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Synthesis of Triisopropyl α-(Trimethylsilyloxy)propargyl Stannanes

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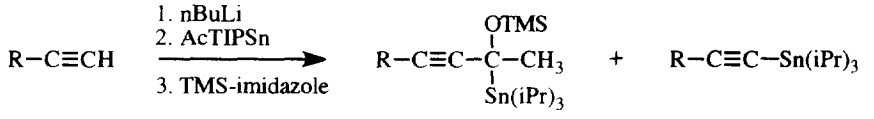
Abstract: *Acetyl(triisopropyl)stannane reacts with alkynyllithium reagents predominantly by way of carbonyl addition to give the title compounds after in situ trimethylsilylation.*

Propargylstannanes are species of considerable synthetic potential, in that they may participate in synthetic transformations as electrophilic, nucleophilic or (masked) radical components. Thus they afford haloallenes by halodestannylation,[1] α-allenyl alcohols from treatment with carbonyl compounds,[2] and S_H2' products with radical sources.[3] In addition, the utility of α-(alkoxy)allylstannanes in synthetic methodology, as demonstrated by Marshall[4] and others,[5] suggests an important synthetic role for α-(oxy)propargylstannane analogues. To our knowledge, however, there exists only one extant route to α-(alkoxy)propargylstannanes, and this was found to be limited to trialkylsilyl-terminated acetylenes.[6]

A conceptually simple approach to α-(oxy)propargylstannanes would entail the addition of alkynylmetals, particularly alkynyllithiums, to acylstannanes. However, neither organomagnesium nor organolithium reagents have been reported to yield useful amounts of carbonyl addition products with acylstannanes, instead affording species derived from organolithium attack at tin.[7,8] In an attempt to invert this behavior, our previous experience with the efficacy of triisopropyl substitution at silicon in inhibiting nucleophilic attack at the metalloid center[9] led us to investigate acetyl(triisopropyl)stannane (AcTIPSn) in this regard.[10] Although treatment of this ketone with methyllithium afforded no carbonyl adduct, we were pleased to find that addition of the alkynyllithiums derived from acetylenes **1a-e** proceeded in a straightforward fashion to afford, after *in situ* trimethylsilylation,[11] the α-(trimethylsilyloxy)propargylstannanes **2a-e** in synthetically useful yields .[12,13] The desired adducts were indeed accompanied by the products of tin attack (**3a-e**), but only in small amounts.[14] Table 1 summarizes these findings.



1 **2** **3**

1-3: a, R = TMS; **b**, R = nBu; **c**, R = tBu; **d**, R = $PhCH_2$; **e**, R = $Me_2C(OTMS)$

Table 1. Reaction of Alkynyllithiums with Acetyl(triisopropyl)stannane[a,b]

RC≡CH, R =	2, % Yield[c]	Ratio, 3:2[d]
TMS	77[e]	1: 21
nBu	65	1: 15
tBu	72	1: 18
$PhCH_2$	67	1: 10
$Me_2C(OTMS)$	71	1: 21

[a]One millimole scale. [b]All new compounds gave satisfactory analytical and spectral data. [c]Yields are of distilled material corrected for by-products as per GC area ratios. [d]Ratios from GC data. [e]Two millimole scale.

Surprisingly, in contrast to the results outlined here for alkylacetylenes, attempts to add lithiated phenylacetylene or 3-methyl-3-buten-1-yne to acetyl(triisopropyl)stannane under these conditions did not lead to significant amounts of adducts. Nevertheless, a wide range of α-(trimethylsilyloxy)propargylstannanes should be accessible by this method, and their utility as synthetic reagents is currently under investigation.

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10. (α-Ethoxyvinyl)triisopropylstannane was prepared from ethyl vinyl ether and TIPSnBr by adaptation of known procedures[15] [bp 52-56°C (0.1 mm)]. Using Ar-purged solvents throughout, enol ether (5.15g) was stirred with ether (50 mL), water (7 mL) and 0.7g TsOH for 4.5h at 25 °C. The aqueous phase was removed, the ether phase stirred with dilute $NaHCO_3$, and dried (Na_2SO_4). Evacuation at 1mm was followed by flash chromatography (silica gel, EtOAc-hexane). Distillation gave 3.84g (82%) of AcTIPSn, bp 85 °C (0.1 mm).
11. α-(Hydroxy)propargylstannanes were unstable upon storage under ambient conditions.
12. These findings presented in part at the Eighth IUPAC Symposium on Organometallic Chemistry Directed Towards Organic Synthesis, Santa Barbara, CA, August 6-10, 1995.
13. Typical procedure: The lithium acetylide prepared from 0.22g (2.2 mmol) of TMSacetylene and 2.2 mmol of nBuLi in 8 mL of ether at 0 °C was treated dropwise with 0.67g (2.3 mmol) of AcTIPSn. The cold bath was removed, and 20 min later the solution was recooled and treated with 0.44 mL (0.42g, 3.0 mmol) of TMS-imidazole. After 2.5h, aqueous workup was followed by kugelrohr distillation (125 °C, 0.1 mm) to give 0.83g (77%) of **2a** [IR: 2140 cm^{-1}; ^1H NMR: δ 0.10 (s, 9H), 0.14 (s, 9H), 1.1-1.7 (m, 21H), 1.68 (s, 3H); ^{13}C NMR: δ 0.0, 2.4, 16.7, 22.3, 30.6, 67.0, 92.3, 113.1]. The sample also contained 4.5% of **3a** and 1.5% of 1-triisopropylstannyl-1-(trimethylsilyloxy)ethene.
14. Small amounts (0.1-2 times the amount of **3**) of the TMS enol ether of AcTIPSn were also present in the product mixtures.
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