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THE REACTIVITY OF SMALL-RING MONOSTANNACYCLOALKANES

I. THE CATALYTIC POLYMERIZATION OF 1,1-DIMETHYL-1-STANNACYCLOPENTANE *

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Summary

A comparative study has been made of the reactivity of small-ring 1,1-dialkyl-1-stannacyclo-pentanes, -hexanes and -heptanes towards a variety of electrophilic and nucleophilic reagents. In the case of the five-membered heterocycles the reactivity of the tin—carbon bonds of the ring is considerably higher than that of the alkyl—tin bonds, indicating substantial ring strain.

1,1-Dimethyl-1-stannacyclopentane was unexpectedly found to be extremely susceptible to polymerization under polar conditions; the half-life at 60°C in methanol is only about 3 h. The resulting $[Me_2Sn(CH_2)_4]_n$ oligomer has an average chain length of $n \approx 7$. Polymerization does not occur under free radical conditions.

Introduction

Although the first heterocycloalkane containing tin, viz. 1,1-diethyl-1-stannacyclohexane, was reported half a century ago [2], the chemistry of monostannacycloalkanes has remained largely unexplored [3]. We recently reported a novel synthesis of small-ring monostannacycloalkanes, involving the intramolecular disproportionation of α,ω-distannaalkanes [4,5] and the first results of a comparative study of the reactivities of monostannacyclo-pentanes, -hexanes and -heptanes are discussed below.

Results and discussion

Reactions with some electrophiles and nucleophiles

In the only paper dealing with the chemical properties of small-ring mono-

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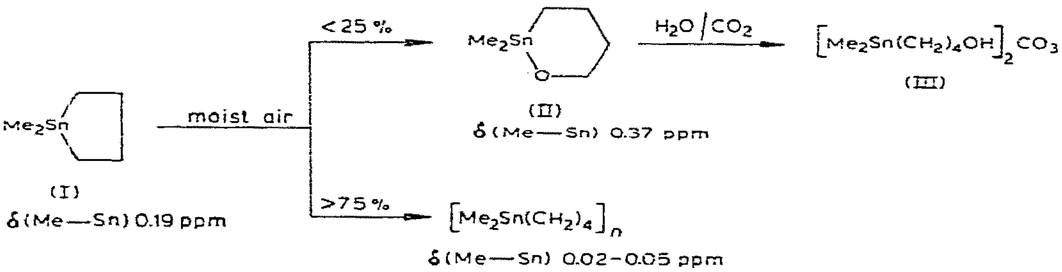
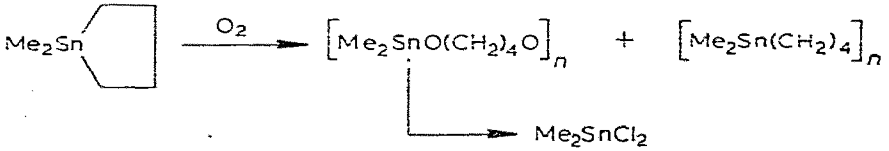
* For preliminary accounts of this work see ref. 1.

stannacycloalkanes, Zimmer and coworkers [6] stated that 1,1-dibutyl-1-stannacyclopentane and -cyclohexane are the sole tetraalkyltin species which undergo tin—carbon bond cleavage even in moist air. We observed that on standing at the atmosphere 1,1-dimethyl-1-stannacyclopentane (I; DMSC-5) decomposed to give a viscous oil after 3 days and finally a vitreous product. The IR absorptions characteristic of the five-membered ring at 1020, 1030 and 1050 cm^{-1} [7]; see also [8,9], disappeared completely, and only very weak absorption bands of carbonate and hydroxide functions were present. According to ^{1}H NMR spectrometry, however, hydrolyte and/or oxidative cleavage occurs only to a minor extent (<25%), the main reaction being polymerization of the ring to give a mixture of $[Me_2Sn(CH_2)_4]_n$ oligomers (see below). The formation of 1,1-dimethyl-1-stanna-2-oxacyclohexane (II) was confirmed by comparison of its spectra with those of an authentic sample of this new compound [10]. Reaction of II with moisture and carbon dioxide gave III, a pure sample of which was isolated. In contrast, the six- and seven-membered ring compounds 1,1-dimethyl-1-stannacyclohexane (DMSC-6) and -cycloheptane (DMSC-7) remain unchanged when exposed to the atmosphere for over one month.



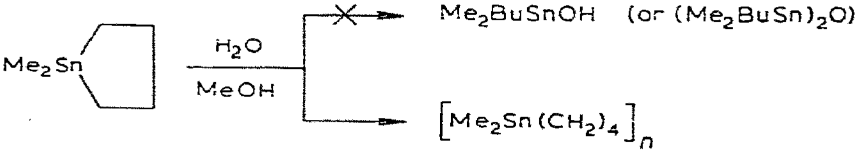
(1)

In carbon tetrachloride solution at room temperature DMSC-5 reacted only slowly with pure oxygen to give oligomeric $[Me_2Sn(CH_2)_4]_n$, together with an inseparable mixture of tin—oxygen species. When that mixture was treated with gaseous HCl in diethyl ether, subsequent GLC analysis showed Me_2SnCl_2 to be the main product (eq. 2).



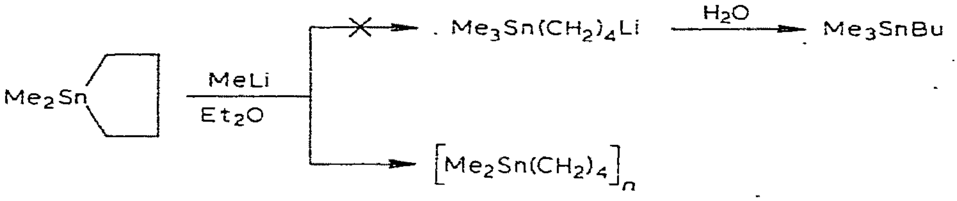
(2)

Reaction of DMSC-5 with one equivalent of water for 2 h at 60°C in methanol gave $[Me_2Sn(CH_2)_4]_n$ oligomers (>90% yield) instead of the expected dimethylbutyltin hydroxide (or bis(dimethylbutyltin) oxide) (eq. 3).



(3)

DMSC-5 reacts rapidly with methyllithium in diethyl ether at room temperature. ^{1}H NMR spectrometry showed the presence of a mixture of polymeric species similar to that formed in reaction 3. No trimethylbutyltin could be detected by GLC in the hydrolyzed reaction mixture.



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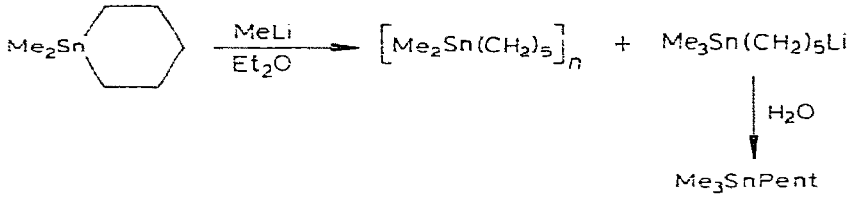
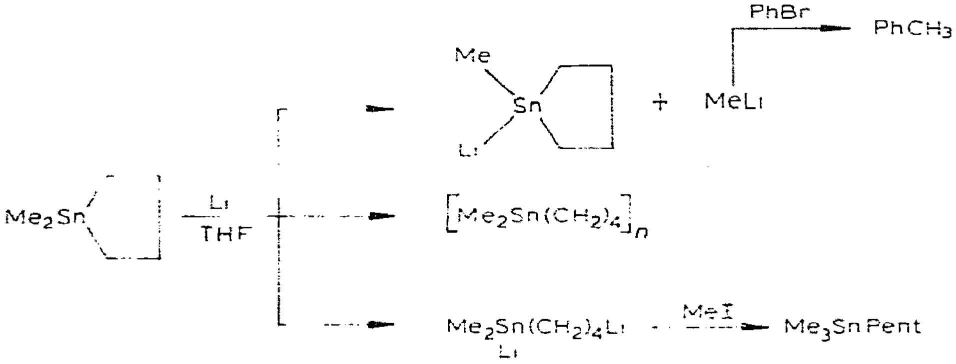
In contrast, DMSC-6 reacts only slowly with methyllithium in boiling diethyl ether to give polymeric material, together with small amounts of the expected cleavage product.



(5)

DMSC-7 was recovered in >75% yield after a similar treatment for 13 h. DMSC-5 resisted treatment for 8 h with a 6 *N* aqueous solution of sodium hydroxide at 70°C. Likewise, DMSC-5 and DMSC-6 failed to react with an excess of lithium aluminium hydride in boiling diethyl ether.

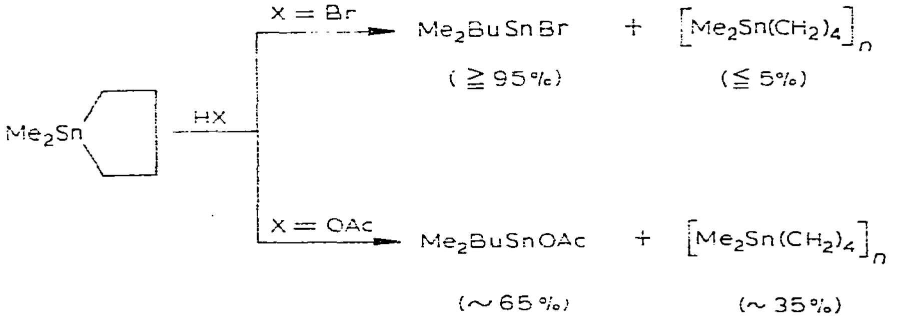
Reaction of DMSC-5 with lithium in THF solution gave a very complex mixture. ^{1}H NMR spectroscopy and GLC analysis of samples treated with bromobenzene, methyl iodide and hydrochloric acid, respectively, indicated that in addition to polymerization, reactions of lithium with both *endo*-cyclic and *exo*-cyclic tin—carbon bonds take place.



(6)

Gaseous hydrobromic acid in carbon tetrachloride gives exclusively cleavage of the ring tin—carbon bond of DMSC-5 within 1 h at 40°C, methyl—tin bond cleavage not being observed. It should be noted that in acid solvolysis of linear tetraalkyltins methyl groups are usually cleaved from tin more readily than higher alkyl groups [11].

With a large excess of acetic acid at 60°C both acid cleavage and polymerization take place. The six-membered heterocyclic (DMSC-6) resists prolonged heating in acetic acid.



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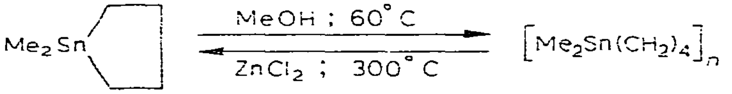
As in many of the reactions discussed above polymerization of the DMSC-5 occurred, rather than the expected substitutions, this feature was investigated in more detail.

Ionic polymerization of stannacyclopentanes

As mentioned already in an earlier paper [4] Lewis acids like zinc chloride and aluminium trichloride catalyze the polymerization of DMSC-5. Comparisons using equivalent amounts of stannacycloalkane and aluminium trichloride showed that the five- and seven-membered ring compounds DMSC-5 and DMSC-7 polymerize much more rapidly (at room temperature) than the six-membered heterocycle DMSC-6, the reactivity decreasing in the order: DMSC-5 > DMSC-7 > DMSC-6 *. Similar trends have been observed by Nametkin and coworkers in their detailed studies of the polymerization of silacycloalkanes in the presence of nucleophilic and electrophilic catalysts (cf. ref. 12 and references cited therein).

Continued studies showed that DMSC-5 is extremely susceptible to polymerization: the half-life time of DMSC-5 at 60°C in anhydrous, oxygen-free methanol is about 3 h. According to the elemental analysis, the oily polymer isolated is a stannahydrocarbon with the same composition as the original monomer. In the IR spectrum the absorptions characteristic of the five-membered ring system at 1020, 1030 and 1050 cm^{-1} [7—9] have disappeared. In the ^1H NMR spectrum the chemical shift of the methyltin protons of DMSC-5 situated at 0.19 ppm (CCl_4 solution) has been replaced by methyltin resonances at 0.00 and 0.04 ppm. The integrated ratio CH_3/CH_2 protons remained unchanged (6 : 8). The polymer mixture can be reconverted into DMSC-5 by thermolysis at 300°C in the presence of a catalytic amount of zinc chloride (cf. ref. 4).



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* The structures of the insoluble, high melting polymers are being studied.

Vapour pressure osmometry in benzene solution gave an average molecular weight of 1427, which corresponds with an average chain length of $n = 7$.

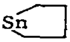
It should be noted that DMSC-6 does not polymerize upon heating for 24 h at 60°C in methanol solution.

The results of a series of polymerization experiments with DMSC-5 are summarized in Table 1. Polymerization does not take place in aprotic apolar solvents such as cyclohexane (ϵ 2.0) or tetrachoroethylene (ϵ 2.3), and is not induced by free radical initiators such as azobis(isobutyronitrile) (AIBN) or by UV light. In the more polar protic solvent methanol (ϵ 32.6), reaction is rapid. Because of the low solubility of the oily polymer in methanol or 3 : 1 methanol/tetrachloroethylene, the reaction mixtures become increasingly inhomogeneous, and this prevents accurate quantitative studies.

Although the polymer itself is soluble in the 1 : 3 methanol/tetrachloroethylene, ring polymerization does not take place in this medium, because of the reduced dielectric constant. In the 3 : 1 methanol/tetrachloroethylene at low concentrations of stannacyclopentane the mixture remains homogeneous, but the rate of polymerization is markedly decreased, which demonstrates that the order of the reaction is >1.

According to Zimmer and coworkers [6], degradation of stannacyclopentanes in air is slower the greater the bulk of the groups bound to tin. Consistently, we observed that the rate of stannacyclopentane polymerization in methanol solution decreases markedly in the order Me > Bu >> i-Bu. As the polar substituent constants of the butyl and isobutyl groups are almost identical the observed rate difference must be largely associated with the difference in steric substituent constants [13].

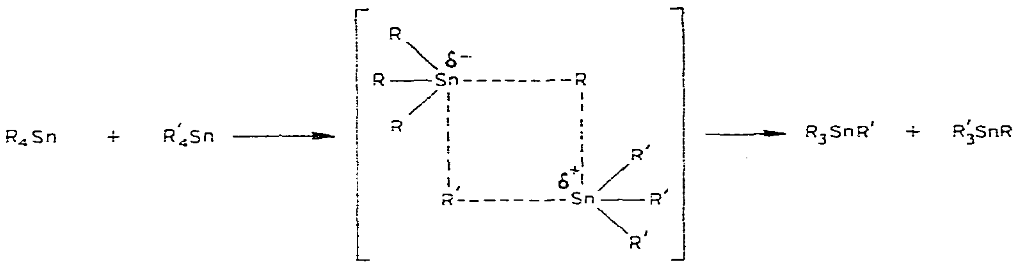
TABLE 1

POLYMERIZATION OF Me_2Sn  AT 60°C AS DETERMINED BY ^1H NMR SPECTROMETRY

Solvent	Concentration (mol l^{-1})	Time (h)	Ring conversion (%)	Remarks
Cyclohexane	0.14	5	0	AIBN [a]
Cyclohexane	0.14	24	3	AIBN [a]
C_2Cl_4	0.44	24	0	
Cyclohexane	1.36	9	Trace	UV [b]
Cyclohexane	0.39	5	Trace	UV [c]
MeOH	0.5	0.5	21	
MeOH	0.5	2	39	Inhomogeneous
MeOH	0.5	5	65	Inhomogeneous
MeOH	0.5	24	87	Inhomogeneous
$MeOH/C_2Cl_4 = 3$	1.36	2	20	Inhomogeneous
$MeOH/C_2Cl_4 = 3$	0.68	2	19	
$MeOH/C_2Cl_4 = 1 : 3$	1.36	2	0	
$MeOH/C_2Cl_4 = 3$	0.14	2	8	
$MeOH/C_2Cl_4 = 3$	0.14	24	32	
MeOH	0.35	24	18	$Bu_2Sn(CH_2)_4$ [d]
MeOH	0.35	48	30	$Bu_2Sn(CH_2)_4$ [d]
MeOH	0.35	48	0	$i\text{-}Bu_2Sn(CH_2)_4$ [d]

[a] At $t = 0$ h and $t = 5$ h 5 mol-percent of AIBN were added. [b] $\lambda = 366$ nm. [c] $\lambda = 254$ nm. [d] Determined by IR spectrometry, by measuring the intensity of the absorptions at 1020, 1030 and 1050 cm^{-1}.

In the absence of more extensive experimental data a discussion of the mechanism of the polymerization reaction 8 is necessarily speculative. Probably the reaction is a special example of a disproportionation reaction between two tetraalkyltin species. This type of reaction proceeds by a polar mechanism involving electrophilic attack of tin on carbon (cf. ref. 5).



(9)

The major driving force for this reaction will be the apparent distortion of bond angles in the case of stannacyclopentanes resulting in a considerably strained ring system of higher energy than unstrained cyclic or linear tetraorganotin compounds.

Further experimental evidence for the enhanced reactivity of the *endo*-cyclic tin—carbon bond of stannacyclopentanes as a result of the ring strain is described elsewhere [10,14].

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. IR spectra were recorded on a Perkin—Elmer Mod. 577 instrument. Elemental analyses were carried out by the Section Elemental Analysis of this Institute.

Typical experiments are described below.

Reaction of 1,1-dimethyl-1-stannacyclopentane (DMSC-5) with atmospheric ambients

A sample of 0.5 g of DMSC-5 was exposed to the atmosphere for 3 days at room temperature. A viscous oil separated upon addition of 1 ml of CCl_4. Evaporation of the CCl_4 solution gave 0.1 g (20%) of impure DMSC-5 (^{1}H NMR). After standing for 7 more days the latter product contained only traces of residual DMSC-5. ^{1}H NMR spectrometry of the resulting viscous oil showed the presence of about 75% of Me_2SnR_2 species [δ(Me—Sn) 0.02, 0.03, 0.05 ppm], possibly $[Me_2Sn(CH_2)_4]_n$, and some 25% of a Me_2RSnX species [δ(Me—Sn) 0.4 ppm], whereas the methyltin resonance of DMSC-5 [δ(Me—Sn) 0.19 ppm] [4,9] was absent. Based on the chemical shift of the methyl—tin protons, the structure of the latter component is tentatively assigned to 1,1-dimethyl-1-stanna-2-oxycyclohexane (II; ref. 10: δ(Me—Sn) 0.38 ppm; $J(^{117/119}Sn—Me)$ 57/59 Hz).

After prolonged exposure the viscous oil turned into a vitreous, partly crystalline material. Treatment with chloroform and acetone gave a small amount of white crystalline solid, the IR spectrum of which contained carbonate and hydroxide absorptions, whereas the absorptions characteristic for stannacyclopentanes [8,9] were absent. These results together with the analyses data suggest structure $[Me_2Sn(CH_2)_4OH]_2CO_3$ (found: C, 29.4; H, 5.6; $C_{13}H_{30}O_5Sn$ calcd.: C, 30.95; H, 5.95%).

No spectral changes were observed with samples of DMSC-6 and DMSC-7. respectively, after exposure to the atmosphere for one month.

Reaction of DMSC-5 with oxygen

A solution of 1.08 g (5.3 mmol) of DMSC-5 in 2 ml of carbon tetrachloride was agitated for 16 days in an atmosphere of pure oxygen. In total 129 ml (~5 mmol) of oxygen had been consumed and two layers had formed. Carbon tetrachloride (2 ml) was added and the viscous insoluble lower phase was extracted four times with 1.5 ml of CCl_4. Evaporation of the combined CCl_4 portions gave 0.4 g of a viscous colourless oil [δ(Me—Sn) 0.06 ppm]. The insoluble lower phase was treated with a dilute solution of HCl in diethyl ether. Evaporation followed by GLC and NMR analysis of the residue showed the presence of Me_2SnCl_2 together with minor amounts of Me_3SnCl and unidentified trimethyltin species.

Reaction of DMSC-5 with water

A solution of 1.07 g (5.2 mmol) of DMSC-5 and 94 μl (5.2 mmol) of water in 8 ml of anhydrous methanol was heated for 5 h at 60°C. An oily liquid separated. ^1H NMR analysis of the residue obtained after evaporation of the solvent showed the presence of three methyltin species with chemical shifts characteristic of a tetraorganotin compound: δ(Me—Sn) 0.19 ppm (~7%; starting material), δ(Me—Sn) 0.05 ppm (42%) and δ(Me—Sn) 0.02 ppm (51%). The methylene protons gave unresolved broad signals in the region 0.4—2 ppm. The integrated ratio of methyltin protons (all together) versus the methylene protons was 6 : 8.05 [$[Me_2Sn(CH_2)_4]_n$, calcd. ratio Me/CH_2 6 : 8]. Methyltin resonances characteristic of a triorganotin species, such as Me_2BuSnX, were absent: e.g. $Me_2BuSnOAc$, δ(Me—Sn) 0.51 ppm [15].

Reaction of DMSC-5 with methyllithium

DMSC-5 (0.270 g, 1.25 mmol) was added to 1.9 ml of a 1.5 *N* solution of methyllithium in diethyl ether. According to ^1H NMR spectrometry about 70% of the DMSC-5 had been converted after 15 min. After standing for one day at room temperature the mixture was treated with a few drops of water. The diethyl ether solution was dried and evaporated to give 0.24 g of oily residue.

^1H NMR spectrometry indicated that the ring had been completely destroyed to give a mixture of $[Me_2Sn(CH_2)_4]_n$ with methyltin resonances situated at 0.00, 0.03 and 0.05 ppm (approximate ratio 3 : 2 : 1). The two broad, unresolved signals of the methylene protons were situated around 0.8 and 1.5 ppm. Integrated ratio methyl protons/methylene protons = 6 : 7.9. No trace of Me_3SnBu was detected by GLC analysis.

The reactions of DMSC-6 and of DMSC-7 with methyllithium were studied similarly. DMSC-6 (0.25 g, 1.15 mmol) was added to 1.6 ml of a 0.72 *N* solution of methyllithium in diethyl ether. After 14 h of reflux GLC analysis of the hydrolyzed mixture demonstrated the presence of 55% of DMSC-6. 40% of high boiling polymeric material and about 5% of $Me_3SnPent$. DMSC-7 was recovered in >75% yield after a similar treatment for 13 h.

Reaction of DMSC-5 with HBr

A solution of 0.62 g (3 mmol) of DMSC-5 in 4 ml of carbon tetrachloride was treated for $\frac{1}{2}$ h with gaseous HBr at 0°C. ^1H NMR spectrometry showed only minor changes. The temperature was raised to 40°C and HBr was passed through the mixture for $\frac{1}{2}$ h. ^1H NMR spectrometry showed that the DMSC-5 had been completely converted to give only a trace of polymeric material [$\leqslant$5%; δ(Me—Sn) 0.06 ppm], the major product being $Me_2BuSnBr$ [δ(Me—Sn) 0.69 ppm; $J(^{117/119}Sn—Me)$ 52/54 Hz; b.p. 44—46°C/0.3 mmHg; n_D^{20} 1.5163] [15].

Reaction of DMSC-5 with acetic acid

A PMR tube was charged with 50 μl (0.69 g, 0.3 mmol) of DMSC-5 and 450 μl of 98% acetic acid. The ^1H NMR spectrum was recorded after 0 h, 5 h and 24 h at 65°C. After 24 h 92% of the DMSC-5 had been converted to give about 32% of polymeric species, δ(Me—Sn) 0.03 ppm and 0.05 ppm, and 60% of $Me_2BuSnOAc$, δ(Me—Sn) 0.51 ppm, $J(^{117/119}Sn—Me)$ 52/54 Hz; m.p. 106—106.5°C [15].

Polymerization of DMSC-5 in methanol solution

A solution of 2 g of DMSC-5 in 22 ml of dry, oxygen-free methanol was heated for 14 h at 60°C. A colourless oil separated. The mixture was evaporated in vacuo to give a viscous liquid; identified as $Me_2Sn(CH_2)_4$; n_D^{20} 1.5360. (Anal.: Found: C, 35.5; H, 7.0; Sn, 57.0; $C_6H_{14}Sn$ calcd.: C, 35.18; H, 6.89; Sn, 57.93%.) ^1H NMR: δ(Me—Sn) 0.00 ppm, $J(^{117/119}Sn—Me)$ 48/50 Hz; δ(Me—Sn) 0.04 ppm, $J(^{117/119}Sn—Me)$ 50/52 Hz.

Osmometric molecular weight determination of the polymeric oil in benzene solution gave an average molecular weight of 1427, which corresponds with an average chain length of $n = 7$ (calcd.: 1434). A 0.2 mg sample of this product was heated at 300°C with a few crystals of $ZnCl_2$ in a distillation flask. GLC analysis showed that the distillate consisted of DMSC-5 (~60%) and tetramethyltin (~25%), together with traces of unidentified products (15%).

Acknowledgements

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