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Synthesis and thermal decomposition of substituted [2-(acyloxy)alkyl]diorganotin compounds, $Bu_2Sn(X)CH_2CHR^1OCOR^2$ (X = halogen, 2,4-pentanedionate, or OCOR), potential sources of organotin catalysts

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Abstract

Halido-, (2,4-pentadionato-*O,O'*)- and (acyloxy)[2-(acyloxy)ethyl]dibutylstannanes, $Bu_2Sn(X)CH_2CHR^1OCOR^2$ (X = halogen, 2,4-pentanedionate, or OCOR) have been prepared, either by hydrostannation of vinyl esters or by condensation of stannyllithium compounds with epoxides followed by esterification. These thermally unstable compounds are easily decomposed in diorganotin compounds with two heteroatom donors. Some are good catalyst sources for silicone curing and polyurethane preparation.

1. Introduction

Bis(acyloxy)diorganostannanes are used in industry [1] as PVC stabilizers and as catalysts for silicone curing [2], polyurethane preparation [3], and esterification reactions [4]. The creation of the silicon–oxygen–silicon network from linear silicones, necessary to induce interesting elastomeric properties, can be obtained by condensation of terminal silicon-hydroxyl groups with a curing agent, either a tetra-alkoxysilane (SiOH–SiOR condensation) or a hydrogenopolysiloxane (SiOH–SiH condensation). Both processes are catalyzed by bis(acyloxy)diorganostannanes. In the polyurethane industry, where high production rates are essential, these stannanes are also used to catalyze the addition of alcohols to isocyanates. Although bis(acyloxy)diorganostannanes are very efficient catalysts, leading to polymers with excellent mechanical properties, they have some drawbacks as condensation reactions start as soon as the mixtures are prepared. A rapid decrease in fluidity results, which may be a problem. This inconvenience can be avoided by using solvents [5] which dilute the active species and thus lower their reactivity, by drying the mixtures [6], by dispersing microcapsules enclosing the catalyst [7], or by using the inactive adduct of a bis(acyloxy)diorganostannane with a sulfonylisocyanate, decomposed by water *in situ* to give the bis(acyloxy)diorganostannane [8].

We recently proposed the use of new catalyst sources, bis[2-(acyloxy)ethyl]diorganostannanes, which can be activated at will by heat [9]. These thermally unstable compounds are not efficient catalysts at room temperature. They induce long pot-lives to the mixtures in which they have been incorporated. However, on moderate heating, they decompose into the usual catalyst inside industrial catalyst mixtures that are then rapidly cured or polymerized.

$$Bu_2Sn(CH_2CHR^1OCOR^2)_2 \xrightarrow{\Delta} Bu_2Sn(OCOR^2)_2 + 2CH_2{=}CHR^1$$

A mechanistic study showed that the reaction rate is determined by the cleavage of the β-carbon–oxygen bond [10] and that this reaction follows an anti-elimination pathway [11]. Here we present results concerning the synthesis and the decomposition of new compounds, $Bu_2Sn(X)CH_2CHR^1OCOR^2$, where X can be a halogen, an acyloxy group or a 2,4-pentanedionate group, and their use as catalyst sources for silicone curing and polyurethane preparation.

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2. Results and discussion

In the thermal decomposition of bis[2-(acyloxy)alkyl]diorganostannanes, the first elimination step should lead to acyloxy[2-(acyloxy)alkyl)]dialkylstannane **1**, that have never been isolated nor detected.

$$Bu_2Sn(CH_2CHR^1OCOR^2)_2 \xrightarrow{-CH_2=CHR^1}$$

$$Bu_2(R^2CO_2)Sn(CH_2CHR^1OCOR^2) \xrightarrow{-CH_2=CHR^1}$$

1

$$nu_2Sn(OCOR^2)_2$$

The (acyloxy)triorganostannanes **1** might show a reduced catalytic activity as the metal is only linked to one oxygen. However, with an acyloxy group in β-position, they are susceptible to β-elimination and thus could be good precursors of known catalysts. Compound **1** ($R^1 = H$, $R^2 = CH_3$) was first prepared in three steps from dibutylstannane and vinyl acetate. UV-induced addition of a five-fold excess of dibutylstannane to vinyl acetate did not give bis[2-(acetyloxy)ethyl]dibutylstannane but provided the expected [2-(acetoxy)ethyl]dibutylstannane in good yield. The substitution of hydrogen by chlorine was achieved by warming [2-(acetyloxy)ethyl]dibutylstannane in carbon tetrachloride. Coupling with silver acetate gave the required stannane **5**.

$$Bu_2SnH_2 \text{ (an excess)} + H_2C{=}CHOCOCH_3 \rightarrow$$

$$Bu_2(H)Sn(CH_2CH_2OCOCH_3)$$

$$Bu_2(H)SnCH_2CH_2OCOCH_3 + CCl_4 \rightarrow$$

$$Bu_2(Cl)SnCH_2CH_2OCOCH_3 + HCCl_3$$

2

$$Bu_2(Cl)SnCH_2CH_2OCOCH_3 + AgOCOCH_3 \rightarrow$$

$$Bu_2(CH_3CO_2)SnCH_2CH_2OCOCH_3 + AgCl$$

5

This is a particularly interesting way to prepare precursors of diorganotin compounds with an acetylacetonate and an acetyloxy group that cannot be obtained by hydrostannation, as vinyl acetylacetonates do not seem to be described. However, this method did not give a pure product, 10% of the $Bu_2Sn(CH_2CHR^1OCOCH_3)_2$ being recovered in the first step. Unfortunately, it could not be purified by distillation because of its thermal sensitivity, nor could it be chromatographied. To get a purer product, the chlorostannane was prepared directly from chlorodibutylstannane [12] and vinyl acetate. When freshly prepared chlorodibutylstannane was used under anaerobic conditions, the addition was very clean and the adducts were isolated in good yield. Otherwise, variable amounts of 1,2-dichlorotetrabutyldistannane and 1,3-dichlorotetrabutyldistannoxane are formed. In these conditions, vinyl laurate and ethyl vinyl ether led also to products, whereas with vinyl benzoate, at 20°C, it decomposed as soon as it formed. The corresponding (acyloxy)stannanes were obtained after coupling with silver acetate or sodium laurate.

$$Bu_2SnHCl + H_2C{=}CHOCOCH_3 \rightarrow$$

$$Bu_2(Cl)SnCH_2CH_2OCOCH_3$$

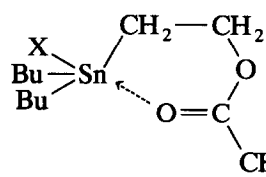
2

$$Bu_2(Cl)SnCH_2CH_2OCOCH_3 + CH_3CO_2Ag \rightarrow$$

$$Bu_2(CH_3CO_2)SnCH_2CH_2OCOCH_3 + AgCl$$

5

These β-substituted organostannanes likely to show an intramolecular chelation of tin by the oxygen of the carbonyl through a six-membered ring [13], were analyzed by ^{119}Sn NMR spectroscopy.



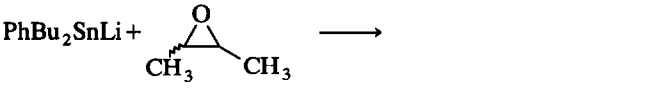
As the tin in [2-(acetoxy)ethyl]tributylstannane resonates at -16.0 ppm (-12.6 ppm for Bu_4Sn) and the shifts of [2-(acetoxy)ethyl]dibutylstannane and [2-(lauroyloxy)ethyl]dibutylstannane are -100.2 ppm and -99.5 ppm respectively (-95.0 ppm for Bu_3SnH) the substituted chain has a low influence on the chemical shift of the tin. The values of 74.6 ppm for chloro[2-(acetoxy)ethyl]dibutylstannane and 34 ppm for acetoxy[2-(acetoxy)ethyl]dibutylstannane were recorded when 140 ppm and 96 ppm were measured for chlorotributylstannane and acetoxytributylstannane respectively. Thus there is an upfield shift of about 65 ppm. An upfield shift of 100 ppm was measured in the case of an established coordination [14]. Therefore, a coordination number higher than four exists in chloro[2-(acetoxy)ethyl]dibutylstannane and (acetoxy)-[2-(acetoxy)ethyl]dibutylstannane. This coordination is intramolecular, like in substituted halogenotriorganostannanes, where a five-membered ring can be formed intramolecularly [15].

Hydrostannation of sterically crowded vinyl esters is often inhibited. For example, even the quite reactive chlorodibutylstannane does not add to propen-2-yl pivalate [16]. Another route has been developed. This involves the addition of a mixed triorganostannyllithium, with an easily removable organic group on the tin, to an epoxide [17]. Thus, butene oxide reacts with phenyldibutylstannyllithium to give (2-hydroxybut-3-

TABLE 1. Decomposition conditions

Compound	Formula	Decomposition temperature (°C)	Time (h) for 100% decomposition
2	$Bu_2Sn(Cl)CH_2CH_2OCOCH_3$	90	1.25
3	$Bu_2Sn(Cl)CH_2CH_2OCO(n\text{-}C_{11}H_{23})$	90	2
4	$Bu_2Sn(Cl)CH_2CH_2OC_2H_5$	150	1.3
5	$Bu_2Sn(CH_3CO_2)CH_2CH_2OCOCH_3$	75	1
6	$Bu_2Sn(n\text{-}C_{11}H_{23}CO_2)CH_2CH_2OCO(n\text{-}C_{11}H_{23})$	75	2
7	$Bu_2Sn(acac)CH_2CH_2OCOCH_3$	120	1
8	$Bu_2Sn(acac)CH_2CH_2OCO(n\text{-}C_{11}H_{23})$	120	3

yl)phenyldibutylstannane, stable enough to be purified by rapid distillation. Care must be taken to not overheat these alcohols, which are susceptible to decomposition [18]. The phenyl group was cleaved at low temperature by iodine. Upon cleavage with bromine or hydrogen chloride, mixtures were obtained. Esterification of this alcohol was achieved with pivaloyl chloride in the presence of pyridine.



$$PhBu_2SnCH(CH_3)CHOHCH_3$$

erythro-**9**, *threo*-**10**

$$PhBu_2SnCH(CH_3)CHOHCH_3 + I_2 \longrightarrow Bu_2Sn(I)CH(CH_3)CHOHCH_3 + PhI$$

erythro-**11**, *threo*-**12**

$$Bu_2Sn(I)CH(CH_3)CHOHCH_3 + {}^tBuCOCl \xrightarrow{\text{pyridine}} Bu_2Sn(I)CH(CH_3)CH(OCO{}^tBu)CH_3 + HCl, \text{pyridine}$$

erythro-**13**, *threo*-**14**

All these compounds were then subjected to thermal decomposition. The results are presented Table 1.

Although stable enough at room temperature to be analyzed and handled easily, these compounds are thermally sensitive and decompose in milder conditions than bis[2-(acyloxy)alkyl]dibutylstannane. For instance, compound **2** was completely decomposed after 1.25 h at 90°C, whereas 3 h at 110°C were necessary to decompose bis[2-(acetyloxy)ethyl]dibutylstannane [10]. The rate constant for the decomposition of **2**, determined by DSC, was found to be larger (150×10^{-4} s^{-1}) than the rate constant measured for bis[2-(acetyloxy)ethyl]dibutylstannane (2.5×10^{-4} s^{-1}). This explains why no unsymmetrical compound had been isolated or detected in the thermolysis of bis[2-(acyloxy)alkyl]dibutylstannane. Chloroether **4** was found to be more stable than the corresponding chloroester **2**, which can be explained because an acyloxy group is a better leaving group. A lauroyloxy group in **3** induced a higher stability than an acetyloxy group in **2**. An identical result was recorded with bis[2-(acetyloxy)ethyl]- and bis[2-lauroyloxy)ethyl]dibutylstannanes [10]. The nature of the electronegative groups or atoms on tin also affects the stability. Acetate **5** was decomposed more easily than chloride **2**, which was less stable than the acetylacetonate **7**. This β-elimination is promoted by the ability of tin to stabilize a β-positive charge [19] and this ability is dependent on delocalization of this charge around the metal. As a heteroatom bearing an unshared electron pair adjacent to a cationic centre increases the stability of such ions [20], the higher stability of bis[2-(acyloxy)alkyl]dibutylstannanes with respect to **1** can be explained by the better stabilizing ability of an oxygen atom compared to an alkyl group. The relative stabilities of **2**, **5** and **7** thus reflect the relative stabilizing effects of chlorine, acetyloxy and 2,4-pentanedionate substituents on an adjacent partial positive charge on tin.

Compound **8** was tested for SiH–SiOR condensation and polyurethane preparation [21]. Two conditions had to be checked to show that this compound can be used; the compositions containing the catalyst precur-

TABLE 2. Pot-lives and gel times induced by latent catalysts

Organotin compound	SiH–SiOR condensation		Polyurethane preparation	
	Pot-life at 30°C (min)	Gel time at 150°C	Pot-life at 27°C	Gel time at 140°C
none	∞	∞	480	21
$Bu_2Sn(acac)_2$	50	10	40	5
$Bu_2Sn(acac)CH_2CH_2OCO(n\text{-}C_{11}H_{23})$	150	10	120	4.5

sor must be more stable at room temperature than compositions with $Bu_2Sn(acac)_2$, and upon heating, compositions containing the catalyst presursor must cure or polymerize rapidly.

Mixtures composed of a α,ω-dihydroxylated polydimethylsiloxane, a small amount of a hydrogenated polydimethylsiloxane, and the diorganotin catalysts or the catalyst precursor were set up at room temperature and the pot-lives measured (Table 2). With the catalyst precursor they are three times longer than with $Bu_2Sn(acac)_2$, which demonstrates the higher stability of the mixtures made with these new stannanes. When heated, at 140°C, gel times of both compositions were identical, indicating the efficiency of the induced catalyst.

The tests for polyurethane preparation were conducted on mixtures containing 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane (isophorone diisocyanate), 1,4-butanediol, poly(ethylene glycol) and an organotin catalyst. As with the silicone experiments, gel times were measured at room temperature to determine pot-lives, and at a higher temperature to ascertain the activity of the new stannanes. They are given in Table 2. At room temperature, gel times with the catalyst precursor was found to be acceptable. After heating at 150°C, gel times of either mixture were identical. These data indicate again the efficiency of the induced catalysts.

3. Experimental details

All reactions were carried out under dinitrogen. THF and benzene were distilled from sodium benzophenone ketyl, and cyclohexane from calcium hydride. Vinyl acetate, vinyl laurate, ethyl vinyl ether, acetyl chloride were distilled before use. Diisopropylamine was distilled from KOH. Dibutylstannane [22], dibutylphenylstannane [23] and chlorobutylstannane [12] were prepared following standard procedures. ^1H NMR spectra were recorded on a Perkin–Elmer–Hitachi R 24 A or a Bruker AC 250 spectrometer (solvent $CDCl_3$, internal reference Me_4Si), ^{119}Sn NMR spectra were taken on a Bruker AC 200 spectrometer (solvent C_6D_6, internal reference Me_4Sn). Irradiations were performed in Pyrex vessels with a Philips HPK 125 UV lamp.

3.1. Chloro[2-(acyloxy)ethyl]dibutylstannanes 2, 3

A degassed solution of vinyl derivative (11.6 mmol) and 12.6 g of Bu_2SnH_2 (53.6 mmol) in 18 ml of anhydrous cyclohexane under dinitrogen at 20°C was irradiated for 24 h. Then the solvent and excess Bu_2SnH_2 were evaporated under vacuum (10^{-4} mmHg) at 20°C. Hydrides were recovered with a 5–10% amount of diadduct [2-(acetyloxy)ethyl]dibutylstannane. ^1H NMR: δ 5.0 (m, 1H), 4.3 (m, 2H, $^3J(Sn-H) = 38$ Hz), 1.8 (s, 3H), 1.5–0.9 (m, 20H); ^{119}Sn NMR: δ −100.0 [2-(lauroyloxy)ethyl]dibutylstannane; ^1H NMR: δ 5.0 (m, 1H), 4.4 (m, 2H, $^3J(Sn-H) = 39$ Hz), 2.3 (t, 2H), 1.6–0.9 (m, 41H); ^{119}Sn: δ −99.5. To a solution of stannane (10 mmol) in 20 ml of degassed benzene was added 1 ml of CCl_4. After 1 h at 50°C, the solvent was evaporated and the chlorostannane isolated as an oil. **2**: ^1H NMR: δ 4.2 (t, 2H, $^3J(Sn-H) = 85$ Hz), 1.7 (s, 3H), 1.6–0.9 (m, 20H); ^{119}Sn NMR: δ 74.6. **3**: ^1H NMR: δ 4.15 (t, 2H, $^3J(Sn-H) = 85$ Hz), 2.2–0.9 (m, 43H); ^{119}Sn NMR: δ 78.2.

3.2. Chloro[2-(acyloxy)ethyl]dibutylstannane 2, 3 and chloro[2-(ethyloxy)ethyl]dibutylstannane 4

A solution of 2.7 g of chlorodibutylstannane (10 mmol) and 10 mmol of unsaturated compound in 20 ml of degassed cyclohexane under dinitrogen was irradiated at 20°C for 3 h. The solvent was then eliminated under vacuum. **4**: ^1H NMR: δ 3.5–2.9 (m, 4H, $^3J(Sn-H) = 66$ Hz), 1.8–0.8 (m, 23H,); ^{119}Sn NMR: δ 103.6.

3.3. (Acyloxy)- and (2,4-pentadionato-O,O')[2-(acyloxy)ethyl]dibutylstannanes 5, 6, 7, 8

To a solution of chloro[2-(acyloxy)ethyl]dibutylstannane (10 mmol) in dry benzene (50 ml) was added silver acetate or potassium laurate or potassium-2,4-pentadionato (50 mmol). After stirring at room temperature (2 h), the suspension was filtered and the solvent evaporated under vacuum. **5**: ^1H NMR: δ 4.4 (m, 2H, $^3J(Sn-H) = 77$ Hz), 2.0 (s, 3H), 1.95 (s, 3H), 1.6–0.9 (m, 20H); ^{119}Sn NMR: δ 34.0. **6**: ^1H NMR: δ 4.4 (m, 2H); 2.0–0.9 (m, 66H); ^{119}Sn NMR; δ 35.9. **7**: ^1H NMR: δ 5.3 (s, 1H), 4.4 (m, 2H, $^3J(Sn-H) = 68$ Hz); 2.0 (s, 3H), 1.8 (s, 6H), 1.7–0.9 (m, 20H); ^{119}Sn NMR: δ 38.8. **8**: ^1H NMR: δ 5.35 (s, 1H) 4.4 (m, 2H), 2.2 (t, 2H), 1.85 (s, 6H), 1.5–0.9 (m, 41H); ^{119}Sn NMR: δ 39.6.

3.4. erythro- and threo-Iodo[3-(pivaloyloxy)but-2-yl]dibutylstannane 13,14

To a solution of phenyldibutylstannyllithium, prepared from 2.2 g (22 mmol) of diisopropylamine, 11 ml of butyllithium (2 M in hexanes) and 6.2 g (20 mmol) of phenyldibutylstannane in 20 ml of THF, was added at 0°C 2.2 g (30 mmol) of *trans* (or *cis*) 2,3-epoxybutane. After stirring at room temperature for 10 h, the mixture was hydrolyzed, extracted with diethyl ether and dried over magnesium sulphate. After evaporation of the solvents, the product was distilled in a Kugelrohr apparatus. **9**: $Eb_{0,001}$ (oven temperature): 150°C. Yield: 71%. ^1H NMR: δ 6.9–7.4 (m, 5H), 3.85 (quintet, 1H, $J = 6$ Hz) 0.5–1.9 (m, 26H); ^{119}Sn NMR: δ 46.4. **10**: $Eb_{0,001}$ (oven temperature): 150°C. Yield 45%. ^1H

NMR: δ 6.9–7.4 (m, 5H), 3.75 (quintet, 1H, $J = 6$ Hz), 0.5–1.9 (m, 26H); ^{119}Sn NMR; δ 47.5. To a solution of 1.9 g (5 mmol) of stannylated alcohol in 10 ml of CCl_4 was added 1.3 g (5 mmol) of iodine. The mixture was then stirred for 1 h and the solvent and iodobenzene evaporated below 50°C at 10^{-4} mmHg. **11**: yield 95%. ^{1}H NMR: δ 3.80 (broad quintet, 1H, $J = 6$ Hz), 0.8–2.2 (m, 26H); ^{13}C NMR: 13.60 (C_δ), 16.80 (C_4), 26.20 (C_1), 26.75 (C_χ), 29.25 (C_β), 41.25 (C_3), 74.20 (C_2); ^{119}Sn NMR: δ 82.8. **12**: yield 97%. ^{1}H NMR: δ 3.85 (broad quintet, 1H, $J = 6$ Hz), 0.8–2.2 (m, 26H); ^{13}C NMR: 13.57 (C_δ), 16.34 (C_4), 25.0 (C_1), 26.62 (C_χ), 29.10 (C_β), 39.25 (C_3), 73.88 (C_2); ^{119}Sn NMR: δ 78.7. To a solution of alcohol (10 mmol) and 1.6 g of pyridine, (10 mmol) in 10 ml of diethylether at 0°C, was added a solution of 1.2 g of pivaloyl chloride (10 mmol) in 10 ml of diethyl ether. After 1 h at 0°C, the mixture was filtered and the solution was washed with 2×20 ml of a cooled saturated $CuSO_4$ solution (1 N) and 2×20 ml of cooled $NaHCO_3$ (1 N). Esters were isolated after drying and evaporation of the solvent below room temperature. They were used as soon as prepared. **13**: yield 85%, ^{1}H NMR: δ 3.80 (quintet, 1H, $J = 6.2$ Hz), 0.7–2.0 (m, 25H), 1.20 (s, 9H); ^{13}C NMR: 8.79 (C_α), 13.59 (C_δ), 25.01 (C_1), 26.19 ($C_{\text{Me ester}}$), 27.01 (C_χ), 28.04 (C_β), 28.60 (C_1), 40.02 ($C_{2\text{ ester}}$), 42.10 (C_3), 75.20 (C_2), 173.99 ($C_{1\text{ ester}}$). **14**: yield 89%, ^{1}H NMR: δ 3.80 (quintet, 1H, $J = 6.2$ Hz), 0.7–2.0 (m, 25H), 1.22 (s, 9H); ^{13}C NMR: 8.69 (C_α), 13.54 (C_δ), 23.91 (C_1), 26.24 ($C_{\text{Me ester}}$), 26.76 (C_χ), 27.18 (C_1), 27.99 (C_β), 39.99 ($C_{2\text{ ester}}$), 40.58 (C_3), 73.14 (C_2), 173.87 ($C_{1\text{ ester}}$).

3.5. SiOH–SiH condensations

In a beaker were placed 23 g of α,ω-dihydroxylated silicone oil (average molecular weight: 42 500, 4.7 meq OH–100 g of oil) 1 g of polyhydrogenomethylsiloxane (SiH contain: 1.5%) and the organotin catalyst (0.712 mmol). The mixture was stirred with a spatula for 1 min. Approximately half of this mixture was then left at room temperature and its viscosity measured periodically until it reached 1500 poises (150 Pa s). The other part was placed in an oven at 150°C until the mixture gelled.

3.6. Polyurethane preparation

In a Schlenk tube under dinitrogen were added 5.26 g of poly(ethyleneglycol) (average molecular weight: 1000), 0.80 g of 1,4-butanediol (9 mmol), and 1 ml of a 0.0075 N solution of the tin catalyst in dry ether. The solvent was evaporated and 3.94 g of 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane (isophorone diisocyanate) (18 mmol) was added. Approximately half of the mixture was then left at room temperature until it gelled to obtain the pot-life, and the other half was placed in an oven at 150°C until the mixture gelled.

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