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Inorganic Condensation Reactions. I. Stannosiloxane Formation[1a]

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Received June 29, 1963

Several $NaOSi(C_6H_5)_3$–organotin chloride reactions carried out at 25° in benzene have been studied in order to establish the fundamentals of a prototype inorganic condensation reaction. It has been shown these reactions are extremely rapid, but free of undesirable secondary processes since quantitative yields of the desired stannosiloxane compounds were obtained. In the course of this study, several new stannosiloxane compounds having the structure $((C_6H_5)_3SiO)_2SnR_2$ were prepared and characterized. Some of these as well as $(C_6H_5)_2Si(OSn(C_6H_5)_3)_2$ were also synthesized by bulk transesterification reactions involving organotin acetates and organoethoxysilanes.

Introduction

In recent years many attempts have been made to synthesize high molecular weight organometallosiloxane polymers by various cohydrolysis,[2] transesterification,[3] and Wurtz-type condensation reactions.[4] However, these efforts have generally yielded products of relatively low molecular weight. This often is attributed to side reactions and bond rearrangement believed to occur during the various polycondensation processes, but relatively little effort has been devoted to elucidating the nature of such reactions or establishing the conditions under which they occur. Little is known about prototype inorganic condensation reactions which lead to well-defined compounds. The present investigation was undertaken to obtain quantitative stoichiometric and, if possible, rate data for a prototype inorganic condensation reaction. The condensation of sodium triphenylsilanolate ($NaOSi(C_6H_5)_3$) with various organotin chlorides in benzene was selected since Post, *et al.*,[5] and Chamberlain[6] have shown this reaction yields well-defined products capable of being fully characterized. The knowledge obtained prompted a preliminary study of the transesterification of organotin acetates with organoethoxysilanes.

Experimental[7]

Materials.—$NaOSi(C_6H_5)_3$ was prepared by the method of Hyde and co-workers.[8] The product isolated had a purity of 96.4 ± 1.4% as determined by neutralization equivalents. Metal and Thermit organotin chlorides and triphenyltin acetate were recrystallized and identified by melting point and elemental analyses before use. Metal and Thermit dibutyltin diacetate, 90% minimum purity, and General Electric XC 3709 diphenyldiethoxysilane, 85% minimum purity, were flash distilled at 10 and 80 mm. pressure, respectively, in order to remove the slight turbidity and discoloration of the commercial materials. Triphenylethoxysilane was prepared by treating triphenylchlorosilane with sodium ethoxide in ethanol. The product was recrystallized from ethanol and identified by melting point and carbon–hydrogen analysis. All solvents were distilled over calcium hydride through a 70-cm. packed column. Thiophene-free benzene was fractionally crystallized before drying and purification by distillation. Infrared spectra were recorded on Perkin-Elmer Model 21 and 237 spectrophotometers. Combined silicon and tin oxides were determined by the method of Gilman and King.[9]

Stannosiloxane Formation.—A series of stannosiloxane compounds was prepared by dissolving 0.006 to 0.010 mole of $NaOSi(C_6H_5)_3$ in 50 ml. of benzene and adding to this solution a stoichiometric amount of the appropriate organotin chloride dissolved in 10–15 ml. of benzene. A slight temperature increase indicated an exothermic reaction. After mixing, the reaction mixture was left 5–15 min. at room temperature before the sodium chloride precipitate was removed by filtration. The clear filtrate was vacuum dried and the solid residue recrystallized. Bis(triphenylsiloxy)dibutylstannane [$(n\text{-}C_4H_9)_2Sn(OSi(C_6H_5)_3)_2$], bis(triphenylsiloxy)dimethylstannane [$(CH_3)_2Sn(OSi(C_6H_5)_3)_2$], and bis(triphenylsiloxy)dibenzylstannane [$(C_6H_5CH_2)_2Sn(OSi(C_6H_5)_3)_2$] were recrystallized from *n*-heptane (−4°). Diethyl ether (−4°) was used for recrystallizing triphenylsiloxytriphenylstannane [$(C_6H_5)_3SiOSn(C_6H_5)_3$] while *o*-xylene (−14°) was employed for bis(triphenylsiloxy)diphenylstannane [$(C_6H_5)_2Sn(OSi(C_6H_5)_3)_2$]. As all the above compounds crystallized slowly, no attempt was made to increase reported yields by repeated concentration and crystallization of the mother liquors.

Several stannosiloxane compounds were also prepared by bulk transesterification reactions. For example, $(C_6H_5)_3SiOSn(C_6H_5)_3$ was synthesized by treating 0.0150 mole (6.13 g.) of triphenyltin acetate with 0.0151 mole (4.56 g.) of triphenylethoxysilane at 172° under nitrogen for 21 hr. The reaction mixture was extracted with *n*-heptane, and the insolubles were recrystallized from ether as before. $(C_6H_5)_3SiOSn(C_6H_5)_3$ was identified by mixture melting point and infrared analysis. The yield of 2.27 g. was 24.3% of the theoretical value. Several additional runs have established that $(C_6H_5)_3SiOSn(C_6H_5)_3$ is also formed at 156 and 185°.

Bis(triphenylsiloxy)dibutylstannane was prepared by heating 0.00920 mole (3.23 g.) of dibutyltin diacetate and 0.0184 mole (5.59 g.) of triphenylethoxysilane under nitrogen at 168° for 23 hr. The reaction mixture was recrystallized from *n*-heptane and the product identified by mixture melting point and infrared analysis. The yield of 4.51 g. was 63.3% of the theoretical value.

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[1] (a) The authors wish to express their gratitude to Materials Central, Wright-Patterson Air Force Base, Ohio, for partial support of this project; (b) submitted in partial fulfillment of the Ph.D. degree.

[2] K. A. Andrianov, T. N. Ganina, and E. N. Khousteleva, *Izv. Akad. Nauk SSSR, Otd. Khim Nauk*, 798 (1956); P. E. Koenig and J. M. Hutchinson, WADC TR 58-44, Part I, May, 1958.

[3] F. A. Henglein, R. Lang, and L. Schmack, *Makromol. Chem.*, **22**, 103 (1957); J. F. O'Brien, WADC TR 57-502, 1957.

[4] P. E. Koenig and R. D. Crain, WADC TR 58-44, Part II, June, 1959.

[5] S. Papetti and H. W. Post, *J. Org. Chem.*, **22**, 526 (1957).

[6] M. M. Chamberlain, "Inorganic Macromolecules Containing a Si–O–M Linkage," Technical Report No. 1, Contract No. Nonr. 1439 (07), Project NR 052-419, Western Reserve University, Sept. 23, 1960.

[7] All melting points were determined by the capillary method and are uncorrected. Carbon–hydrogen analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Mich.; Microanalytical Laboratory, Skokie, Ill.; and Galbraith Laboratories, Inc., Knoxville, Tenn.

[8] J. F. Hyde, O. K. Johannson, W. H. Daudt, R. F. Fleming, H. B. Laudenslager, and M. P. Roche, *J. Am. Chem. Soc.*, **75**, 5615 (1953).

[9] H. Gilman and W. B. King, *ibid.*, **51**, 1213 (1929).

TABLE I

PHYSICAL PROPERTIES AND ANALYSES OF THE STANNOSILOXANE COMPOUNDS

Compound	Method of prepn.	M.p., °C.	Yield, %	Calculated, %			Found, %		
				C	H	Combined oxides	C	H	Combined oxides
$(C_6H_5)_3SiOSn(C_6H_5)_3$	Silanolate condensation	139–140	59.7	69.15	4.80	33.72	69.33	4.84	33.77, 33.66
$(C_6H_5)_3SiOSn(C_6H_5)_3$[a]	Transesterification	139–140	24.3						
$(CH_3)_2Sn(OSi(C_6H_5)_3)_2$	Silanolate condensation	155–156	64.9	65.26	6.01	38.74	65.44	5.92	38.72, 38.23
$(n\text{-}C_4H_9)_2Sn(OSi(C_6H_5)_3)_2$	Silanolate condensation	69–70	79.5	67.46	6.90	34.59	67.61	6.57	34.22, 34.23
$(n\text{-}C_4H_9)_2Sn(OSi(C_6H_5)_3)_2$[a]	Transesterification	69–70	63.3						
$(C_6H_5)_2Sn(OSi(C_6H_5)_3)_2$	Silanolate condensation	148.5–149.5	40.2	70.01	5.83	32.90	70.05	5.64	32.72, 32.65
$(C_6H_5CH_3)_2Sn(OSi(C_6H_5)_3)_2$	Silanolate condensation	122–123	78.3	70.36	5.39	31.82	70.41	5.31	31.71, 31.83
$(C_6H_5)_2Si(OSn(C_6H_5)_3)_2$	Transesterification	94.5–96.5	34.5	63.06	4.38	. . .	63.05	4.49	. . .

[a] Identified by mixture melting point and infrared analysis.

$(n\text{-}C_4H_9)_2Sn(OSi(C_6H_5)_3)_2$ has also been prepared at 156 and 185°.

Bis(triphenylstannyloxy)diphenylsilane [$(C_6H_5)_2Si(OSn(C_6H_5)_3)_2$] was prepared by treating 0.0140 mole (4.24 g.) of triphenyltinacetate with 0.00520 mole (1.41 g.) of diphenyldiethoxysilane at 156° under nitrogen for 7 hr. The product was recrystallized twice from *n*-heptane and identified by melting point, infrared, and carbon–hydrogen analysis. The yield of 1.64 g. was 34.5% of theoretical.

Stoichiometry.—Stoichiometry of the reactions of $NaOSi(C_6H_5)_3$ with triphenyltin chloride, dimethyltin dichloride, and dibutyltin dichloride in benzene was established by obtaining closed material balances around reaction systems involving 0.255 to 0.492 mequiv. of reactants. The average closure achieved was 99.8% and the standard deviation (σ) was ±1.4%.

The reactions were initiated by pipetting 0.0157 to 0.0984 *M* reactant solutions into a 50-ml. erlenmeyer flask. The amount of $NaOSi(C_6H_5)_3$ taken was that necessary to give a 1:1 reaction ratio assuming 100% purity. Since the silanolate actually was only 96.4 ± 1.4% pure, a small organotin chloride excess (~3.6%) existed in all runs. After mixing, the reaction mixtures were left at room temperature (25 ± 2°) for a known period before being filtered. The solids retained by the filter were extracted with several aliquots of water which then were combined and titrated with standard silver nitrate using dichlorofluorescein as the indicator. The per cent sodium chloride yield for each reaction mixture was calculated from the milliequivalents of silver nitrate used. The reliability of this extraction and titration procedure was established by suspending known amounts of sodium chloride in the reactor with benzene solutions of $(C_6H_5)_3SiOSn(C_6H_5)_3$ or various organotin chlorides. When these mixtures were treated as outlined above, an average chloride recovery of 99.0%, σ ±0.2%, was observed. Only dimethyltin dichloride affected the analysis, but this was small (~1%).

Following the chloride analysis, the filters used were dried and extracted with benzene. The benzene extracts were added to the clear filtrate obtained initially, and the combined mixture was vacuum dried to constant weight. The weight per cent stannosiloxane compound present in each solid residue was then determined spectrophotometrically.

A simple spectrophotometric procedure was used since preliminary experiments established that all of the stannosiloxane compounds had a characteristic infrared peak lying at 10.2 to 10.6 μ with which neither the reactants nor potential secondary products interfered significantly. Thus, Beer's law calibration curves were prepared, and the weight per cent yield of a stannosiloxane compound in a given reaction mixture was determined using these plots. Cyclohexane was employed as the solvent for all $(C_6H_5)_3SiOSn(C_6H_5)_3$ and $(n\text{-}C_4H_9)_2Sn(OSi(C_6H_5)_3)_2$ runs, and carbon disulfide was used for the $(CH_3)_2Sn(OSi(C_6H_5)_3)_2$ runs.

A measure of the error in the spectrophotometric procedure is given by the scatter of the data about the calibration curves. The average deviation from the $(C_6H_5)_3SiOSn(C_6H_5)_3$, $(CH_3)_2Sn(OSi(C_6H_5)_3)_2$, and $(n\text{-}C_4H_9)_2Sn(OSi(C_6H_5)_3)_2$ plots was ±1.1, ±1.0, and ±1.6%, respectively. This scatter is attributed to instrumental errors, since nine duplicate determinations of $(n\text{-}C_4H_9)_2Sn(OSi(C_6H_5)_3)_2$ had an average difference of 1.5%.

Results

Physical properties and elemental analyses of the stannosiloxane compounds prepared are shown in Table I. All are white crystalline compounds with well-defined melting points. $(C_6H_5)_3SiOSn(C_6H_5)_3$, $(n\text{-}C_4H_9)_2Sn(OSi(C_6H_5)_3)_2$, $(C_6H_5CH_3)_2Sn(OSi(C_6H_5)_3)_2$, and $(CH_3)_2Sn(OSi(C_6H_5)_3)_2$ dissolve readily in most organic solvents upon heating, but $(C_6H_5)_2Sn(OSi(C_6H_5)_3)_2$ is soluble only in hot *o*-xylene. All of these compounds are sparsely soluble in alcohols.

The stannosiloxanes are readily identified by a characteristic absorption band between 10.2 and 10.6 μ. The peak lies at 10.2 μ in $(C_6H_5)_2Si(OSn(C_6H_5)_3)_2$, and at 10.3 to 10.4 μ in $(C_6H_5)_3SiOSn(C_6H_5)_3$. It is shifted to 10.6 μ in $(n\text{-}C_4H_9)_2Sn(OSi(C_6H_5)_3)_2$, and lies at 10.4 μ in $(CH_3)_2Sn(OSi(C_6H_5)_3)_2$ and $(C_6H_5CH_3)_2Sn(OSi(C_6H_5)_3)_2$. This characteristic peak is reported to be at 10.2 μ for trimethylsiloxy–trialkylstannane compounds and is attributed to the Si–O–Sn bond.[10]

Stoichiometric data for the reactions of $NaOSi(C_6H_5)_3$ with triphenyltin chloride, dibutyltin dichloride, and dimethyltin dichloride at 25 ± 2° in benzene are given in Table II. All runs were made with a small organotin chloride excess (~3.6%). The reported yields represent averages of two to five determinations and are consistent, in all cases, with the over-all equations

$$NaOSi(C_6H_5)_3 + (C_6H_5)_3SnCl \longrightarrow (C_6H_5)_3SiOSn(C_6H_5)_3 + NaCl$$

$$2NaOSi(C_6H_5)_3 + (n\text{-}C_4H_9)_2SnCl_2 \longrightarrow (n\text{-}C_4H_9)_2Sn(OSi(C_6H_5)_3)_2 + 2NaCl$$

$$2NaOSi(C_6H_5)_3 + (CH_3)_2SnCl_2 \longrightarrow (CH_3)_2Sn(OSi(C_6H_5)_3)_2 + 2NaCl$$

There is no evidence of significant side reactions over the concentration range investigated. Since the Na-

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(10) R. Okawara and K. Sugita, *J. Am. Chem. Soc.*, **83**, 4480 (1961).

$OSi(C_6H_5)_3$ was only 96.4 ± 1.4% pure, the reported yields correspond to total consumption of reactants. No dependence on initial reactant concentration was observed. The small discrepancy (2.0–2.2%) between sodium chloride and $(C_6H_5)_3SiOSn(C_6H_5)_3$ yields is regarded as within experimental error. Although the $R_2Sn(OSi(C_6H_5)_3)_2$ data appear to scatter considerably, the average deviation of $R_2Sn(OSi(C_6H_5)_3)_2$ yields from that predicted by chloride analysis is only ±1.6%.

A measure of the rate of the $NaOSi(C_6H_5)_3$–organotin chloride reaction in benzene was obtained by isolating, after known reaction times, the sodium chloride by-product which precipitated. Representative data presented in Table III show that sodium chloride formation is essentially complete within 1 min. at 25°. This indicates the silanolate condensation reaction is extremely fast.

Several well-defined stannosiloxane compounds prepared by the $NaOSi(C_6H_5)_3$–organotin chloride reaction were also synthesized by bulk transesterification. An attempt to cause triphenyltin acetate to react with triphenylethoxysilane in refluxing dichlorobenzene failed, but a bulk reaction involving these reactants yielded $(C_6H_5)_3SiOSn(C_6H_5)_3$. Likewise, the bulk reaction of triphenylethoxysilane with dibutyltin diacetate gave $(n\text{-}C_4H_9)_2Sn(OSi(C_6H_5)_3)_2$, while $(C_6H_5)_2Si(OSn(C_6H_5)_3)_2$ was isolated as a product of the triphenyltin acetate and diphenyldiethoxysilane reaction. Significantly, all of these transesterification processes were slow and required prolonged reaction periods at temperatures of 150° or more. Since these severe conditions invite undesirable secondary processes, it was not surprising to discover that both triphenyltin acetate and dibutyltin diacetate decomposed significantly when heated. After 22 hr. at 168°, dibutyltin diacetate changed from a liquid to a waxy solid, and infrared analysis indicated few unreacted acetate groups remained. A similar decrease in acetate concentration was observed when triphenyltin acetate was heated at 168°. This decomposition process has not been studied further, but it undoubtedly is a significant and limiting factor in any prolonged polycondensation process carried out at elevated temperatures.

TABLE II

REPRESENTATIVE STOICHIOMETRIC DATA FOR STANNOSILOXANE FORMATION IN BENZENE AT 25°

Stannosiloxane compound	Initial $NaOSi(C_6H_5)_3$ concn., N	NaCl yield, %	Stannosiloxane yield, %
$(C_6H_5)_3SiOSn(C_6H_5)_3$	0.00783	95.7	97.9
$(C_6H_5)_3SiOSn(C_6H_5)_3$	0.0299	96.7	98.8
$(C_6H_5)_3SiOSn(C_6H_5)_3$	0.0490	94.9	96.9
$(n\text{-}C_4H_9)_2Sn(OSi(C_6H_5)_3)_2$	0.0127	97.8	96.4
$(n\text{-}C_4H_9)_2Sn(OSi(C_6H_5)_3)_2$	0.0260	96.4	90.8
$(n\text{-}C_4H_9)_2Sn(OSi(C_6H_5)_3)_2$	0.0492	97.6	97.7
$(CH_3)_2Sn(OSi(C_6H_5)_3)_2$	0.0136	96.2	94.5
$(CH_3)_2Sn(OSi(C_6H_5)_3)_2$	0.0260	97.1	96.4

TABLE III

SODIUM CHLORIDE YIELD AS A FUNCTION OF REACTION TIME AT 25°

Compound	Initial $NaOSi(C_6H_5)_3$ concn., N	Reaction time, min.	NaCl yield, %
$(C_6H_5)_3SiOSn(C_6H_5)_3$	0.0134	0.9	93.4
		5.4	94.3
$(C_6H_5)_3SiOSn(C_6H_5)_3$	0.0299	0.8	96.3
		5.6	96.8
$(C_6H_5)_3SiOSn(C_6H_5)_3$	0.0490	0.8	94.2
		54.7	95.2
$(n\text{-}C_4H_9)_2Sn(OSi(C_6H_5)_3)_2$	0.0490	0.8	94.6
		50.4	95.1
$(CH_3)_2Sn(OSi(C_6H_5)_3)_2$	0.0260	0.9	96.4
		54.6	96.9
$(C_6H_5)_2Sn(OSi(C_6H_5)_3)_2$	0.0299	0.8	95.8
		1.0	96.8

Discussion

Most of the stannosiloxane compounds listed in Table I are new. However, the $(C_6H_5)_3SiOSn(C_6H_5)_3$ reported here corresponds to that obtained by Post and Papetti,[5] and the $(CH_3)_2Sn(OSi(C_6H_5)_3)_2$ reported here appears to be the same material obtained by Chamberlain[6] for which only a melting point was given. Both authors treated $NaOSi(C_6H_5)_3$ with the appropriate organotin chloride in anhydrous ether. Koenig[2] also reported the synthesis of $(CH_3)_2Sn(OSi(C_6H_5)_3)_2$, m.p. 165–166°, by the bulk reaction of $[(CH_3)_2SnO]_x$ with triphenylsilanol, but gave only silicon and tin analyses. The failure of Koenig and Crain[4] to isolate $(C_6H_5)_2Sn(OSi(C_6H_5)_3)_2$ as a product of the heterogeneous reaction of triphenylsilanol with $((C_6H_5)_2SnO)_x$ indicates the reaction of polymeric organotin oxides with triphenylsilanol is not a satisfactory synthetic route to well-defined stannosiloxane compounds. This is also true of the heterogeneous cohydrolysis procedures employed by Okawara[11] and Andrianov.[2] Stannosiloxane compounds ultimately may be isolated as products of these complex reaction systems, but their isolation and identification could be difficult, especially if they have not been prepared previously. A more fruitful approach is to prepare well-defined stannosiloxane compounds by the relatively simple $NaOSi(C_6H_5)_3$–organotin chloride reaction. This synthesis is rapid, involves mild reaction conditions which minimize undesirable side reactions, and may offer a convenient route to many metallosiloxane compounds. Once the physical and chemical properties of a series of compounds formed in this way have been characterized, attempts can be made to follow the more complex processes mentioned above.

The preparation of $(C_6H_5)_3SiOSn(C_6H_5)_3$, $(n\text{-}C_4H_9)_2Sn(OSi(C_6H_5)_3)_2$, and $(C_6H_5)_2Si(OSn(C_6H_5)_3)_2$ by bulk transesterification is believed to be the first reaction of this type which has yielded well-defined stannosiloxane compounds. Although Henglein and O'Brien[3] reported transesterification reactions were used to prepare stannosiloxane polymers, they never established

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[11] R. Okawara, D. G. White, K. Fujitani, and H. Sato, *J. Am. Chem. Soc.*, **83**, 1342 (1961).

that –Si–O–Sn– bonds actually were formed. Okawara and co-workers[11] reported they failed to isolate $(CH_3)_3SiOSn(CH_3)_3$ or $(CH_3)_2Sn(OSi(CH_3)_3)_2$ as products of the reaction of trimethyltin formate or dimethyltin diformate with trimethylethoxysilane. Significantly, $(C_6H_5)_2Si(OSn(C_6H_5)_3)_2$ is the first well-defined noncyclic compound containing a stable $-\underset{|}{\overset{|}{\mathrm{Sn}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Sn}}}-$ bond sequence. All previous well-defined stannosiloxane compounds contained either $-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Sn}}}-$ or $-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Sn}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}-$ bond sequences.

Recently, some question concerning the stability of $-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Sn}}}-\mathrm{O}-$ bonds has developed since Okawara[11] reported the cohydrolysis of trimethylchlorosilane with dialkyltin dichlorides in the presence of excess base gave tetraalkyl-1,3-(trimethylsiloxy)distannoxanes and not bis(trimethylsiloxy)dialkylstannanes. Cohydrolysis involving equivalent amounts of aqueous ammonia yielded compounds with compositions that correspond closely to the formula $R_2Sn(OSi(CH_3)_3)_2$, but these reportedly decomposed on standing with the evolution of $(CH_3)_3SiOSi(CH_3)_3$.

$$2(CH_3)_3SiOSnR_2OSi(CH_3)_3 \longrightarrow (CH_3)_3SiOSi(CH_3)_3 + (CH_3)_3SiO(SnR_2O)_2Si(CH_3)_3$$

A very slow decomposition of bottled $(CH_3)_3SiO(SnR_2O)_2Si(CH_3)_3$ was also reported. Schmidbaur and Schmidt[12] have since reported that stable $(CH_3)_2Sn(OSi(CH_3)_3)_2$, m.p. 48°, can be prepared in good yield by the reaction of $LiOSi(CH_3)_3$ with dimethyltin dichloride in anhydrous ether, but the question of stannosiloxane stability still persists. Although no specific attempt was made to quantitatively investigate stability in the present study, there never was any indication that the stannosiloxane compounds in Table I are unstable. A sample of $(n\text{-}C_4H_9)_2Sn(OSi(C_6H_5)_3)_2$ has been stored at room temperature for 1 year and no change in its physical appearance or infrared spectra is evident. The synthesis of $(C_6H_5)_3SiOSn(C_6H_5)_3$, $(n\text{-}C_4H_9)_2Sn(OSi(C_6H_5)_3)_2$, and $(C_6H_5)_2Si(OSn(C_6H_5)_3)_2$ in good yields by prolonged reactions at temperatures of 156–185° is evidence for their thermal stability.

The stoichiometric and qualitative rate data of this study show that pure $NaOSi(C_6H_5)_3$ reacts rapidly in an aprotic solvent with stoichiometric amounts of R_3SnCl or R_2SnCl_2 to give quantitative yields of the corresponding stannosiloxane compound. Assuming the principles established for organic polycondensations are applicable to the present system,[13] this lack of side reactions implies the reaction of pure $(NaO)_2Si(C_6H_5)_2$ with pure R_2SnCl_2 in an aprotic solvent will yield stannosiloxane structures composed of regular alternating $(-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Sn}}}-\mathrm{O}-)$ units. Linear high polymer formation may be limited by cyclic formation or kinetic factors, but $-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}-$ or $-\underset{|}{\overset{|}{\mathrm{Sn}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Sn}}}-$ linkages should not be formed under normal reaction conditions unless a linear polymeric chain composed of $(-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Sn}}}-\mathrm{O}-)$ units is inherently unstable and undergoes bond rearrangement such as that exhibited by $(-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\mathrm{Sn}-)$ polymers.[14] Such bond rearrangement would be minimized by the low reaction temperatures required.

In conclusion, it should be noted there is a great deal of similarity between the silanolate–organotin chloride reaction and the fast irreversible reactions generally utilized in interfacial polycondensation.[15] This suggests an interfacial polymerization of $(NaO)_2Si(C_6H_5)_2$ and R_2SnCl_2 may yield truly high molecular weight linear stannosiloxane polymers if a suitable solvent system can be found.

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(12) H. Schmidbaur and M. Schmidt, *J. Am. Chem. Soc.*, **83**, 2963 (1961).

(13) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, New York, N. Y., 1953, Chapter III.

(14) E. D. Hornbaker and F. Conrad, *J. Org. Chem.*, **24**, 1858 (1959).

(15) E. L. Wittbecker and P. W. Morgan, *J. Polymer Sci.*, **40**, 289 (1959); P. W. Morgan and S. L. Kwolek, *ibid.*, **40**, 299 (1959).