Organometallics **1994,** *13,* 1034–1038

Air Activated Organotin Catalysts for Silicone Curing and Polyurethane Preparation

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Received May 3, 1993[●]

Summary: Upon exposure to air, 1,2-bis(acyloxy)tetraalkyldistannanes incorporated in mixtures of either silicone oils and curing agent, or of isocyanates and alcohols, are oxidized to 1,3-bis(acyloxy)tetraalkyldistannoxanes which show excellent catalytic properties for curing silicones or for preparing polyurethanes. Under nitrogen, they induce longer pot-lives than the usual bis(acyloxy)dialkylstannane catalysts. Peralkylpolycyclostannanes, obtained either by the palladium-catalyzed decomposition of dialkylstannanes or by reduction of dichlorodialkylstannanes with metals, are also very good latent catalysts for silicone curing. When incorporated into reactive mixtures under nitrogen, they do not catalyze the condensation. Upon exposure to air, they are oxidized to active catalysts which cure silicones. These di- or polystannanes can be considered air-activated latent organotin catalysts.

In the plastics industry, the most important reactions catalyzed by bis(acyloxy)dialkylstannanes[1] are the curing of silicones, which need to be cured to show their interesting elastomeric properties,[2] the preparation of polyurethanes,[3] which has to be accelerated when high production rates are needed, and esterification processes. Organotin catalysts are used in these reactions because of their high efficiency, their low cost, and their moderate toxicity. Such high efficiency may cause inconvenience, however, as condensation or addition reactions start as soon as reactants and catalyst are mixed together.[4] We recently designed and prepared new latent organotin catalysts, bis[2-(acyloxy)alkyl]diorganostannanes,[5] which provide long pot-lives for the mixtures into which they have been incorporated and which can be activated at will by heating. These tetraorganostannanes are inactive, but upon heating, they undergo an *anti* β-elimination reaction leading to catalytically active bis(acyloxy)dialkylstannanes.[6]

$$R^1{}_2Sn(CH_2CHR^2OCOR^3)_2 \rightarrow R^1{}_2Sn(OCOR^3)_2 + 2H_2C{=}CHR^2$$

To broaden the scope of these latent catalysts to room temperature applications, we desired a nonthermal activation process. As the active catalysts all have tin–oxygen bonds, whereas the inactive precursors do not, activations involving an oxidation were chosen for study. Moreover, as a number of organotin compounds are sensitive to atmospheric oxygen, this research looked very promising.

1,2-Bis(acyloxy)tetraalkyldistannanes were first chosen as oxygen activatable latent catalysts. These compounds, in which each tin atom bears only one acyloxy group, have been thought to show a reduced catalytic activity and would thus be likely to induce reasonable pot-lives. As the tin–tin bond is easily oxidizable, exposure to air leads to 1,3-bis(acyloxy)tetraalkyldistannoxanes, where each tin atom bears two oxygen atoms, thus showing the usual catalyst structure. These distannoxanes have already proven useful in polyurethane formation catalysts.[7]

$$R^1{}_2(R^2CO_2)Sn{-}Sn(O_2CR^2)R^1{}_2 + {}^1\!/_2O_2 \rightarrow R^1{}_2(R^2CO_2)Sn{-}O{-}Sn(O_2CR^2)R^1{}_2$$

The distannanes have been prepared in two ways, either by decomposition of unstable (acyloxy)dialkylstannanes[8] or by exchange between 1,2-dichlorotetraalkyldistannanes and acid salts.[9] To increase the rate of the first reaction, dichlorobis(triphenylphosphine)palladium has been used as catalyst and the usual solvent, pentane,[10b] exchanged for the more polar THF. Under these conditions, the preparation of the distannane is complete within 3 h at room temperature instead of after 36 h.

$$R^1{}_2SnH_2 + R^1{}_2Sn(O_2CR^2)_2 \rightarrow 2[R^1{}_2Sn(H)O_2CR^2]_2 \xrightarrow[-H_2]{(PPh_3)_2PdCl_2} R^1{}_2(R^2CO_2)Sn{-}Sn(O_2CR^2)R^1{}_2$$

Another attractive way, involving the cleavage of two alkyl

[●] Abstract published in *Advance ACS Abstracts,* December 1, 1993.

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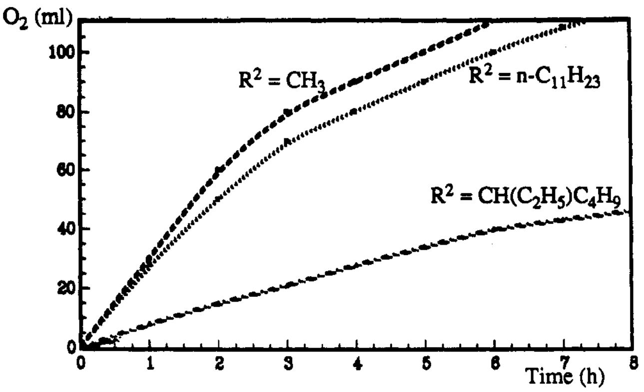


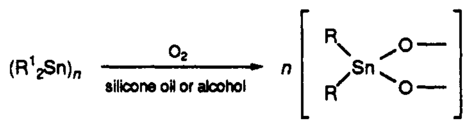
Figure 1. Comparison of oxygen absorptions by solutions (5 mmol) of 1,2-bis(acyloxy)tetrabutyldistannanes in heptane (20 mL), at 25 °C, under 100-W sunlamp irradiation.

groups of a hexaalkylditin by a halogenated carboxylic acid,[11] failed when the more industrially interesting butyl or octyl groups where used. This method seems limited to a labile methyl group and to halogenated carboxylic acids.

As reported earlier for the oxidation of hexaethylditin,[12] two oxidation mechanisms seem to be involved when 1,2-bis(acyloxy)tetraalkyldistannanes are exposed to oxygen. In the dark, the oxygen consumption by a solution of 1,2-bis(acetoxy)tetrabutyldistannane in heptane was slow, whereas, upon exposure to light (100-W lamp), it was much more rapid, leading to quantitative formation of 1,3-bis(acetoxy)tetrabutyldistannoxane. The oxidation rate has been measured as a function of the acyloxy moiety, in heptane solution. When acetoxy or lauroyloxy groups were used, oxidation rates were found to be in the same range. With more substituted acyloxy groups, the absorption of oxygen is considerably slower (see Figure 1). This can be due either to the steric effects around the tin–tin bond (each acyloxy group is coordinated to the neighboring tin atom[13]) or to the electronic effects of more branched groups, which make the tin–tin bond stronger. To avoid any interference with the palladium catalyst in this study, the distannanes were prepared by the spontaneous slow decomposition of (acyloxy)dialkylstannanes.

The catalytic activity of 1,3-bis(acyloxy)tetrabutyl- and 1,2-bis(acyloxy)tetraoctyldistannoxane has been compared to that of the corresponding known bis(acyloxy)dialkylstannane catalysts for SiH/SiOH condensations (see Table 1). They have been found to be more active, as gel times were reached almost twice as rapidly as with the corresponding carboxylate for (lauroyloxy)- and [(2-ethylhexanoyl)oxy]distannoxanes. 1,3-Bis(acetyloxy)tetraalkyldistannoxane showed an activity slightly lower than bis(acetyloxy)dialkylstannane. Tests in SiOH/SiOR condensations showed a slightly reduced activity for the distannoxanes. The distannane precursors were also tested in both condensations, under nitrogen and under air, to ascertain their latency properties. Results are gathered in Table 2. For both SiOH/SiOR and SiH/SiOH condensations, pot-lives under nitrogen were found to be much longer than those of the corresponding bis(acyloxy)dibutylstannane, from 30 (compare entries 1 and 5) to more than 40 times (entries 9 and 13) for the first one and from 3 to 4 for the other one (entries 2 and 6, and entries 10 and 14). 1,2-Bis(acyloxy)tetrabutyldistannanes were also tested as polyurethane preparation catalysts with 3-(isocyanatomethyl)-3,5,5-trimethylcyclohexyl isocyanate and a mixture of 1,4-butanediol and poly(ethylene glycol). The results are presented Table 3. As for silicone curing, 1,3-bis(acyloxy)distannoxanes showed very good catalytic properties. Under nitrogen, pot-lives were 10 times longer than those with the usual catalysts, and under air, the catalytic properties were recovered very rapidly. It has been checked that the platinum catalyst left in the distannanes had no influence on the course of the polymerization.

As the change of an acyloxy bond of a diacyloxystannane into an oxygen–tin bond of a stannoxane improved the activity of the catalysts, latent catalysts able to give only tin–oxygen bonds upon oxidation, without acyloxy groups, have been tested. These potential catalysts were poly(dialkylstannanes). The oxidation products of poly(diorganostannanes) are solid amorphous insoluble diorganotin oxides. They might have been discarded because of this insolubility. However, despite the lack of earlier reports, it has been suspected that oxidation occurring at low concentration with species such as silanols, alcohols, or isocyanates, able to react or interact with oxidation products, would lead to soluble compounds where the tin bears two oxygen atoms.



Poly(diorganostannanes) can be prepared either by the decomposition of diorganostannanes catalyzed by amines or sodium methoxide or by the condensation of diorganostannanes with dialkyoxy- or diaminodiorganostannanes.[14] Cyclic poly(organostannanes)[15] of various ring sizes (three to nine membered ring) have been fully characterized with phenyl,[16,17,21] methyl,[16,18] ethyl,[19,20] isobutyl,[21] *tert*-butyl,[21,22] or even bulkier[23] substituents.

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Table 1. Activity of 1,3-Bis(acyloxy)tetraalkyldistannoxanes in a SiH/SiOH Polycondensation

catalyst	gel time (min)	catalyst	gel time (min)
$(n\text{-}C_4H_9)_2Sn(O_2CCH_3)_2$	8	$(n\text{-}C_8H_{17})_2Sn(O_2CCH_3)_2$	9
$[(n\text{-}C_4H_9)_2Sn(O_2CCH_3)]_2O$	12	$[(n\text{-}C_8H_{17})_2Sn(O_2CCH_3)]_2O$	15
$(n\text{-}C_4H_9)_2Sn(O_2CC_{11}H_{23})_2$	12	$(n\text{-}C_8H_{17})_2Sn(O_2CC_{11}H_{23})_2$	15
$[(n\text{-}C_4H_9)_2Sn(O_2CC_{11}H_{23})]_2O$	9	$[(n\text{-}C_8H_{17})_2Sn(O_2CC_{11}H_{23})]_2O$	8
$(n\text{-}C_4H_9)_2Sn(O_2CCH(C_2H_5)C_4H_9)_2$	35	$(n\text{-}C_8H_{17})_2Sn(O_2CCH(C_2H_5)C_4H_9)_2$	30
$[(n\text{-}C_4H_9)_2Sn(O_2CCH(C_2H_5)C_4H_9)_2]_2O$	20	$[(n\text{-}C_8H_{17})_2Sn(O_2CCH(C_2H_5)C_4H_9)_2]_2O$	15

Table 2. Activity of Distannanes in SiOH/SiOR and SiH/SiOH Polycondensations

catalyst	entry	SiOH/SiOR gel time (h)	entry	SiH/SiOH gel time (min)
$Bu_2Sn(O_2CCH_3)_2$	1	1.5	2	8
$[Bu_2Sn(O_2CCH_3)]_2O$	3	1.2	4	12
$[Bu_2Sn(O_2CCH_3)]_2$ (N_2)	5	45	6	43
$[Bu_2Sn(O_2CCH_3)]_2$ (air)	7	4.5	8	23
$Bu_2Sn(O_2CC_{11}H_{23})_2$	9	3.2	10	12
$[Bu_2Sn(O_2CC_{11}H_{23})]_2O$	11	2.7	12	9
$[Bu_2Sn(O_2CC_{11}H_{23})]_2$ (N_2)	13	>120	14	36
$[Bu_2Sn(O_2CC_{11}H_{23})]_2$ (air)	15	8.5	16	26

Table 3. Organotin Promoted Polyurethane Preparation

catalyst	gel time (min)
$Bu_2Sn(O_2CCH(C_2H_5)C_4H_9)_2$	14
$[Bu_2Sn(O_2CCH(C_2H_5)C_4H_9)]_2O$	20
$[Bu_2Sn(O_2CCH(C_2H_5)C_4H_9)]_2$ (N_2)	150
$[Bu_2Sn(O_2CCH(C_2H_5)C_4H_9)]_2$ (air)	30
no	500

Table 4. Preparation of Polydibutylpolycyclostannanes by Palladium-Catalyzed Decomposition of Dibutylstannane

solvent	T (°C)	t (h)	yield (%)	Sn_5/Sn_6
pentane	15	12	95	90/10
silicone	20	6	80	70/30
THF	-50	2	95	[a]
	15	0.5	95	80/20
	50	0.2	90	70/30

[a] Sn_5, 29%; Sn_6, 25%; Sn_7, 15%; Sn_8, 13%; Sn_9, 10%; higher oligomers, 8%.

Table 5. Preparation of Polydialkyl Polystannanes from R_2SnCl_2

R_2SnCl_2	metal	activation[a]	T (°C)	t (h)	solvent	yield (%)[b]
Bu_2SnCl_2	Mg	B	–5	2	THF	83 (40/60)
Bu_2SnCl_2	Mg	A	60	1	THF	90 (45/55)
Bu_2SnCl_2	Mg	C	10	0.2	THF	75 (70/30)
Bu_2SnCl_2	Li	B	60	1	THF	71 (45/55)
Bu_2SnCl_2	Mg	B	40	1	Et_2O	50 (40/60)
Bu_2SnCl_2	Na		110	3	tol	50 (40/60)
Oct_2SnCl_2	Mg	A	60	1	THF	86 (30/70)

[a] A: 1,2-dibromoethane. B: Stirring. C: Ultrasound. [b] $Sn_5 + Sn_6$ (Sn_5/Sn_6).

With the industrially more interesting butyl[21,24] and octyl group, analytical data are scarce. As it gave rapid and clean results with trialkylstannanes,[10a] the palladium-catalyzed decomposition of the corresponding diorganostannanes have been used to prepare perbutyl- and peroctylpolystannanes. Indeed, the reaction proceeded quite well, leading after 12 h in pentane at 15 °C, from dibutylstannane to a 95% yield of a mixture of 90% decabutylcyclopentastannane and 10% dodecabutylcyclohexastannane. As reported above, a more polar solvent increased the reaction rate. In THF, only 30 min was necessary for the complete condensation. At low temperatures (–50 °C), a mixture of 29% cyclopentastannane, 25% cyclohexastannane, 15% cycloheptastannane, 13% cyclooctastannane, and 10% cyclononastannane, together with 8% higher oligomers, was isolated (see Table 4). This showed that the kinetic products of the reaction were cyclic oligomers whereas the cyclopenta- and cyclohexastannanes were the thermodynamic products. The cyclopenta- and the cyclohexastannane showed behaviors different from that of the dodecamethylcyclohexastannane which spontaneously and reversibly rearranges to a mixture of cyclopenta- and cyclohexastannanes.[18] Under the same conditions, at 20 or 80 °C in benzene, the dodecabutylcyclohexastannane was found to be stable, as were mixtures of penta- and hexamers of different compositions. This is probably due to the higher stability of the tin–tin bond in the butylated compounds than in methylated ones.[27] The composition of the mixture was determined by reversed-phase HPLC,[26] and the oligomers were identified by ^{119}Sn NMR spectroscopy and HPLC coupled FAB mass spectrometry. Decabutylcyclopentastannane and dodecabutylcyclohexastannane were isolated by reversed-phase preparative HPLC. In ^{119}Sn NMR, they gave very close signals, with the expected pattern of satellites,[23e] at –201.2 and –202.5 ppm, respectively, for $(Bu_2Sn)_5$ and $(Oct_2Sn)_5$, and –202.4 and –202.9 ppm, respectively, for $(Bu_2Sn)_6$ and $(Oct_2Sn)_6$. Tin–tin coupling constants for both pentamers [$(Bu_2Sn)_5$ $^1J_{Sn-Sn} = 476$ Hz, $^2J_{Sn-Sn} = 461$ Hz; $(Oct_2Sn)_5$ $^1J_{Sn-Sn} = 473$ Hz, $^2J_{Sn-Sn} = 446$ Hz] and both hexamers [$(Bu_2Sn)_6$ $^1J_{Sn-Sn} = 462$ Hz, $^2J_{Sn-Sn} = 386$ Hz, $^3J_{Sn-Sn} = 81$ Hz; $(Oct_2Sn)_6$ $^1J_{Sn-Sn} = 459$ Hz, $^2J_{Sn-Sn} = 372$ Hz, $^3J_{Sn-Sn} = 80$ Hz] were found smaller than those in the corresponding $(Me_2Sn)_5$ and $(Me_2Sn)_6$,[18] which is the usual effect when a methyl group is replaced by a heavier group.[27,28] Mass spectra showed molecular peaks at *m/e* 1170 (^{120}Sn) for $(Bu_2Sn)_5$ and at *m/e* 1404 for $(Bu_2Sn)_6$.

As the preparation of these compounds involved dialkylstannanes, difficult to purify in the octyl case, a more straightforward route, using commercially available starting materials, was desired. The reduction of dibutyl- or dioctyldichlorostannanes by metals was tested (see Table 5). This route gave us good results with stannoxanes[29] and has been described for di-*tert*-butyl-[21] and diphenyldichlorostannanes[16] to give the tetra- and hexamer, respectively. Indeed, it worked well, giving high yields of mixtures of equimolar amounts of pentamer and hexamer. The use of magnesium, previously activated either by 1,2-dibromoethane or by a prolonged stirring[30] under nitrogen,

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(24) The sodium methoxide catalyzed decomposition of dibutylstannane was reported[21] to give a 93% yield of dodecabutylcyclohexastannane. In our hands the reaction was far from being so selective: it led to an 80% yield of a mixture of 28% decabutylcyclopentastannane and 72% dodecabutylcyclohexastannane. As Sita[25] and ourselves[26] have pointed out, modern structural investigations reveal some discrepancies about the characterization of polytins.

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Table 6. SiH/SiOH Polycondensation Catalyzed by $(R_2Sn)_n$ (Gel Time)

conditions	$(Bu_2Sn)_n$	$Bu_2Sn(OAc)_2$	$(Oct_2Sn)_2$	$Oct_2Sn(OAc)_2$
N_2	8 h		10 h	
air	8 min	8 min	8 min	9 min

in THF at 60 °C, gave the best results. Activation by ultrasound allowed complete reduction at low temperatures. When THF was replaced by diethyl ether, the yield of polystannanes diminished, as when lithium or sodium was used instead of magnesium. Dichlorodioctylstannane gave the same results as dichlorodibutylstannane. In both cases, the pentamer was much more reactive toward oxygen than the more stable hexamer. Upon exposure to air, a solution of the pentamer decomposed almost immediately, while the hexamer was decomposed more slowly.

These polystannanes were tested for silicone curing catalysis. It was first checked that no precipitation occurred when a dilute solution of the mixture of cyclic oligomers in silicone oil under nitrogen was exposed to air. As anticipated, the oxidation products stayed in solution. The catalytic properties were tested for SiH/SiOH polycondensation (Table 6). When a solution of silicone oil, curing agent, and a mixture of decabutylcyclopentastannane and dodecabutylcyclohexastannane (45/55) was exposed to air, a very rapid condensation occurred. The reaction was as fast (8 min) as when the usual bis(acetyloxy)dibutylstannane catalyst was used. The remaining palladium catalyst in the cyclopolystannanes, susceptible to interaction with the silicon–hydrogen bond of the siloxane, did not interfere with this condensation reaction. The peralkylated cyclopolystannanes are thus excellent catalysts for SiH/SiOH polycondensation. However, when these reactive solutions were kept under nitrogen, they remained fluid for a very long time: 8 h for the butylated polystannanes and 10 h for the octylated polystannanes. Pot-lives were thus 60 times longer with the cyclopolystannanes than with the ordinary catalysts, which demonstrates the latency property of these organotin compounds.

In conclusion, 1,3-bis(acyloxy)tetraalkyldistannoxanes and dialkyltin oxides have been found to be excellent catalysts for silicone curing and polyurethane preparation. These compounds can be obtained in industrial mixtures by *in situ* oxidation of 1,2-bis(acyloxy)tetraalkyldistannanes and peralkylcyclopolystannanes, respectively. As 1,2-bis(acyloxy)tetraalkyldistannanes and peralkylcyclopolystannanes themselves show very poor catalytical properties, they form a new class of air activatable organotin catalysts.

Experimental Section

All reactions were carried out under a nitrogen atmosphere, except oxidation reactions, which were conducted under air or oxygen. THF, diethyl ether, pentane, and cyclohexane were distilled from sodium benzophenone ketyl (with added diphenyl ether for hydrocarbons). Dichlorodibutylstannane was recrystallized before use. Dibutylstannane,[31] dioctylstannane,[32] 1,2-dichlorotetrabutyldistannane and 1,2-dichlorotetraoctyldistannane,[10b] and 1,3-bis(acyloxy)dialkyldistannoxanes[33] were prepared according to known procedures. ^1H NMR spectra were recorded on a Perkin-Elmer-Hitachi R 24B or a Bruker AC-250 spectrometer (in $CDCl_3$, internal reference Me_4Si), ^{13}C NMR spectra on a JEOL FX90Q spectrometer at 22.63 MHz (solvent C_6D_6, internal reference Me_4Si), and ^{119}Sn NMR spectra on a Bruker AC-200 spectrometer at 74.5 MHz (solvent C_6D_6, internal reference Me_4Sn). Tests for condensation reactions were repeated at least three times. Average values are given in the tables.

1,2-Bis(acyloxy)tetraalkyldistannanes. The preparation of 1,2-bis(acetyloxy)tetrabutyldistannane is representative.

First Method. In a Schlenk tube, under nitrogen, 30 mmol of dibutylstannane (7.05 g) and 30 mmol of bis(acetyloxy)dibutylstannane (10.53 g) were mixed. After 5 min 0.015 mmol of dichlorobis(triphenylphosphore)palladium (10.5 mg) was added and the mixture stirred for 2 h at room temperature. The resulting oils were used without further purification. They were found to be >94% pure by ^{119}NMR spectroscopy, the main impurity being bis(acetyloxy)dibutylstannane.

Second Method. In a Schlenk tube under nitrogen were mixed 30 mmol of dibutylstannane (7.05 g) and 30 mmol of dichlorodibutylstannane (9.12 g) in pentane (30 mL). After 15 min, 0.03 mmol of dichlorobis(triphenylphosphine)palladium (22 mg) in pentane (30 mL) was added. After 2 h, a 5-fold excess of sodium acetate (12.30 g, 150 mmol) was added. Silver or potassium salts were also convenient. The mixture was stirred for 1 h and filtered and the solvent evaporated. The resulting distannanes were more than 95% pure. 1,2-Bis(acetyloxy)tetrabutyldistannane: ^1H NMR δ 0.9–1.65 (36H, m), 1.9 (6H, s); ^{13}C NMR δ 183.4, 29.2, 27.2, 23.5, 18.2, 13.9; ^{119}Sn NMR δ −126.8 ($^1J_{Sn-Sn}$ = 11 272 Hz). 1,2-Bis(lauroyloxy)tetrabutyldistannane: ^1H NMR δ 0.8–1.8 (78H, m), 1.9–2.3 (4H, m); ^{13}C NMR δ 185.9 (0.5C), 179.7 (0.5C), 37.5 (0.5C), 36.6 (0.5C), 31.3, 30.2, 30.0, 29.9, 29.3, 27.2, 26.2, 23.7, 18.2, 14.4, 14.0; ^{119}Sn NMR δ −135.8 ($^1J_{Sn-Sn}$ = 11 662 Hz). 1,2-Bis[(2-ethylhexanoyl)oxy]tetrabutyldistannane: mp 24 °C; ^1H NMR δ 0.8–1.8 (72H, m), 1.9–2.3 (2H, m); ^{13}C NMR δ 191.5, 50.7, 33.1, 30.6, 29.5, 27.4, 26.6, 23.3, 18.5, 14.4, 14.0, 12.5; ^{119}Sn NMR δ −140.0 ($^1J_{Sn-Sn}$ = 10 857 Hz). 1,2-Bis(lauroyloxy)tetraoctyldistannane: ^1H NMR δ 0.8–1.8 (94H, m), 1.9–2.3 (4H, m); ^{119}Sn NMR δ −140.0 ($^1J_{Sn-Sn}$ = 11 662 Hz).

Peralkylcyclopolystannanes. Palladium-Catalyzed Condensation. In a Schlenk tube under nitrogen protected from light, 20 mmol of dialkylstannane and 0.015 mmol of dichlorobis(triphenylphosphine)palladium (10 mg) were mixed in the appropriate solvent (20 mL). After completion of H_2 evolution (an equal volume of pentane was added when THF or Et_2O was used), the mixture was filtered through a short column of silica under nitrogen and the first fraction recovered. The solvent was evaporated.

Metal Induced Condensation. Activation by 1,2-Dibromoethane. Into a three-necked flask were introduced 0.41 mol of magnesium (10 g), 20 mL of THF, and 0.5 mL of 1,2-dibromoethane. After reaction, a solution of 40 mmol of dichlorodialkylstannane in 50 mL of THF was added dropwise and the mixture refluxed for 1 h.

Activation by Stirring.[30] Into a three-necked flask was introduced 0.5 mol of magnesium turnings (12 g). After stirring for 48 h, the flask was internally coated with a mirror of metal and the turnings were finely divided. THF (20 mL) was then added followed dropwise by a solution of 40 mmol of dichlorodialkylstannanes in 50 mL of THF. The reaction was exothermic. The mixture was refluxed for 1 h.

Activation by Ultrasound. After cleaning a stoichiometric amount of the metal by irradiation for 30 min at 0 °C in 50 mL of the solvent mentioned Table 5, the dichlorodialkylstannane (40 mmol) in 40 mL of solvent was added dropwise. Once the reduction was complete, 100 mL of degassed pentane was added. The resulting mixture was filtered under nitrogen and transferred to a Schlenk tube containing 50 mL of degassed water. After drying and filtration through a short column of silica under nitrogen, the solvents were evaporated and the cyclostannanes recovered as light-yellow oils. They were purified by preparative reversed-phase chromatography. Decabutylcyclopentastannane: ^{119}Sn NMR δ −201.2 ($^1J_{Sn-Sn}$ = 476 Hz, $^2J_{Sn-Sn}$ = 461 Hz). Anal. Calcd for $C_{40}H_{90}Sn_5$: C, 41.25; H, 7.79. Found: C,

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39.68; H, 7.21. Dodecabutylcyclohexastannane: ^{119}Sn NMR δ -202.4 ($^1J_{Sn-Sn} = 462$ Hz, $^2J_{Sn-Sn} = 386$ Hz, $^3J_{Sn-Sn} = 81$ Hz). Anal. Calcd for $C_{48}H_{108}Sn_6$: C, 41.25; H, 7.79. Found: C, 39.82; H, 7.34. Decaoctylcyclopentastannane: ^{119}Sn NMR δ -202.5 ($^1J_{Sn-Sn} = 473$ Hz, $^2J_{Sn-Sn} = 446$ Hz). Anal. Calcd for $C_{80}H_{170}Sn_5$: C, 55.68; H, 9.93. Found: C, 55.27; H, 9.35. Dodecaoctylcyclohexastannane: ^{119}Sn NMR δ -202.9 ($^1J_{Sn-Sn} = 459$ Hz, $^2J_{Sn-Sn} = 372$ Hz, $^3J_{Sn-Sn} = 80$ Hz). Anal. Calcd for $C_{96}H_{204}Sn_6$: C, 55.68; H, 9.93. Found: C, 55.04; H, 9.31.

SiOH/SiOR Condensations. Into a Schlenk tube were placed 60 g of degassed α,ω-dihydroxylated silicone oil (average molecular weight 42 500; 4.7 mequiv of OH/100 g of oil), 0.84 g (3.2 mmol) of tetrapropoxysilane, and the organotin catalyst (1.14 mequiv of Sn). The mixture was vigorously stirred for 1 min. Approximately half of this mixture was then left at room temperature under nitrogen until the mixture gelled. The other half was placed under air until the gel state was reached.

SiH/SiOH Condensations. Into a Schlenk tube were placed 23 g of degassed α,ω-dihydroxylated silicone oil (average molecular weight 42 500; 4.7 mequiv of OH/100 g of oil), 1 g of poly(hydrogenomethylsiloxane) (SiH content: 1.5%), and the organotin catalyst (0.712 mequiv of Sn). The mixture was stirred for 1 min. Approximately half of this mixture was then left at room temperature under nitrogen until it formed a gel. The other half was placed under air until the mixture gelled.

Polyurethane Preparation. Into a Schlenk tube were added 5.26 g of poly(ethylene glycol) (average molecular weight: 1000), 0.80 g of 1,4-butanediol (9 mmol), and 1 mL of a 0.0075 equiv of Sn/L solution of the tin catalyst in ether. The solvent was evaporated, and 3.94 g of 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane (isophorone diisocyanate) (18 mmol) was added. After mixing, approximately half of the mixture was left in the Schlenk tube until it gelled (pot-life value) and the other half poured into a beaker under air until the mixture gelled.

Acknowledgment. We are indebted to Schering-France for a generous gift of organotin compounds.

OM930283M