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Efficient One-Pot Synthesis of Propargylstannanes from Propargylic Alcohol Derivatives *via* Allenyltitaniums

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Abstract

Successive treatment of propargylic carbonates with a Ti(O-*i*-Pr)4 / 2*i*-PrMgCl reagent and Bu3SnCl afforded propargylstannanes in excellent yields, thus opening up an easy access to a variety of propargylstannanes, including those containing functional groups such as halide, carbonate and acetal.
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Allenyl- and propargylstannanes are valuable synthetic reagents, and thus, their preparation has attracted much interest.[1] Substitution reactions of propargylic alcohol derivatives such as halides or sulfonates with stannyl anions which proceed *via* an S_N2'-pathway provide general and convenient access to a variety of allenylstannanes.[2] Allenylstannanes are sometimes synthesized by electrophilic stannylation reaction of an allenylmagnesium[3a,b] or allenylsilver(I)[3c] species.[4] Synthesis of propargylstannanes, however, has been less well developed compared to allenylstannanes. Preparation of propargylstannanes usually is carried out by the stannylation reaction of propargylmagnesium compounds.[5,6] A problem associated with this method is that accessible propargylmagnesium compounds are limited in variety. The fact that propargylstannanes may be isomerized to allenylstannanes under thermal, acidic, or nucleophilic conditions, although the position of equilibrium may be influenced by steric factors, also makes it difficult to prepare some kinds of propargylstannanes.[7] We report here a general and efficient method for synthesizing propargylstannanes which is based on the stannylation of allenyltitanium compounds with Bu3SnCl.

Recently, we have developed an efficient entry to allenyltitanium compounds by the reaction of a Ti(O-*i*-Pr)4 / 2*i*-PrMgCl (**1**) reagent and propargylic alcohol derivatives such as halides, sulfonates, acetates, or carbonates.[8] Since a γ-alkoxyallenyltitanium [prepared from

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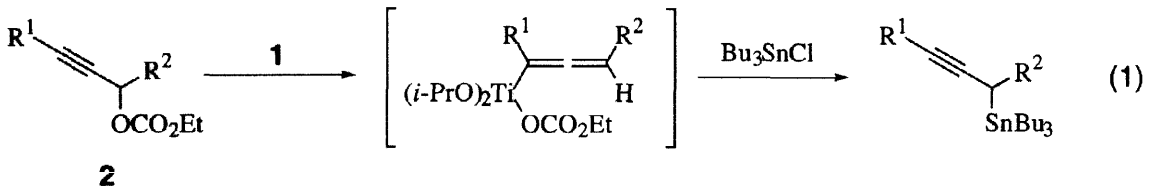
the corresponding propargylic ether by successive treatment with *t*-BuLi and Ti(O-*i*-Pr)4] had been reported to react with Bu_3SnCl to afford the γ-alkoxypropargylstannane,[6b,9] we anticipated that treatment of the reaction product of propargylic alcohol derivatives and **1** with Bu_3SnCl might open up one-pot access to propargylstannanes. Table 1 summarizes the results of a successive treatment of a variety of propargylic carbonates **2** with **1** and Bu_3SnCl (eq 1).[10]

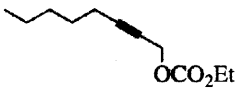
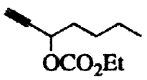
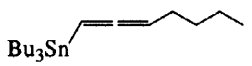
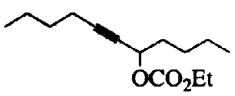
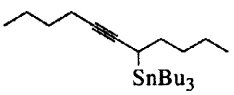
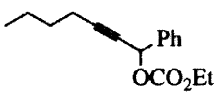
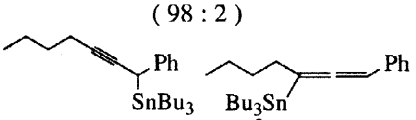
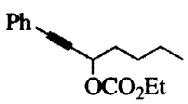
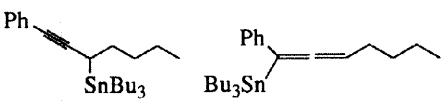
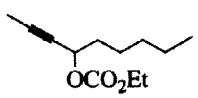
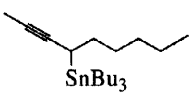
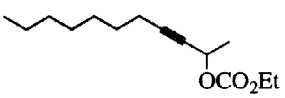
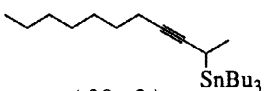
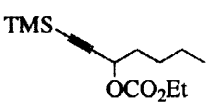
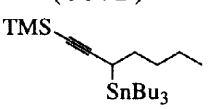
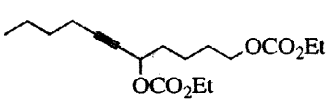
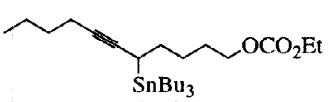
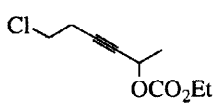
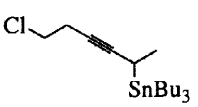
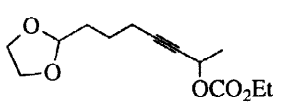
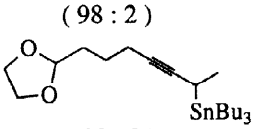


(1)

As shown in entry 1 in Table 1, primary propargylic carbonate **2** (R^1=alkyl, R^2=H) afforded the expected propargylstannane and its allenyl isomer in a ratio of 96:4 in 66% combined yield. Terminal propargylic carbonate **2** (R^1=H, R^2=alkyl), however, provided the corresponding allenylstannane exclusively (entry 2). Secondary propargylic carbonate **2** (R^1, R^2=alkyl) having an internal triple bond afforded the propargylstannane almost exclusively and in excellent yield (entry 3). However, in the case of **2** where either R^1 or R^2 is a phenyl group, the reaction gave a mixture of propargyl- and allenylstannanes (entries 4 and 5). This might be due to the isomerization of the resulting propargylstannanes to allenyl ones under the workup conditions, because the ratio of both stannanes was somewhat dependent on the workup conditions (entry 4). Thus, the present methodology offers an efficient method for synthesizing primary propargylstannanes and secondary dialkyl substituted propargylstannanes having an internal triple bond. The latter stannanes are not necessarily accessible by the existing methods available so far. We, therefore, carried out the synthesis of a variety of secondary propargylstannanes from the corresponding propargylic carbonates and the results are shown in entries 6-11 in Table 1. Especially noteworthy is the fact that, since the functional groups of propargylic alcohol derivatives can tolerate the reaction with **1**,[8] the reaction opens up an easy access to propargylstannanes containing functional groups such as carbonate (entry 9), chloride (entry 10) and acetal (entry 11).

In conclusion, a highly efficient one-pot method for synthesizing propargylstannanes from propargylic carbonates has been developed. Thus, it now becomes possible to synthesize not only allenylstannanes[2] but also propargylstannanes from propargylic alcohol derivatives.

Table 1. One-pot Synthesis of Propargylstannanes from Propargylic Carbonates and Ti(O-*i*-Pr)$_4$ / 2*i*-PrMgCl.[a]

Entry	Propargylic Carbonate	Products (Ratio of Propargyl- and Allenylstannane)[b]	Yield, %[c]
1		 (96 : 4)	66[d]
2		 (2 : 98)	71[d]
3		 (98 : 2)	80
4		 (63 : 37)[e]	57[e]
5		 (53 : 47)	85
6		 (97 : 3)	72
7		 (98 : 2)	77
8[f]		 (99 : 1)	87
9		 (98 : 2)	80
10		 (98 : 2)	82
11		 (98 : 2)	76

[a]Propargylic carbonate : Ti(O-*i*-Pr)$_4$: *i*-PrMgCl : Bu_3SnCl = 1 : 1.5 : 3 : 1.2. [b]Ratio was determined by ^1H nmr analysis. For characteristic ^1H NMR data of the propargylstannanes, see reference 11. [c]Total isolated yield of propargyl- and allenylstannane after short column chromatography. [d]Propargylic carbonate : Ti(O-*i*-Pr)$_4$: *i*-PrMgCl : Bu_3SnCl = 1 : 1 : 2 : 1.2. [e]Workup in the presence of Et_3N gave propargyl- and allenylstannane in a ratio of 78:22 (87% total yield). [f]The corresponding propargylic acetate and phosphate afforded almost the same ratio and combined yield.

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[9] Since highly regioselective lithiation of usual dialkyl substituted alkynes is almost impossible, this synthetic protocol of propargylstannanes has severe limitation.

[10] Typical procedure: to a solution of ethyl 6-undecyn-5-yl carbonate (240 mg, 1.0 mmol) and Ti(O-*i*-Pr)$_4$ (444 μL, 1.5 mmol) in ether (10 mL) was added dropwise *i*-PrMgCl (2.7 mL, 1.11 M in ether, 3.0 mmol) at -50 °C. The resulting clear yellow solution was stirred for 2 h at -50 ~ -40 °C. During this period color of the solution changed from orange to red-brown. After cooling to -78 °C, to this was added Bu_3SnCl (326 μL, 1.2 mmol) and then the mixture was gradually warmed to 0 °C over 1 h. The reaction mixture was quenched with aqueous saturated $NaHCO_3$ and extracted with *n*-hexane. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was chromatographed using a silica-gel short column with Et_3N to give an oil which consisted of 5-tributylstannyl-6-undecyn and 5-tributylstannyl-5,6-undecadiene in a 98:2 ratio (80% total yield).

[11] ^{1}H NMR (300MHz, $CDCl_3$) data: **entry 1** δ 2.13(tt, J=2.4, 6.9 Hz, 2H, C≡CC$\underline{H}_2$CH$_2$). **entry 3** δ 1.90-1.97(m, 1H, C≡CC$\underline{H}$SnBu$_3$), 2.17(dt, J=2.4, 6.9 Hz, 2H, C≡CC$\underline{H}_2$). **entry 6** δ 1.81(d, J=2.7 Hz, C≡CC$\underline{H}_3$), 1.87-1.94(m, 1H, C≡CC$\underline{H}$SnBu$_3$). **entry 7** δ 1.93(tq, J=2.7, 7.2 Hz, 1H, C≡CC$\underline{H}$SnBu$_3$), 2.16(dt, J=2.4, 6.9 Hz, 2H, C≡CC$\underline{H}_2$). **entry 8** δ 0.11(s, 9H, C≡CSi(C$\underline{H}_3$)$_3$), 2.02(dd, J=3.3, 8.9 Hz, 1H, C≡CC$\underline{H}$SnBu$_3$). **entry 9** δ 1.88-1.95(m, 1H, C≡CC$\underline{H}$SnBu$_3$), 2.15(dt, J=2.4, 6.6 Hz, 2H, C≡CC$\underline{H}_2$), 4.12(t, J=6.6 Hz, 2H, OC$\underline{H}_2$CH$_2$), 4.17(q, J=7.2 Hz, 2H, OC$\underline{H}_2$CH$_3$). **entry 10** δ 1.92(tq, J=2.4, 7.2 Hz, 1H, C≡CC$\underline{H}$SnBu$_3$), 2.63(dt, J=2.4, 7.5 Hz, 2H, C≡CC$\underline{H}_2$), 3.53(t, J=7.5, 2H, C$\underline{H}_2$Cl). **entry 11** δ 1.92(tq, J=2.4, 7.2 Hz, 1H, C≡CC$\underline{H}$SnBu$_3$), 2.22(dt, J=2.9, 7.5 Hz, 2H, C≡CC$\underline{H}_2$), 3.81-3.98(m, 4H, (C$\underline{H}_2$O)$_2$CH), 4.86 (t, J=4.6, 1H, (CH$_2$O)$_2$C$\underline{H}$).