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ALKALINE HYDROLYSIS OF METHYL[TRIS(TRIMETHYLSILYL)METHYL]DICHLOROSTANNANE

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Summary

The compound $(Me_3Si)_3CSnMeCl_2$ reacts with MeOH/MeOK to give the cyclotristannoxane, $\mathrm{Me[(Me_3Si)_3C]\overline{SnOSn[C(SiMe_3)_3](Me)OSnO}[CH(SiMe_3)_2]Me}$, the structure of which was determined by full X-ray crystallography. Crystals of $C_{30}H_{82}O_3Si_8Sn_3$ are monoclinic, $a = 13.931(2)$, $b = 18.465(4)$, $c = 21.245(4)$ Å, $\gamma = 104.31(2)^0$, $D_c = 1.43$ g/cm^3, $Z = 4$, space group $P2_1/n$. The final R factor is 0.059.

Introduction

While investigating tris(trimethylsilyl)methyl derivatives of germanium and tin [1,2] we studied the hydrolysis of $(Me_3Si)_3CSnMeCl_2$ (I) by alcoholic alkali.

The growth of interest in the chemistry of tris(trimethylsilyl)methylsilanes is due to their structure and reactivity [3]. Thus, Eaborn and coworkers [4,5] have shown, that in the reaction of $TsiSiR_2X$* with alcoholic alkali the cleavage of a Si–C bond in the trisyl group occured and $(Me_3Si)_2CHSiR_2OMe$ was formed. The alkaline hydrolysis of $TsiMR_2Cl$ (M = Ge, Sn) was not followed by the cleavage of a Si–C bond [3,6,7]. According to Glockling and coworkers [7], the reaction of $TsiSnMeCl_2$ with $NaOH/H_2O$ in dioxan proceeds without cleavage of $SiMe_3$ group and leads to the linear trimer MeTsiSn(OH)OSn(Me)(Tsi)OSn(OH)TsiMe (II). So, the trisyl derivatives of germanium and tin have not shown the usual behaviour observed for the silicon analogues.

But, in accordance with our results, the hydrolysis of I leads to cyclotristannoxane $\mathrm{Me[(Me_3Si)_3C]\overline{SnOSn[C(SiMe_3)_3](Me)OSnO}[CH(SiMe_3)_2]Me}$ (III). The data of elemental analysis of compounds II and III practically coincide. Found: C 33.62; 33.85; H 7.79; 7.97. $C_{30}H_{82}O_3Si_8Sn_3$ calcd: C 33.62; H 7.71%. The structure of III was determined by full X-ray structure analysis, which showed that the cleavage of a Si–C bond took place along with hydrolysis of Sn–Cl bonds.

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* Tsi ("Trisyl") = $(Me_3Si)_3C$.

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Experimental

Synthesis

Methyl[tris(trimethylsilyl)methyl]dichlorostannane [1] (5.22 g) was heated with excess of potassium hydroxide in a mixture of the methanol and THF (1 : 1) for 1.5 h. The reaction mixture was diluted with water and extracted with ether. The ether layer was separated, then was dried over anhydrous Na_2SO_4. Colourless solid cyclotristannoxane (III), m.p. 181–182°C (MeOH) (with decomposition) was obtained (2.18 g, 51%) after removing the solvent in vacuo.

X-ray crystallography

The experimental intensities were collected on a Syntex P$\bar{1}$ four-circle automatic diffractometer using λ(Mo-K_α) radiation, a graphite monochromator, and the $\theta/2\theta$ scan method; $2\theta_{max} = 48°$. The final set of 5650 unique reflections with $I \geqslant 3\sigma(I)$ was corrected for Lorentz and polarization effects, but not for absorption (μ(Mo) = 16.4 cm^{-1}). Crystallographic parameters: $C_{30}H_{82}O_3Si_8Sn_3$, monoclinic, a = 13.931(2), b = 18.465(4), c = 21.245(4) Å, γ = 104.31(2)°, D_c = 1.43 g/cm^3, Z = 4, space group $P2_1/n$.

The structure was solved by the direct method using the MULTAN program and was refined * by full-matrix least squares with anisotropic (Sn, O, C, Si(1)–Si(5)) and isotropic (Si(7)–Si(9)) ** thermal parameters. The methyl hydrogen atoms were not localized. The final R value is 0.059. All calculations were performed on the Nova-3 computer incorporated in Nicolet R3 crystallographic system.

Discussion

The conformation of the molecule III is shown in Fig. 1 (for clarity the C atoms of the trimethylsilyl groups are not given). Unlike the hexakis(tert-butyl)cyclotristannoxane [8] having a planar 6-membered ring, the structure investigated here exhibits the heterocycle as substantially non-planar (a conformation of the strongly flattened boat). The atoms Sn(1), O(3), O(1) and Sn(2) are coplanar within 0.027 Å, the atoms Sn(3) and O(2) are out of this plane by 0.217 and 0.328 Å in opposite directions. The planes Sn(1)O(2)Sn(2) and O(3)Sn(3)O(1) form with the plane Sn(1)O(3)O(1)Sn(2) angles of 24.7 and 10.5°, respectively. This non-planarity may be due to the steric hindrance caused by the presence of the bulky substituents.

The interatomic distances and valence angles around Sn atoms are given in Tables 1 and 2. The mean values: Sn–C 2.153 Å, Sn–O 1.957 Å, O–Sn–O 104.8°, Sn–O–Sn 133.2°, C–Sn–C 117.4° are in a good agreement with the published data [8]. The Si–C distances are in the limits 1.867–1.936 Å (mean value 1.894 Å corresponds to the known ones), the coordination of Si atoms is practically ideally tetrahedral.

It is the formation of III that is of interest by itself. As it is known, alkaline hydrolysis of dialkyl(or diaryl)dihalogenstannanes leads to polymeric products, which are usually considered as analogues of polyorganosilanes [9] $(R_2SnO)_n$ or as coordinative polymers of the types [10]:

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* The table of positional and thermal atomic parameters may be obtained from the authors.

** These atoms are statistically ordered with respect to the Sn(3)–C(23) bond.

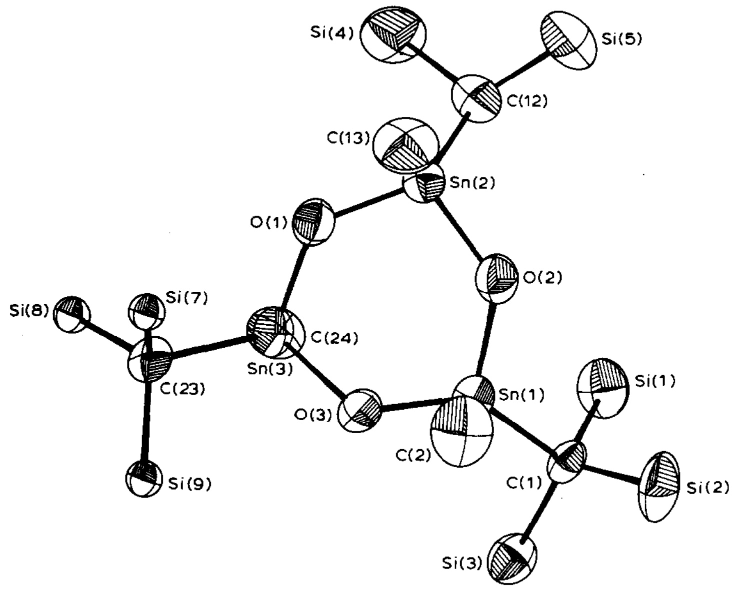
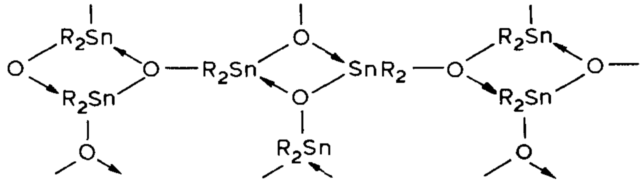


Fig. 1. ORTEP (50%) drawing of the molecule of III.



The only exception is t-Bu_2SnCl_2, the alkaline hydrolysis of which yields cyclotristannoxane [8].

The other distinguishing feature of the reaction of $TsiSnMeCl_2$ with alcoholic alkali is the cleavage of a Si–C bond, as was found in the reaction of $TsiSiR_2X$ with MeONa/MeOH but did not occur for $TsiGeR_2X$. Nucleophilic cleavage of a C–$SiMe_3$ bond, followed by fast protonation, probably proceeds in tris[tris(trimethylsilyl)methyl]cyclotristannoxane (IV), formed in the first stage.

TABLE 1

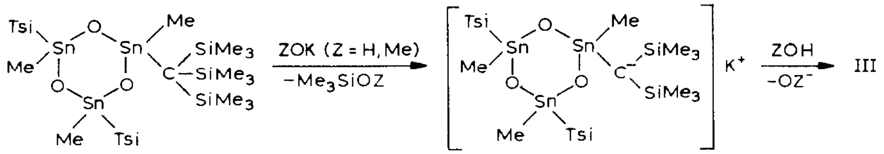
INTERATOMIC DISTANCES (Å) AND THEIR e.s.d.'s (in parentheses) FOR THE Sn ENVIRONMENT

Sn(1)–C(1)	2.167(11)	Sn(1)–O(2)	1.931(9)
Sn(1)–C(2)	2.158(14)	Sn(1)–O(3)	1.958(8)
Sn(2)–C(12)	2.116(14)	Sn(2)–O(1)	1.961(8)
Sn(2)–C(13)	2.143(15)	Sn(2)–O(2)	1.968(9)
Sn(3)–C(23)	2.191(11)	Sn(3)–O(1)	1.967(9)
Sn(3)–C(24)	2.142(12)	Sn(3)–O(3)	1.955(8)

TABLE 2

VALENCE ANGLES (deg.) AND THEIR e.s.d.'s (in parentheses) FOR THE Sn ENVIRONMENT

O(2)-Sn(1)-O(3)	105.1(3)	O(2)-Sn(2)-C(13)	108.3(5)
O(2)-Sn(1)-C(1)	108.2(4)	C(12)-Sn(2)-C(13)	118.8(6)
O(2)-Sn(1)-C(2)	107.6(5)	O(1)-Sn(3)-O(3)	104.7(3)
O(3)-Sn(1)-C(1)	111.2(4)	O(1)-Sn(3)-C(23)	109.5(4)
O(3)-Sn(1)-C(2)	105.5(5)	O(1)-Sn(3)-C(24)	109.3(4)
C(1)-Sn(1)-C(2)	118.5(5)	C(3)-Sn(3)-C(23)	111.0(4)
O(1)-Sn(2)-O(2)	104.6(3)	O(3)-Sn(3)-C(24)	107.0(4)
O(1)-Sn(2)-C(12)	110.9(4)	C(23)-Sn(3)-C(24)	114.9(4)
O(1)-Sn(2)-C(13)	107.1(5)	Sn(2)-O(1)-Sn(3)	133.4(4)
O(2)-Sn(2)-C(12)	106.2(4)	Sn(1)-O(2)-Sn(2)	132.4(5)
		Sn(1)-O(3)-Sn(3)	133.7(4)



(IV)

The heating (III) in the alkaline solution leads to the further cleavage of other Me_3Si-groups.

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