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Preliminary communication

Synthesis of acylsilanes via transmetalation of 1-triorganosilyloxyvinyltin derivatives *

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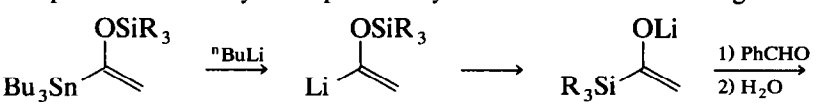
Abstract

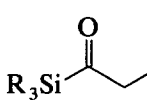
Transmetalation of 1-triorganosilyloxyvinyltin derivatives occurs with a reverse Brook rearrangement. Subsequent trapping with various electrophiles affords new acylsilanes.

We have previously reported that 1-triorganosilyloxyvinyltin derivatives are of considerable value as acyl anion precursors [1]. They react smoothly with organic halides via palladium catalysed cross-coupling, yielding silyl enolates which can be used in numerous useful synthetic transformations or readily hydrolyzed to the corresponding ketones. We now report the preparation of organolithium compounds of this masked acyltin and their trapping with various electrophiles.

We have found that 1-triorganosilyloxyvinyltins undergo a rapid transmetalation with ^{n}BuLi at −78°C to give the corresponding organolithium compounds and that 1–2 anionic rearrangement of silicon takes place [2–4]. For instance, when trapping occurred with benzaldehyde, a complex reaction mixture was obtained from which the major isolated product was an acylsilane [5]. The formation of this compound could only be explained by a reverse Brook rearrangement (eq. 1).



(1) (A) (B)



(1)

The substitution of the ethylenic positions of the organotin precursor was expected to prevent reaction at this position (**B**), but even in the case of transmeta-

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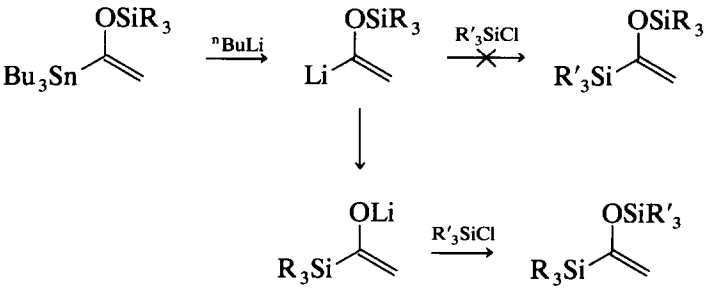
* Dedicated to Professor Alwyn G. Davies, in recognition of his important contributions to organometallic chemistry.

lation of **3** (Table 1), a reverse Brook rearrangement was observed, although some isolated products indicated that direct trapping of the vinyllithium species (**A**) occurred.

In order to elucidate this reverse Brook rearrangement [6–8], triorganochlorosilanes were used as electrophiles, because lithium enolates (**B**) are readily derivatized producing silyl enol ethers [9] unambiguously, and vinyllithium reagents (**A**) are also silylated. The groups bound to the silicon atom were chosen to be different from those on the silicon in the organotin precursor (Table 1). It was thus possible to distinguish by ^{29}Si NMR analysis which silicon atom was linked to the oxygen or to the sp^2 carbon atom (eq. 2).

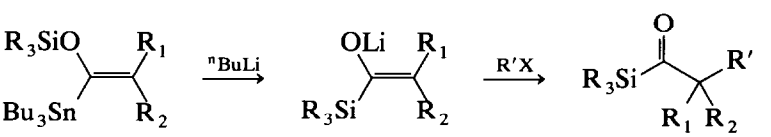


(2)

First, the chemical shift of the silicon linked to the oxygen shifted downfield with respect to the other silicon atom. By various INEPT experiments using selective decoupling of some of the organic groups bound to silicon, it is possible to measure the coupling constants of this silicon with various hydrogen atoms in the molecule. For example, the identification of the $SiMePh_2$ group was made by the observation of five peaks due to coupling of Si with the four *ortho* aromatic protons ($^3J = 4.6$ Hz) when the methyl group was selectively decoupled. In the case of entries 1 or 2 (Table 1) the coupling constants of the vinylic silicon with the two unequivalent ethylenic protons was measured ($^3J = 3.5$ or 3.7 Hz and $^3J = 10.5$ or 10.7 Hz respectively for the *cis* and *trans* hydrogen). With two methyl groups at the ethylenic position (entry 4), the two silicon atoms were identified by their chemical shifts by comparison with entry 2. Secondly, the identification of the $SiEt_3$ and $SiMe_3$ group was made by measuring the coupling constants $^2J = 6.3$ Hz and $^3J = 7.2$ Hz (Et) and $^2J = 6.7$ Hz (Me). The INEPT spectra were simulated with the aid of a simulation program [10]. ^5J and ^4J coupling constants were observed respectively between the ethylenic methyl groups and the $SiEt_3$ and $SiMe_3$ substituents.

In conclusion, a reverse Brook rearrangement is observed in all cases, even when the silicon atom is substituted with bulky groups. It appears that the stabilization energy gained when the negative charge is on oxygen rather than on carbon outweighs the energy lost by putting the silicon on carbon rather than on oxygen.

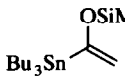
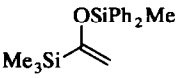
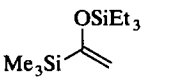
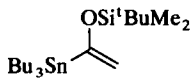
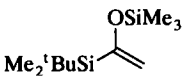
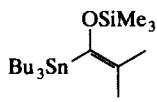
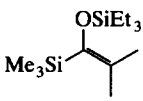
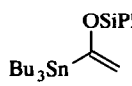
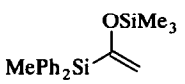
In a second type of experiment the enolates arising from the rearrangement were trapped by various organic halides providing acylsilanes (eq. 3).



(3)

Table 1

Reverse Brook rearrangement of silicon

Entry	Vinyltin derivatives	Electrophiles	Products	^{29}Si NMR, δ (ppm), J (Hz)	Yield (%)
1	 (1)	$Ph_2MeSiCl$	 (6)	−5.87 ($OSiPh_2Me$) $^3J = 4.6$, $^2J = 5.0$ −6.93 ($SiMe_3$) $^2J = 7.1$, $^3J = 3.5$, $^3J = 10.5$	64
2	1	Et_3SiCl	 (7)	−7.45 ($SiMe_3$) $^2J = 6.8$, $^3J = 3.7$, $^3J = 10.7$ 17.73 ($OSiEt_3$)	70
3	 (2)	Me_3SiCl	 (8)	15.27 ($OSiMe_3$) $^2J = 6.6$ −0.63 (Si^tBuMe_2)	73
4	 (3)	Et_3SiCl	 (9)	16.14 ($OSiEt_3$) $^2J = 6.3$, $^3J = 7.2$, $^5J = 0.5$ −8.34 ($SiMe_3$) $^2J = 6.7$, $^4J = 1.1$	66
5	 (4)	Me_3SiCl	 (10)	17.07 ($OSiMe_3$) $^2J = 6.6$ −16.49 ($SiPh_2Me$)	63

In general, as shown in Table 2, the reaction gave acylsilanes in reasonable yields, although some double condensation resulting from further enolization and alkylation of the acylsilane happened. With methyl iodide, the reaction was rather slow as revealed by the high proportion of unalkylated acylsilane. When trapping occurred with benzoyl chloride, the only contamination was due to *O*-acylation producing enol benzoate. We have not tried to optimize the yields, our present goal being to obtain evidence for a reverse Brook rearrangement.

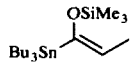
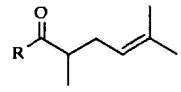
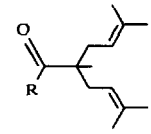
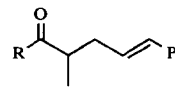
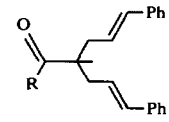
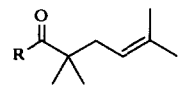
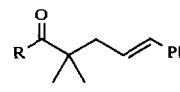
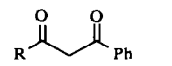
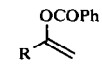
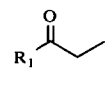
In conclusion, 1-triorganosilyloxyvinyltin derivatives undergo rapid Sn–Li exchange followed by 1–2 anionic rearrangement to enolates at −78°C. The enolates can be trapped by alkyl halides to give acylsilanes.

Experimental section

Organotin compounds **1–3** and **5** were synthesized according to published procedure [1]. Compound **4** was obtained similarly. The general procedure for the transmetalation is the following. ^{n}BuLi (2.5 *M* in hexane, 2 ml, 5 mmol) was added to a solution of 1-trialkylsilyloxyvinyltin (5 mmol) in THF at −78°C under dinitro-

Table 2

Synthesis of acylsilane by [1,2] anionic rearangement [a]

Entry	Vinyltin derivatives	Electrophiles	Products (distribution)		Isolated yield (%)
1	 (5)	$(CH_3)_2C{=}CHCH_2Br$	 (11) (86)	 (14)	56
2	5	$PhCH{=}CHCH_2Br$	 (12) (87)	 (13)	50
3	3	$(CH_3)_2C{=}CHCH_2Br$	 (13)	–	54
4	3	$PhCH{=}CHCH_2Br$	 (14)	–	60
5	1	PhCOCl	 (15) (72)	 (28)	61
6	2	CH_3I	 (16) (46)	R_1COCH_3 (18) $R_1COCH(CH_3)_2$ (36)	51

[a] $R = SiMe_3$, $R_1 = Si^tBuMe_2$.

gen. After 10 min, 5 mmol of electrophilic reagent was added dropwise to the solution at −78°C. The solution was allowed to reach room temperature, diluted with pentane and washed (water), dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (SiO_2, 1% ether/pentane) or bulb-to-bulb distillation.

Physical data

4: ^1H NMR (60 MHz, $CDCl_3$): $\delta = 0.7$ (s, 3H), 0.5–1.6 (m, 27H), 4.2 (s, 1H), 4.8 (s, 1H), 7.1–7.6 (m, 10H), B.p.: 170°C/0.3 mmHg.

6: ^1H NMR (60 MHz, $CDCl_3$): $\delta = 0.01$ (s, 9H), 0.60 (s, 3H), 4.35 (s, 1H), 4.61 (s, 1H), 7.0–7.5 (m, 10H). MS: m/z (%) 312 (M^+, 2.8), 297 ($M^+ - Me$, 8.2), 219 ($M^+ - PhO$, 50.7), 209 ($Me_3SiOSiMePh^+$, 44.2), 197 ($SiPh_2Me^+$, 100).

7: ^{1}H NMR (60 MHz, $CDCl_3$): $\delta = 0.01$ (s, 9H), 0.6 (q, $J = 8$ Hz, 6H), 0.9 (t, $J = 8$ Hz, 9H), 4.4 (s, 1H), 4.7 (s, 1H). B.p.: 50°C/0.5 mmHg. MS: m/z (%) 230 (M^+, 0.5), 201 ($M^+ - Et$, 12.1), 175 ($Me_3SiOSiEt_2^+$, 43.3), 161 ($Me_2SiOSiEt_2H^+$, 23.5), 147 ($Me_3SiOSiEtH^+$, 100), 115 ($SiEt_3^+$, 47.8), 87 ($HSiEt_2^+$, 52.7), 73 ($SiMe_3^+$, 36.2).

8: ^{1}H NMR (60 MHz, $CDCl_3$): $\delta = 0.1$ (s, 6H), 0.3 (s, 9H), 1.0 (s, 9H), 4.5 (s, 1H), 4.8 (s, 1H). MS: m/z (%) 215 ($M^+ - Me$, 0.3), 147 ($Me_3SiOSiMe_2^+$, 100), 133 ($Me_3SiOSiMeH^+$, 17.7), 73 (Me_3Si^+, 29.5).

9: ^{1}H NMR (60 MHz, CCl_4): $\delta = 0.1$ (s, 9H), 0.7 (q, $J = 8$ Hz, 6H), 0.9 (t, $J = 8$ Hz, 9H), 1.7 (s, 6H). MS: m/z (%) 258 (M^+, 24.4), 175 ($Me_3SiOSiEt_2^+$, 48.2), 147 ($Me_3SiOSiMe_2^+$, 100), 87 ($HSiEt_2^+$, 22.0), 73 (Me_3Si^+, 25.5).

10: ^{1}H NMR (60 MHz, CCl_4): $\delta = 0.01$ (s, 9H), 0.5 (s, 3H), 4.35 (s, 1H), 4.75 (s, 1H), 7.0–7.5 (m, 10H). MS: m/z (%) 312 (M^+, 8.4), 234 ($M^+ -$ PhH, 21.4), 219 ($M^+ -$ PhO, 59.1), 209 ($Me_3SiOSiMePh^+$, 100), 197 ($SiPh_2Me^+$, 83.7), 73 (Me_3Si^+, 39.1).

11: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.01$ (s, 9H), 0.74 (d, 3H, $J = 7$ Hz), 1.39 (s, 3H), 1.47 (s, 3H), 1.6–1.7 (m, 1H) (CH_2C=), 2.03–2.14 (m, 1H) (CH_2C=), 2.6–2.79 (m, 1H) (CHCO), 4.7–4.9 (t, 1H). ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = -2.7$ (Me_3Si), 14.1 (*Me*CH), 17.7 (*Me*C = *trans*/H), 25.7 (*Me*C = *cis*/H), 29.6 (CH_2), 50.4 (CH), 121.8 (CH_2C=), 133.0 (=*C*Me_2), 202 (CO). MS: m/z (%) 198 (M^+, 0.8), 183 ($M^+ -$ Me, 8.9), 73 (Me_3Si^+, 100).

12: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.08$ (s, 9H), 0.89 (d, $J = 6.9$ Hz, 3H), 2.0 (m, 1H) (CH_2C=), 2.4 (m 1H) (CH_2C=), 2.95 (m, $J = 6.9$ Hz, 1H) (CHCO), 5.9 (m, 1H) (=C*H*CH_2), 6.2 (m 1H) (=C*H*Ph), 7.0–7.25 (m, 5H). MS: m/z (%) 247 ($M + 1$, 1.3), 246 (M^+, 4.7), 161 (6.6), 73 (Me_3Si^+, 100).

13: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.01$ (s, 9H), 0.8 (s, 6H), 1.36 (s, 3H), 1.45 (s, 3H), 1.9 (d, $J = 7.4$ Hz, 2H), 4.7 (t, $J = 7.4$ Hz, 1H). ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = -1.083$ (Me_3Si), 17.66 (*Me*C = *trans*/H), 21.93 (Me_2C), 25.67 (*Me*C = *cis*/H), 35.78 (CH_2), 52.59 (*C*CO), 119.56 (CH_2C=), 133.49 (=*C*Me_2), 203.52 (CO). MS: m/z (%) 212 (M^+, 1.0), 197 ($M^+ -$ Me, 8.0), 73 (Me_3Si^+, 100). IR: (NaCl) 1630, 1250 cm^{-1}.

14: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.11$ (s, 9H), 0.96 (s, 6H), 2.2 (d, $J = 7.9$ Hz, 2H), 5.9 (m, 1H), 6.2 (m, 1H), 6.99–7.18 (m, 5H). ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = -0.68$ (Me_3Si), 22.52 (Me_2C), 41.27 (CH_2), 52.68 (*C*CO), 126.14 (*p*-CH), 126.19 (*o*-CH), 127.19 (CH_2CH=), 128.57 (*m*-CH), 132.86 (=*C*HPh), 137.47 (C quat), 203.5 (CO). MS: m/z (%) 260 (M^+, 2.5), 161 (10.8), 117 ($PhCH{=}CHCH_2^+$, 5.7), 73 (Me_3Si^+, 100).

15: ^{1}H NMR (60 MHz, CCl_4): $\delta = 0.1$ (s, 9H), 6.0 (s, 2H), 7.1–7.8 (m, 5H).

16: ^{1}H NMR (60 MHz, CCl_4): $\delta = 0.05$ (s, 6H), 0.81 (s, 9H), 2.35 (q, 2H), 1.0 (t, 3H).

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