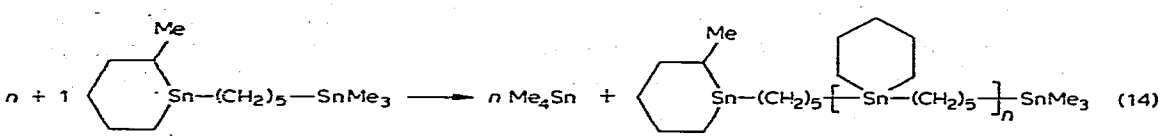

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In a small-scale experiment, from thermolysis of XV at 250—280°C about 60% of distillate was collected. As determined by GLC-MS analysis the distillate consisted of about 60% of DMSC-6 (eq. 13) and 6% of the tin spirocycle (eq. 12), together with some 22% of tetramethyltin.

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. ^{1}H NMR spectra were recorded using Varian Associates HA 60 and HA 100 spectrometers. Elemental analyses were carried out by the Elemental Analysis Section of this Institute.

Typical experiments are described below.

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

A solution of 5.19 g (0.02 mol) of $SnCl_4$ in 10 ml of CCl_4 was added dropwise to a solution of 4.13 g (0.02 mol) of DMSC-5 in 20 ml of CCl_4 at 0°C. ^{1}H NMR

spectrometry showed that the reaction was immediately complete. The crude product obtained by evaporation of the solvent was recrystallized from light-petroleum (b.r. 40—60°C), yielding 8.15 g (88%) of pure I, m.p. 44—46°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%.)

1,4-Bis(dichloromethylstannyl)butane (II)

A 1.1 g (2.4 mmol) sample of I (m.p. 44—46°C) was heated for 2 h at 150°C. Attempted recrystallization of the resulting high melting solid failed. An 0.55 g sample of the crude product was washed thoroughly with chloroform and dried in vacuo to give 0.4 g (73%) of pure II, m.p. 206—210°C. (Anal.: Found: C, 16.2; H, 3.2; Cl, 30.3. $C_6H_{14}Cl_4Sn_2$ calcd.: C, 15.49; H, 3.03; Cl, 30.47%.)

1-(Chlorodimethylstannyl)-4-(dichloromethylstannyl)butane (III)

Following the procedure for I, reaction of 2.23 g (0.011 mol) of DMSC-5 with 2.62 g (0.011 mol) of $MeSnCl_3$ in 10 ml of CCl_4 gave 3.8 g (78%) of III, m.p. 110—112°C. (Anal.: Found: C, 18.6; H, 3.8. $C_7H_{17}Cl_3Sn_2$ calcd.: C, 18.90; H, 3.85%.)

1,4-Bis(chlorodimethylstannyl)butane (IV)

A solution of 2.14 g (0.01 mol) of DMSC-5 and 2.30 g (0.01 mol) of Me_2SnCl_2 in 14 ml of CCl_4 was refluxed for 15 h. ^1H NMR analysis showed that about 90% of DMSC-5 had reacted to give IV. The solvent was evaporated and the residue was heated for 8 h at 90°C. Recrystallization from tetrachloroethylene gave 3.9 g (87%) of IV, 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-(Chlorodimethylstannyl)-4-(trichlorogermyl)butane (V)

A mixture of 4.38 g (0.021 mol) of DMSC-5, 4.60 g (0.021 mol) of $GeCl_4$ and 20 ml of nitromethane (two phases) was heated for 11 h at 50°C (after about 7 h the mixture became homogeneous). Distillation gave 2.6 g (30%) of V, b.p. 128—131°C/10 mmHg, n_D^{20} 1.5390. On standing the product turned into a low melting solid (m.p. < 30°C). Analysis of all distillation fractions collected by GLC-MS as well as by ^1H NMR analysis showed the presence of $MeGeCl_3$ (δ(Me—Ge) 1.83 ppm), but 1-chloro-1-methyl-1-stannacyclopentane could not be demonstrated.

Reaction of DMSC-5 with mercuric chloride

A solution of 1.02 g (0.005 mol) of DMSC-5 and 1.36 g (0.005 mol) of $HgCl_2$ in 12.5 ml of nitromethane was stirred for 2 h at room temperature. ^1H NMR spectrometry showed the presence of about 7% of MeHgCl (δ(Hg—Me) 1.04 ppm; $J(^{199}Hg—Me)$ 202 Hz) and about 7% of an unidentified MeR_2SnX species (δ(Me—Sn) 0.64 ppm), possibly $MeClSn(CH_2)_4$. The chemical shift of the main product (85%; δ(Me—Sn) 0.63 ppm; $J(^{117}Sn—Me)$ 54 Hz) was characteristic of the structure MeR_2SnX, most probably $Me_2ClSn(CH_2)_4HgCl$.

Evaporation of the solvent and subsequent recrystallization of the solid residue gave 1.3 g (55%) of crude $Me_2ClSn(CH_2)_4HgCl$ (m.p. 60—72°C), contaminated with MeHgCl. Repeated recrystallization gave a product (m.p.

77—81°C) consisting of (^{1}H NMR; analysis data) the mixture $Me_2ClSn(CH_2)_4$-HgCl/MeHgCl 8/1. (Anal.: Found: C, 13.3; H, 2.7; Sn, 20.0. $Me_2ClSn(CH_2)_4$-HgCl/MeHgCl 8/1 calcd.: C, 13.06; H, 2.61; Sn, 19.94%.)

Dimethyl(4-chlorobutyl)tin chloride

A solution of 2.08 g (0.01 mol) of DMSC-5, 0.8 ml (1.35 g, 0.01 mol) of sulphuryl chloride and 0.1 g (0.4 mmol) of benzoyl peroxide in 3 ml of CCl_4 was heated for 3 h at 70°C. Distillation gave 1.5 g (54%) of pure $Me_2ClSn(CH_2)_4Cl$, b.p. 98—100°C/0.7 mmHg, n_D^{20} 1.5208. (Anal.: Found: C, 26.2; H, 5.2; Cl, 25.9. $C_6H_{14}Cl_2Sn$ calcd.: C, 26.13; H, 5.12; Cl, 25.71%.)

Dimethyl(5-chloropentyl)tin chloride

According to the procedure given above reaction of DMSC-6 with sulphuryl chloride gave a 45% yield of $Me_2ClSn(CH_2)_5Cl$, b.p. 117—120°C/0.8 mmHg, n_D^{20} 1.5172. (Anal.: Found: C, 29.3; H, 5.6; Cl, 25.1. $C_7H_{16}Cl_2Sn$ calcd.: C, 29.01; H, 5.56; Cl, 24.47%.)

1-Chloro-1-methyl-1-stannacyclohexane (VI)

A solution of 12.2 g (0.047 mol) of $SnCl_4$ in 7 ml of nitromethane was added slowly to a heterogeneous mixture of 10.2 g (0.047 mol) of DMSC-6 and 25 ml of nitromethane at —30°C. The resulting homogeneous yellowish solution was kept for 2 days at —25°C. According to ^{1}H NMR spectrometry DMSC-6 had been completely converted to give about 80% of (VI) (δ(Me—Sn) 0.71 ppm; $MeNO_2$ solution) and 20% of 1-(chlorodimethylstannyl)-5-(trichlorostannyl)-pentane (δ(Me—Sn) 0.63 ppm). In addition to the major product $MeSnCl_3$ minor amounts of Me_2SnCl_2 were found to be present.

A similar reaction course was observed in acetonitrile. Repeated fractionation gave a 60% yield of pure VI, b.p. 61—62°C/0.7 mmHg, n_D^{20} 1.5465. The product solidified on standing, m.p. 27—28°C. (Anal.: Found: C, 30.4; H, 5.7; Cl, 14.8. $C_6H_{13}ClSn$ calcd.: C, 30.11; H, 5.48; Cl, 14.81%.)

Reaction of DMSC-6 with mercuric chloride in nitromethane gave after 2 days at —30°C (^{1}H NMR) MeHgCl (δ(Me—Hg) 1.04 ppm, $J(^{119}Hg—Me)$ 210 Hz) and ~95% of VI, together with about 5% of a by-product, possibly $Me_2ClSn(CH_2)_5HgCl$ (δ(Me—Sn) 0.62 ppm).

1-Chloro-1-methyl-1-stannacycloheptane

In a similar way reaction of DMSC-7 with $SnCl_4$ in nitromethane solution at —20°C gave (^{1}H NMR) exclusively 1-chloro-1-methyl-1-stannacycloheptane and methyltin trichloride, no other methyl—tin resonances being detectable. Careful fractionation gave a 65% yield of pure $MeClSn(CH_2)_6$, b.p. 80—81°C/0.6 mmHg; n_D^{20} 1.5472. (Anal.: Found: C, 33.6; H, 6.3; Cl, 13.9; Sn, 46.6. $C_7H_{15}ClSn$ calcd.: C, 33.19; H, 5.97; Cl, 13.99; Sn, 46.85%.)

1,1'-Oxybis(1-methylstannacyclohexane) (VIII)

A solution of 2.0 g (8.4 mmol) of VI in 25 ml of diethyl ether was treated three times with 3 ml aqueous 6 *N* NH_4OH. Evaporation of the diethyl ether gave 1.35 g (76%) of pure (VIII), b.p. 106—107°C/0.2 mmHg, n_D^{20} 1.5480. (Anal.: Found: C, 33.8; H, 6.3. $C_{12}H_{26}OSn_2$ calcd.: C, 34.02; H, 6.18%.)

The IR spectrum shows, in addition to the absorptions characteristic of the six-membered ring-system at 908 and 970 cm^{-1} [5], the very strong absorption due to the ν_{as} (Sn—O—Sn) mode at 760—780 cm^{-1}.

On standing in the air compound VIII gradually was converted into the corresponding carbonate IX, m.p. 92—94°C. (Anal.: Found: C, 33.4; H, 5.5; O, 10.0; Sn, 50.8. $C_{13}H_{26}O_3Sn_2$ calcd.: C, 33.38; H, 5.60; O, 10.26; Sn, 50.75%.)

1-Methyl-1-(iodomethyl)-1-stannacyclohexane (VII)

A THF solution containing 30 mmol of ICH_2ZnI [18] was added slowly to a solution of 3.9 g (16.3 mmol) of VI in 10 ml of THF at 30°C. The mixture was heated for 3 h at 40°C. After the addition of 18 ml of benzene the mixture was treated four times with 40 ml of a 5% solution of aqueous HCl. The organic phase was dried and evaporated. Distillation gave 3.8 g (70%) of VII, b.p. 70—71°C/0.2 mmHg, n_D^{20} 1.5879. (Anal.: Found: C, 24.5; H, 4.6; I, 37.0. $C_7H_{15}ISn$ calcd.: C, 24.39; H, 4.39; I, 36.81%.)

1-Methyl-1-[5-(trimethylstannyl)pentyl]-1-stannacyclohexane (XIV)

A solution of 3.14 g (10 mmol) of $Me_3Sn(CH_2)_5Br$ [21] in 12 ml of diethyl ether was slowly added to a suspension of 0.4 g (16 mg-at.) of magnesium powder in 2 ml of boiling diethyl ether. The mixture was refluxed for 1.5 h. Drop-wise addition of a solution of 2.4 g (10 mmol) of VI in 5 ml of diethyl ether resulted in a slightly exothermal reaction. After reflux for two more hours the mixture was decomposed with 5 ml of a saturated aqueous solution of ammonium chloride. After the usual work-up, distillation gave 3.05 g (68%) of a product which was indicated by GLC analysis to be about 80% pure. Redistillation raised the purity to only about 86%. The identity of the main compound was confirmed by GLC-MS analysis. ^1H NMR: $\delta(Me_3—Sn)$ 0.04 ppm, δ(Me—Sn) 0.06 ppm, integrated ratio 3/1.

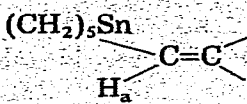
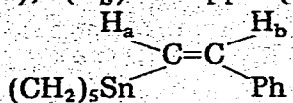
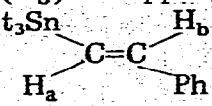
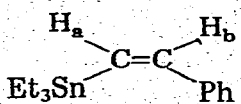
A sample of 0.44 g (1 mmol) of XIV was heated in a distillation apparatus for $\frac{1}{2}$ h at 260—280°C. A small amount of distillate was collected: 0.25 g (58%). GLC-MS showed the product to consist of 22% of Me_4Sn, 60% of DMSC-6 (fragments: *m/e* 220, $Me_2SnC_5H_{10}$; *m/e* 205, $MeSnC_5H_{10}$; *m/e* 177, $MeSnC_3H_6$; *m/e* 150, Me_2Sn; *m/e* 135, MeSn; *m/e* 120, Sn) and 6% of 6-stannaspiro[5.5]-undecane (fragments: *m/e* 260, $(CH_2)_5Sn(CH_2)_5$; *m/e* 190, $(CH_2)_5Sn$; *m/e* 162, $(CH_2)_3Sn$; *m/e* 148, $(CH_2)_2Sn$; *m/e* 134, CH_2Sn; *m/e* 120, Sn).

1-Hydrido-1-methyl-1-stannacyclohexane (X)

A solution of 9.6 g (0.04 mol) of VI in 25 ml diethyl ether was added drop-wise to 2.4 g (0.06 mol) of $LiAlH_4$ in 15 ml of diethyl ether. The mixture was refluxed for 1 h, decomposed by means of 4 ml of water, filtered, dried and evaporated. Distillation gave 5.3 g (65%) of X, b.p. 55—66°C/24 mmHg, n_D^{20} 1.5165. (Anal.: Found: C, 34.9; H, 7.0. $C_6H_{14}Sn$ calcd.: C, 35.18; H, 6.89%.)

Addition of 1-hydrido-1-methyl-1-stannacyclohexane to phenylacetylene

A mixture of 0.68 g (3.3 mmol) of X and 700 µl (6.3 mmol) of PhC≡CH was heated for 12 h at 70°C. Distillation gave 0.55 g (53%) of adducts, b.p. 108—110°C/0.3 mmHg, n_D^{20} 1.5844. (Anal.: Found: C, 54.0; H, 6.6. $C_{14}H_{20}Sn$ calcd.: C, 54.77; H, 6.57%.) ^1H NMR spectrometry showed that the mixture consisted

of 30% *cis*- and 70% *trans*-adduct:  (*trans*): δ(Me—Sn) 0.24 ppm; δ(H_a) 6.78 ppm (d); δ(H_b) 6.78 ppm (d); J_{ab} 0.8 Hz. J(^{117}Sn—CH_a) 71 Hz; J(^{117}Sn—CH_b) 71.5 Hz.  (*cis*): δ(Me—Sn) 0.04 ppm; δ(H_a) 6.17 ppm (d); δ(H_b) 7.52 ppm (d); J_{ab} 13.5 Hz. J(^{117}Sn—CH_a) 66 Hz; J(^{117}Sn—CH_b) 142 Hz.  (*trans*) [19]: δ(H_a) 6.83 ppm; δ(H_b) 6.83 ppm; J(^{117}Sn—CH_a) = J(^{117}Sn—CH_b) 64 Hz.  (*cis*) [19]: δ(H_a) 6.15 ppm (d); δ(H_b) 7.55 ppm; J_{ab} 13.6 Hz. J(^{117}Sn—CH_a) 66 Hz; J(^{117}Sn—CH_b) 148 Hz.

1,1'-Bis(1-methyl-1-stannacyclohexane) (XIII)

A mixture of 3.23 g (15.8 mmol) of X and 0.12 ml of hexylamine was stirred at 85°C. Over a period of 8 h about 14.2 mmol (90%) of hydrogen was collected. Distillation gave 1.35 g (42%) of pure XIII, b.p. 115—118°C/0.5 mmHg, n_D^{20} 1.5896. (Anal.: Found: C, 35.4; H, 6.6; Sn, 58.4. $C_{12}H_{26}Sn_2$ calcd.: C, 35.35; H, 6.43; Sn, 58.22%.)

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