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Transmetallation of β-allenyl silanes: efficient synthesis of dienyl chlorostannanes and chlorostibines†

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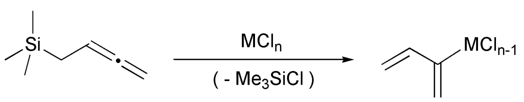
The reaction of 1-trimethylsilylbuta-2,3-diene with tin tetrachloride, antimony trichloride or antimony pentachloride gave the corresponding buta-1,3-dien-2-yl halostannane or stibine derivatives; this ligand exchange was extended to other β-allenylsilanes.

Since Calas established in 1974 that allyltrimethylsilane could efficiently add to aldehydes or ketones under Lewis acid activation,[1] this method has became a very popular procedure to prepare homoallylic alcohols. In this context and to explain the observed selectivities, the aldehydes coordinated to Lewis acids generally react with allylsilanes through an antiperiplanar open transition state and *via* a S_E2' mecanism pathway.[2] However, numerous authors have suggested that the allylsilane could be transmetallated by the Lewis acid involved generating *in situ* a new allylic species which could react with the aldehyde through a Zimmerman-Traxler transition state. In 1988, Denmark and Wilson demonstrated that the formation of allyltrichlorostannane from allyltrimethylsilane with tin tetrachloride was efficient at low temperature.[3] More recently, Dias *et al.* have confirmed these results by a NMR study, of the transmetallation reaction between $SnCl_4$ and a chiral allylsilane.[4] In addition, we have previously described the preparation of β-allenyltrimethylsilanes **1** from allylsilanes in two steps.[5] To broaden the synthetic potentialities of β-allenylsilanes, we planned to prepare various β-allenyl or buta-1,3-dien-2-yl organometallic reagents by ligand exchange. In this paper, we report the scope and limitations of the reaction of Lewis acids bearing halide ligands with β-allenylsilanes **1** which could have had a similar reactivity to that of unsaturated stannanes (vinylic, allylic propargylic or allenyl derivatives) as recently described.[6]

Our investigation began with the ligand exchange between tin chloride species and β-allenylsilane **1a**. The reaction was run at 0.1 M in $CDCl_3$ solution with 1.1 equiv of $SnCl_4$ under an argon atmosphere; in all cases, direct ^{13}C (75.5 MHz), ^1H (300 MHz), and ^{119}Sn (111.92 MHz) NMR observations were made. Upon addition of $SnCl_4$ to β-allenylsilane **1a** at −40 °C, it was immediately observed that the colourless solution became slightly orange and heterogeneous.‡ The ^1H NMR spectrum of the slightly yellow solution at room temperature showed complete consumption of the silane **1a** within 1 min and quantitative formation of Me_3SiCl. Significantly, the resonances for the allenic protons (Fig. 1, ESI†) disappeared and five different signals appeared between 5.40 and 6.70 ppm which exhibit numerous tin-hydrogen constants (Fig. 2, ESI†). On the basis of ^1H, ^{13}C and ^{119}Sn NMR spectra (Table 1), this new compound was identified as buta-1,3-dien-2-yltin trichloride **2a** which could be obtained from **1a** *via* a S_E' pathway. Moreover, treatment of **2a** with butyllithium (3.5 eq.) gave buta-1,3-dien-2-yl-tributylstannane in 86% yield.[7] Conducting the experiment at room temperature led to an identical result (95% yield). In both cases, no amount of β-allenyltrichlorostannane was observed; that remained true even when the experiment was conducted at low temperature (−60 °C).

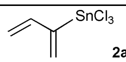
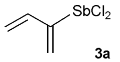
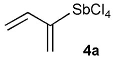
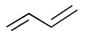
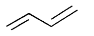
In order to examine the scope of the transmetallation reaction, we also examined other halide salts (Scheme 1). Results are summarised in Table 2. First, in order to prepare di- or



1a **2-4**

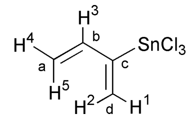
Scheme 1

Table 2 Reactivity of **1a** with diverse metal halides

Entry	MCln	Solvent, *T*/°C, time		Yield (%)
1	$SnCl_4$	$CHCl_3$, −40 °C, 1 min	 **2a**	96
2	$SnCl_4$ (0.5 eq.)	″	″	45
3	$SbCl_3$	$CHCl_3$, −45 °C, 1 min	 **3a**	87[a]
4	$SbCl_5$	$CDCl_3$, −45 °C, 1 min	 **4a**	70
5[b]	$TiCl_4$	$CHCl_3$, −45 °C, 1 min		9
6[b]	$BF_3·Et_2O$	$CHCl_3$, 0 °C, 1 min		12
7	$SiCl_44$	$CHCl_3$, 60 °C, 12h	—	—
8	$GeCl_4$	″	—	—
9	$AsCl_3$	″	—	—

[a] Obtained as a mixture with 13% of butadiene. [b] Quantitative conversions in butadiene were obtained by using a large excess of Lewis acid.

Table 1 NMR data of **2a**

	^1H NMR (400 MHz, $CDCl_3$) δ (ppm)	**^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm)
	H^4 5.46 (dd, J = 1.1, 10.4, $^4J_{Sn-H}$ = 15.8 Hz) H^5 5.60 (dd, J = 1.1, 16.8, $^4J_{Sn-H}$ = 14 Hz) H^1 5.88 (d, J = 1.1, $^3J_{Sn-H}$ = 193–202 Hz) H^2 6.20 (d, J = 1.1, $^3J_{Sn-H}$ = 456–476 Hz) H^3 6.71 (ddt, J = 1.1, 10.4, 16.8, $^3J_{Sn-H}$ = 303–317 Hz)	C^a 122.4 ($^3J_{Sn-C}$ = 52 Hz) C^d 133.4 ($^2J_{Sn-C}$ = 49.3 Hz) C^b 136.2 ($^2J_{Sn-C}$ = 106 Hz) C^c148.2 ($^1J_{Sn-C}$ = 947–992Hz) **^{119}Sn NMR (149 MHz, $CDCl_3$)** δ (ppm): −65.3

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† Electronic supplementary information (ESI) available: NMR spectra of compounds **1a** and **2a**. See http://www.rsc.org/suppdata/cc/b1/b111580b/

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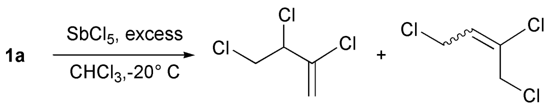
tributadienyl chlorostannanes, we examined the reactivity of **1a** with a substoichiometric amount (0.5 eq.) of tin tetrachloride (entry 2). In this case, butadienyltrichlorotin **2a** was obtained along with the starting silane **1a** (1 : 1 mixture), implying that these compounds do not react with each other. To explain this non-reactivity and the selectivity in favour of **2a** (*vs* bis(butadienyl)dichlorostannane), we think that the butadienyl ligand of **2a** largely decreases the electrophilic character of the tin atom.

The reaction at 20° C of $SbCl_3$ with silane **1a** in $CDCl_3$ gave dienyldichlorostibine **3a**§ in 87% yield as a mixture with butadiene and trimethylsilyl chloride (entry 3).[8] Equally, $SbCl_5$ reacts at low temperature (−60 °C) with **1a** and yields butadienyltetrachlorostibine **4a**¶ and quantitatively trimethylsilyl chloride (entry 4). The dienylstibine **4a** exhibited a low stability at room temperature and decomposed after a few hours.

In contrast, reaction of **1a** with excess of stibine pentachloride (3 eq.) at −20° C did not afford **4a** but a mixture of trichlorobutene derivatives was quantitatively obtained (Scheme 2). To explain the trichlorinated products, we postulate that the reaction would proceed *via* the formation of **4a** which, in the presence of $SbCl_5$, would undergo a chlorine–antimony exchange followed by 1,2 or 1,4 electrophilic chlorination of the diene moiety.[9]

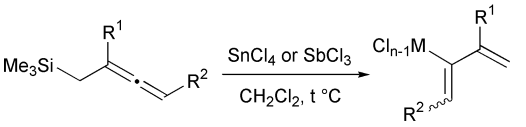


Scheme 2

No reaction was observed between compound **1a** and $SiCl_4$, $GeCl_4$ or $AsCl_3$ even at 80 °C (entries 7–9). With titanium tetrachloride (entry 5) or boron trifluoride (entry 6) which are strong Lewis acids, we were not able to establish the formation of butadienyl derivatives. For example, with 1 equivalent of $BF_3{\cdot}Et_2O$, approximately 12% conversion of **1a** into butadiene was observed while a large excess of Lewis acid (more than 10 equivalents) was necessary to observe complete conversion into butadiene and trimethylsilyl fluoride as observed by ^1H NMR. This partial protolysis of **1a** already observed during the Lewis acid promoted reaction of allylsilanes is difficult to explain, nevertheless we think that a minor amount of HCl could be present in $TiCl_4$ and acts in this partial protolysis reaction.

In order to evaluate the scope of the reaction, we then tested other β-allenylsilanes (Scheme 3). Reaction of tin tetrachloride or stibine trichloride with a range of β-allenyl trimethylsilanes proceeded with regiocontrol to give substituted butadienyl chlorostannanes or stibines respectively with fair yields (Table 3).

In conclusion, we have shown that the reaction of Lewis acidic halides such as tin tetrachloride or stibine trichloride with β-allenylsilanes leads only to the corresponding butadienyl derivatives, *via* a transposition reaction. This approach allows the synthesis of new butadienyl tin or antimony derivatives. Other Lewis acid halide derivatives such as $GeCl_4$, $SiCl_4$, BF_3 or $TiCl_4$ were found non reactive.

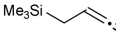
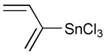
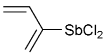
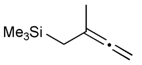
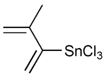
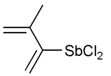
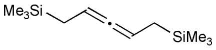
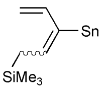
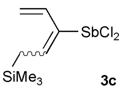


1a-c

2a-c M=Sn
3a-c M=Sb

Scheme 3

Table 3 Reactivity of **1a–c** with $SnCl_4$ and $SbCl_3$

Entry	Allenylsilanes 1	MCl_n[a]	Dienylstannanes 2	Yield (%)
1	 **1a**	$SnCl_4$	 **2a**	96
2	″	$SbCl_3$	 **3a**	87
3	 **1b**	$SnCl_4$	 **2b**	83
4	″	$SbCl_3$	 **3b**	75
5	 **1c**	$SnCl_4$	 **2c**	85[b]
6	″	$SbCl_3$	 **3c**	78[b]

[a] Transmellation reactions with tin tetrachloride and antimony trichloride were respectively conducted at 20 °C and −40 °C in CH_2Cl_2. [b] A 1 : 1 mixture of *E* and *Z* isomers was obtained.

Notes and references

‡ Filtration of the suspension led to a very small amount by weight of precipitate insoluble in either $CDCl_3$ or CD_2Cl_2 . ^1H and ^{13}C NMR analyses carried out in DMSO-d_6 did not permit the precise structure of the product to be obtained.

§ ^1H NMR (400 MHz, $CDCl_3$) δ(ppm): 5.38 (d, J = 10.5 Hz, 1H^4); 5.55 (d, J = 17.6 Hz, 1H^5); 6.20 (s, 1 H^1); 6.46 (s, H^2); 7.06 (dd, J = 10.5, 17.6 Hz, 1H^3). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 118.8 (C^a); 129.6 (C^d); 137.6 (C^b); 160.0 (C^c).

¶ ^1H NMR (300 MHz, $CDCl_3$) δ(ppm): 5.54 (d, J = 10.7 Hz, 1H^4); 5.66 (d, J = 16.9 Hz, 1H^5); 6.19 (bs, 1H^1); 6.21 (bs, 1H^2); 6.75 (dd, J = 10.7, 16.9 Hz, 1H^3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 122.3 (C^a); 127.2 (C^d); 132.7 (C^b); 158.9 (C^c).

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