$$\begin{array}{c} H \\ N \\ HB \diagdown BNH_2 \\ | \quad | \\ HN \quad NH \\ \diagdown B \diagup \\ NH_2 \end{array}$$

Niedenzu and Dawson[21] have pointed out that 2,-4,6-triaminoborazine is quite unstable. They could not isolate 2,4,6-triaminoborazine as a pure compound. The instability of Fraction I is thus consistent with the supposition that it is an amino-substituted borazine, 2,4-diaminoborazine. Niedenzu and Dawson prepared several aminoborazines in which the amine nitrogen was substituted. In all of these compounds a very strong peak at 6.7 μ and another at 7.4 μ was noted in the infrared spectra. The infrared spectrum of Fraction I shows a strong band at 6.7 μ and a weaker one at 7.4 μ, again consistent with the supposition that the major component is 2,4-diaminoborazine.

The Structure of the Material Volatile at 90° in a Sublimator, Fraction IV.—Melting points and a preliminary mass spectral analysis suggest that Fraction IV is a mixture. It seems logical to assume that higher molecular weight products would be of the same type as those already described for $B_5N_5H_8$, $B_6N_6H_{10}$ and $B_3N_5H_8$. The mass spectrum shows a strong series of peaks about m/e of 185. These might be due to an anthracene-like $B_7N_7H_{10}$ (mol. wt. 184) or to a diamino-substituted analog of biphenyl, $B_6N_8H_{12}$ (mol. wt. 189). The series of peaks about m/e of 173 might be due to a monoamino-substituted analog of biphenyl, $B_6N_7H_{11}$ (mol. wt. 174), or to the fused tricyclic molecule $B_6N_7H_9$ (mol. wt. 172). The infrared spectrum is consistent with the above supposition. It shows B–H and N–H stretching vibrations and the characteristic borazine ring vibration.

The Structure of the Material Nonvolatile at 90° in a Sublimator, Fraction V.—All of the observations made on this material are consistent with the

(21) K. Niedenzu and J. W. Dawson, THIS JOURNAL, 81, 3561 (1959).

assumption that it is a highly condensed boron–nitrogen framework approaching that of boron nitride but still containing B–H and N–H bonds. The infrared spectrum of Fraction V shows some similarity to that of boron nitride but also shows that B–H and N–H bonds are present.

Comparison of the Pyrolysis of Borazine and Benzene.—The experimental data available do not allow one to write a detailed mechanism for the thermal decomposition of borazine. However, the observation of first order kinetics does suggest that a free radical mechanism is involved. The intermediate compounds obtained indicate that on pyrolysis borazine must first form dicyclic boron–nitrogen compounds by loss of hydrogen. These compounds in turn lose hydrogen to form an extended boron–nitrogen framework like that of boron nitride. The compounds which were isolated imply that at least two types of reaction are taking place. The existence of $B_5N_5H_8$ and $B_3N_5H_8$ indicate that there is some breakdown of the borazine ring. The production of $B_6N_6H_{10}$ does not require the breaking of the borazine ring but only intermolecular dehydrogenation.

The thermal decomposition of borazine is not completely analogous to the thermal decomposition of benzene. Intermediates in the thermal decomposition of benzene are biphenyl, terphenyls and triphenylene.[22] No modern worker has been able to isolate any naphthalene from the thermal decomposition products of benzene. Intermolecular dehydrogenation without the breaking of benzene rings, therefore, is the important mechanism in the thermal decomposition of benzene. This process of intermolecular dehydrogenation is also important in the thermal decomposition of borazine. However, the presence of $B_5N_5H_8$ and $B_3N_5H_8$ in the decomposition products of borazine require that ring cleavage must be another important mechanism in its thermal decomposition. Thus the thermal decomposition of borazine proceeds in a more complicated manner than does the thermal decomposition of benzene.

(22) C. R. Kinney and E. DelBel, Ind. Eng. Chem., 46, 548 (1954).

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Preparation and Properties of Tetraalkyl-1,3-bis-(trimethylsiloxy)-distannoxanes

BY ROKURO OKAWARA, DAVID G. WHITE,[1] KAZUSHI FUJITANI AND HIROYASU SATO

The cohydrolysis of trimethylchlorosilane with a dialkyltin dichloride has been studied as a means of preparing compounds containing the Si–O–Sn linkage. Crystalline tetraalkyl-1,3-bis-(trimethylsiloxy)-distannoxanes, $Me_3SiO(SnR_2O)_2SiMe_3$, are obtained by hydrolyzing a mixture of Me_3SiCl and R_2SnCl_2 (R = Me, Et, n-Pr, n-Bu) in benzene with excess aqueous ammonia in petroleum ether. Bis-(trimethylsiloxy)-dialkyltin compounds, $Me_3SiOSnR_2OSiMe_3$, are formed when an equivalent amount of aqueous ammonia is used, but these compounds are unstable and cannot be isolated in a pure state. Tetraalkyl-1,3-bis-(trimethylsiloxy)-distannoxanes also are produced by the cohydrolysis of Me_3SiCl with a tetraalkyl-1,3-dichlorodistannoxane. Some chemical and physical properties of these compounds have been investigated, and characteristic infrared absorption frequencies are given.

The search for polymers with greater stability at high temperatures has brought about a recent

interest in the preparation of modified organosiloxanes, in which some of the silicon atoms in the siloxane chain are replaced by various metallic

atoms. Stannosiloxanes of this type have been investigated by Koenig and co-workers, and they prepared a polymeric material containing both Me_2SnO and Me_2SiO units by hydrolyzing a mixture of dimethyltin dichloride and dimethyldichlorosilane with aqueous ammonia.[2] However, the yield was very poor (less than 5%). Okawara and Rochow[3] obtained a liquid with thin oily to viscous properties in 70–85% yield by improving the hydrolysis conditions used by Koenig. Henglein, Lang and Schmack[4] prepared certain polymers of a similar type by transesterification, i.e., by the reaction of dimethyldiethoxysilane with tin(II) acetate or dialkyltin diacetate.

These previous investigations have not determined definitely whether these polymeric materials actually contain the Si–O–Sn linkage or are just mixtures of the polymers $(Me_2SiO)_n$ and $(R_2SnO)_m$. Alkyl compounds with the Si–O–Sn bond were first reported by Tatlock and Rochow[5] who treated sodium or potassium trimethylsilanolate with Me_2SnCl_2, $SnCl_2$ and $SnCl_4$. They claimed to have obtained bis-(trimethylsiloxy)-dimethyltin, tin-(II) trimethylsilanolate and tin(IV) trimethylsilanolate, but very few analytical data are given. The purpose of our study has been to synthesize well-defined compounds containing the Si–O–Sn bond and to determine their properties and the characteristic infrared absorption of this linkage.

We failed to obtain $Me_3SiOSnMe_3$ and compounds of the type $Me_3SiO(SnMe_2O)_nSiMe_3$ by the transesterification of trimethylethoxysilane with trimethyltin formate or dimethyltin diformate. The reactions of $Me_2Sn(OCOH)_2$ with Me_3SiCl, Me_2SnO with Me_3SiCl and Me_2SnCl_2 with Me_3-SiOEt were also unsuccessful, and only Me_2-$SnCl_2$ was isolated in each case.

The cohydrolysis of a mixture of Me_3SiCl and R_2SnCl_2 ($R = CH_3$, C_2H_5, n-C_3H_7 and n-C_4H_9) in benzene solution with excess aqueous ammonia (about twice the equivalent amount) has been found to yield a crystalline compound with the formula $Me_3SiO(SnR_2O)_2SiMe_3$. The conditions of the hydrolyses and the product yields are given in Table I. Almost a quantitative yield of crystals is obtained when an excess of Me_3SiCl is cohydrolyzed with Me_2SnCl_2, but when the mole ratio of Me_3SiCl/Me_2SnCl_2 is reduced to 1, the yield is only 30%. Therefore a Si/Sn mole ratio of about 4 or greater was used in the cohydrolyses of the other dialkyltin dichlorides. Convincing evidence for the distannoxane structure of these compounds is the fact that the cohydrolysis of Me_3SiCl with $ClR_2SnOSnR_2Cl$ gives the same product. The melting points and analyses of these compounds are presented in Table II.

Although the presence of excess ammonia in the hydrolyzing medium appears to favor the formation of the tetraalkyl-1,3-bis-(trimethylsiloxy)-distannoxanes, the cohydrolyses with just the equiva-

(2) P. E. Koenig and J. H. Hutchinson, WADC Technical Report 58-44, Part I.

(3) R. Okawara and E. G. Rochow, Technical Report ONR, Harvard University, February 1960, Contract No. Nonr-1866(13).

(4) F. A. Henglein, R. Lang and L. Schmack, Makromol. Chem., 22, 103 (1957).

(5) W. S. Tatlock and E. G. Rochow, J. Org. Chem., 17, 1555 (1952).

TABLE I

Cohydrolysis of R_2SnCl_2 and Me_3SiCl with Aqueous NH_3[a]

| R_2SnCl_2, g.	Me_3SiCl, ml.	Mole ratio, Si/Sn	Yield,[b] %
	R = CH_3		
4.4	2.6	1	30
4.4	5.12	2	80
6.6	19.5	5	95
4.4	20.5	8	95
	R = C_2H_5		
10.1	19.2	3.7	90
	R = n-C_3H_7		
8.28	25.6	6.6	85
	R = n-C_4H_9		
6.06	12.8	5	95

[a] The hydrolyzing medium in each experiment was about twice the equivalent amount of aqueous NH_3 added to 200 ml. of petroleum ether. [b] Yield of crude product containing mainly $Me_3SiO(SnR_2O)_2SiMe_3$.

TABLE II

Properties of Tetraalkyl-1,3-bis-(trimethylsiloxy)-distannoxanes

| Compound (R = Me_3SiO)	M.p.,[a] °C.	Sn, % Found (calcd.)	C, % Found[b] (calcd.)	H, % Found[b] (calcd.)
$(RSnMe_2)_2O$	167–168	48.25 (48.26)	24.89 (24.41)	6.01 (6.15)
$(RSnEt_2)_2O$	126–130	43.41 (43.32)	30.56 (30.68)	6.77 (6.99)
$[RSn(n\text{-}Pr)_2]_2O$	107–108	39.62 (39.40)	35.80 (35.78)	7.65 (7.68)
$[RSn(n\text{-}Bu)_2]_2O$	108–109	36.02 (35.96)	40.31 (40.02)	8.35 (8.24)

[a] Melting points are uncorrected. [b] Carbon and hydrogen analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

lent amount of aqueous ammonia give compounds with compositions that closely correspond to the formula $Me_3SiOSnR_2OSiMe_3$. However, these compounds undergo decomposition on standing, and it is difficult to characterize them accurately. Since, for example, $Me_3SiO(SnEt_2O)_2SiMe_3$ crystallizes from the oily bis-(trimethylsiloxy)-diethyltin on standing, and some vapor, presumably Me_3-SiOSiMe_3, is liberated, bis-(trimethylsiloxy)-dialkyltin compounds appear to decompose

$$2Me_3SiOSnR_2OSiMe_3 \longrightarrow Me_3SiOSiMe_3 + Me_3SiO(SnR_2O)_2SiMe_3$$
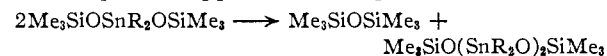
Some chemical and physical properties of the $Me_3SiO(SnR_2O)_2SiMe_3$ compounds were studied. They are soluble in aliphatic and aromatic hydrocarbon solvents, but when they are added to oxygen-containing solvents such as ethanol, ether, dioxane and acetone, slow decomposition occurs to yield the white, insoluble dialkyltin oxide. Although these compounds are insoluble in water, moisture promotes the decomposition reaction. A very slow decomposition (presumably to $Me_3SiOSiMe_3$ and $Me_3SiO(SnR_2O)_nSiMe_3$) may proceed even in the absence of water; thus a bottled sample of Me_3-SiO(SnPr_2O)_2SiMe_3 (m.p. 107–108°) only partially melted at 97° (some solid remained at 110°) after standing for a few weeks.

A similar cohydrolysis of Me₃SiCl with tin(II) chloride produced a 34% yield of unstable, crystalline Me₃SiO(SnO)₂SiMe₃, which decomposed into a yellow powder after several days. Analysis for tin showed that this change must have occurred

$$n\text{Me}_3\text{SiO-(Sn-O-)}_2\text{SiMe}_3 \longrightarrow$$

$$\text{Me}_3\text{SiO-(Sn-O-)}_{2n}\text{SiMe}_3 + (n-1)\text{Me}_3\text{SiOSiMe}_3$$
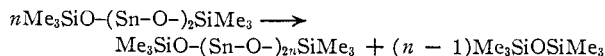
In the infrared region 700 to 3500 cm.⁻¹, two common strong bands characteristic to all tetraalkyl-1,3-bis-(trimethylsiloxy)-distannoxanes are found at 910 ± 5 and 980 ± 5 cm.⁻¹. These two bands are not observed with either dialkyltin oxide or hexamethyldisiloxane. The spectrum of the stannous derivative shows strong bands at 870 and 1065 cm.⁻¹; the latter is associated with the Si-O-Si bond in hexamethyldisiloxane[6] which is formed by decomposition.

Experimental[7]

Materials.—Dimethyltin dichloride (m.p. 106°) was supplied by the Metal and Thermit Corporation. Diethyltin dichloride, di-n-propyltin dichloride and di-n-butyltin dichloride (technical) were obtained from the Nitto Chemical Co. and were recrystallized before use. Trimethylchlorosilane was supplied by the Shin-Etsu Chemical Company.

Tetramethyl-1,3-dichlorodistannoxane was prepared by hydrolyzing dimethylchloroacetoxystannane.[8] The recrystallized solid had a Sn content of 61.27%. Calcd. for C₄H₁₂Sn₂OCl₂: Sn, 61.75. The compounds provided by the Nitto Chemical Company were tetraethyl-1,3-dichlorodistannoxane, m.p .174-176°. Found: Sn, 53.99. Calcd. for C₈H₂₀Sn₂OCl₂: Sn, 53.90. Tetra-n-propyl-1,3-dichlorodistannoxane, m.p. 121°. Found: Sn, 47.31. Calcd. for C₁₂H₂₈Sn₂OCl₂: Sn, 47.80. Tetra-n-butyl-1,3-dichlorodistannoxane, m.p. 112°. Found: Sn, 43.38. Calcd. for C₁₆H₃₆Sn₂OCl₂: Sn, 42.95.

Cohydrolysis of Me₃SiCl and R₂SnCl₂.—An alkaline medium is necessary to hydrolyze dialkyltin dichlorides. In the experiments shown in Table I, about twice the equivalent amount of aqueous ammonia was used. This was mixed with 200 ml. of petroleum ether in a three-necked flask fitted with a stirrer, reflux condenser and dropping funnel. The contents were cooled with an ice-bath and stirred vigorously, and the solution of the reactants in 150 ml. of benzene was added from the dropping funnel. The rate of addition had no appreciable effect on the yield of product. After this addition, about 200 ml. of water was added, and the rapid stirring was continued for an additional ten minutes. Then the organic layer was separated, washed twice with water, dried with Na₂SO₄ and distilled under reduced pressure. Removal of all of the Me₃SiOSiMe₃, formed by the hydrolysis of the excess Me₃SiCl, was insured by warming the residue in a vacuum. The solid product was recrystallized from benzene or petroleum ether.

Cohydrolysis of Me₃SiCl and ClR₂SnOSnR₂Cl.—These cohydrolyses were carried out using a slight excess of aqueous ammonia (1.1 times the equivalent amount). The colorless crystals obtained were identified as tetraalkyl-1,3-bis-(trimethylsiloxy)-distannoxanes by their melting points and analyses.

Cohydrolysis of Me₃SiCl and R₂SnCl₂ with the Equivalent Amount of Ammonia.—A mixture of Me₃SiCl and Et₂SnCl₂ was cohydrolyzed with the equivalent (or slightly less than the equivalent) amount of ammonia. The product was washed with water repeatedly until the water layer became neutral to methyl orange. The solvents were driven off by simple distillation, and the oily residue was evacuated by a rotary pump at room temperature to take off hexamethyldisiloxane completely. A pale yellow oil thus obtained had a Sn content of 34.63 %. Calcd. for Me₃SiOSnEt₂OSiMe₃: Sn, 33.42. After standing for one day at room temperature, this oil had experienced a weight loss of about 20% and changed to crystals. Additional loss in weight was not so remarkable but occurred slowly. Analysis of these crystals, m.p. 101°, gave a Sn content of 39.48%. Calcd. for Me₃SiO(SnEt₂O)₂SiMe₃: Sn, 43.32.

Cohydrolysis of Me₃SiCl and SnCl₂.—The procedure was similar to that described above: 38.4 ml. of Me₃SiCl and 5.7 g. of SnCl₂ (mole ratio Si/Sn = 10) dissolved in 150 ml. of diethyl ether was introduced into a cooled mixture of 200 ml. of petroleum ether and about twice the equivalent amount of aqueous ammonia. The reaction mixture contained a large amount of a white precipitate. After separation of the water layer and the precipitate, the solution was evaporated to a small volume and cooled to room temperature. Fine hexagonal crystals of Me₃SiO(SnO)₂SiMe₃ were produced, which were recrystallized from benzene; yield, 2.2 g. (34%), m.p. 150-168°.

Anal. Found: Sn, 55.59. Calcd. for C₆H₁₈Si₂O₃Sn₂: Sn, 54.98.

This compound appeared to be stable in solution, but the solid decomposed readily. When it was placed in a vacuum at room temperature for several days, there was an increase in the tin content: 55.59 % Sn (originally), 64.25% Sn (3 days later), 70.11 % Sn (8 days later).

Analysis of Products.—The gravimetric analyses for Sn and Si were conducted by treatment of a weighed sample in a Pt crucible with concentrated H₂SO₄, followed by careful heating to dryness. After the addition of a few drops of HNO₃, the residue was heated to a red heat for 15 minutes and then weighed as SnO₂ plus SiO₂. Concentrated HF and a few drops of H₂SO₄ then were added, and the mixture was gently heated to dryness. The residue (SnO₂) was again heated to a red heat for 15 minutes and weighed. The loss in weight corresponds to the weight of SiO₂.

Although this method gave accurate analyses for tin, the percentages of silicon (not reported) were always lower than the calculated values and varied with the heating conditions. This was caused by the formation of volatile Me₃SiOSiMe₃ by the action of hot, concentrated H₂SO₄.

Infrared Spectra.—The infrared absorption spectra were recorded using a Perkin–Elmer Model 21 double-beam spectrophotometer. The spectra were obtained using pressed KBr discs.

(6) N. Wright and M. J. Hunter, THIS JOURNAL, **69**, 803 (1947).

(7) Melting points are uncorrected.

(8) R. Okawara and E. G. Rochow, THIS JOURNAL, **82**, 3285 (1960).