Tetrahedron Letters, Vol.31, No.50, pp 7253-7256, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

A NEW TRANSMETALLATION ROUTE TO MIXED TRIMETHYLSTANNYLCUPRATES: $Me_3Sn(R)Cu(CN)Li_2$#

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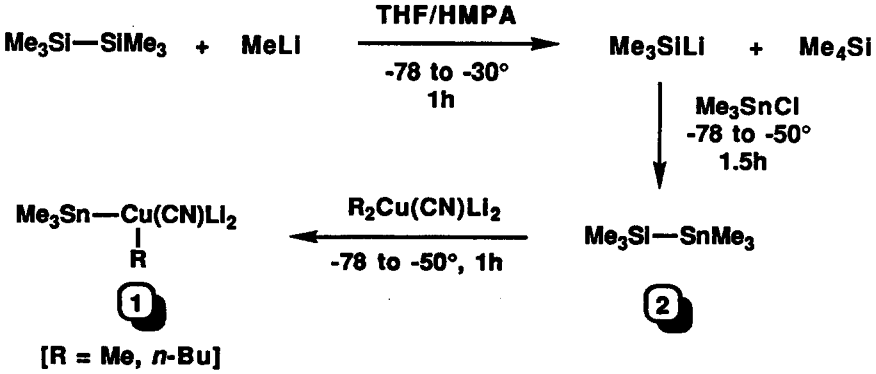
Abstract. Higher order stannylcuprates, $Me_3Sn(R)Cu(CN)Li_2$ can be prepared in a one-flask operation by treatment of Me_3Sn-$SiMe_3$ (prepared *in situ* from Me_3Si-$SiMe_3$, MeLi and Me_3SnCl) with $R_2Cu(CN)Li_2$. These reagents selectively deliver the Me_3Sn moiety to a variety of organic substrates.

As part of our program on polyene stitching aimed at developing rapid constructions of conjugated, skipped and doubly skipped olefins *via* new organometallic procedures, we needed a simple route for introducing the trimethystannyl moiety into organic substrates. Previously, it has been shown that both Me_3SnH[1] and Me_3Sn-$SnMe_3$[2] are receptive toward transmetallations with $R_2Cu(CN)Li_2$ to form reactive cuprates $Me_3Sn(R)Cu(CN)Li_2$ (1),[3,4] thereby providing inroads to the lynchpins designed. Although both methods are efficient, the former is most applicable to larger scale reactions, while the latter is costly. Moreover, both procedures discard half of the available tin in the educt as Me_3SnR. We now report that by utilizing the trimethysilyl group as a proton surrogate, quantitative *in situ* generation of Me_3Sn-$SiMe_3$ (2), followed by ligand exchange with a trivial cuprate $R_2Cu(CN)Li_2$ [3, R = Me or *n*-Bu] affords reagents 1. Once formed, these cuprates participate in the usual cuprate coupling reactions to deliver the Me_3Sn group with virtually complete selectivity, all operations being carried out in a single flask.



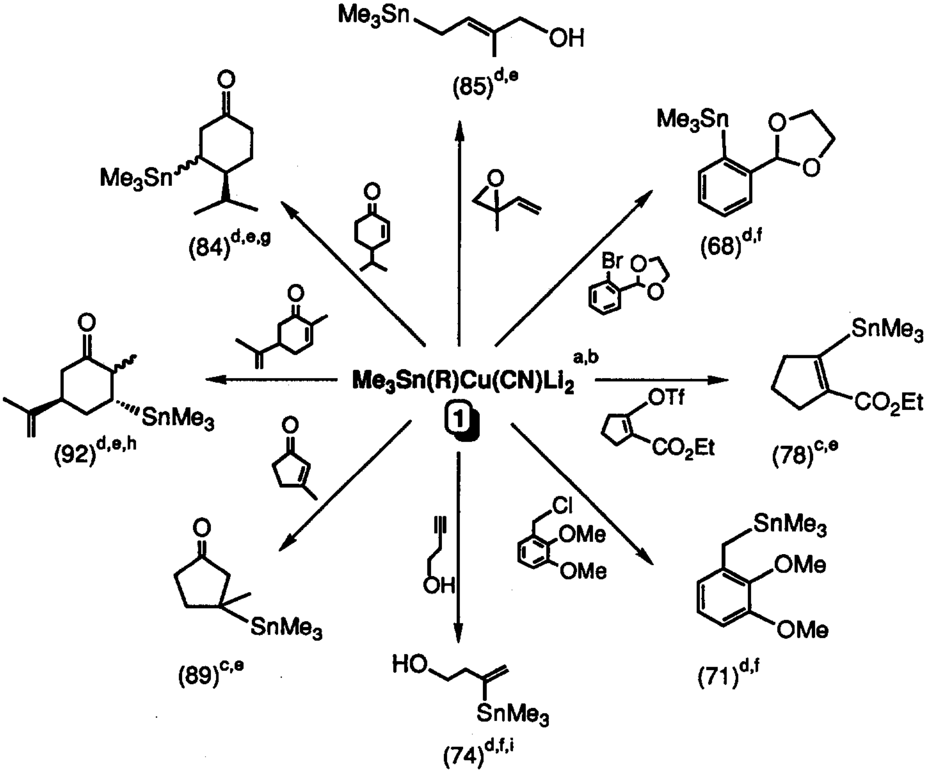
Scheme 1. Formation of higher order trimethylstannylcyanocuprates 1.

#Submitted in honor of Professor **Harry H. Wasserman** on the occasion of his 70th birthday.

Hexamethylsilylstannane **2** is easily formed from treatment of commercially available Me_3Si-$SiMe_3$ in THF/HMPA with MeLi at low temperatures (Scheme 1).[5] The resulting solution of Me_3SiLi is converted to **2** using Me_3SnCl,[1] and then subjected directly to transmetallation[6] with preformed $R_2Cu(CN)Li_2$ (**3**) in THF at low twmperatures. Attack by **3** at silicon (to generate an inert by-product Me_3SiR) was anticipated from earlier work by Chenard,[7] as well as some of our own.[8]

Scheme 2 summarizes our results using this single flask scenerio. Representative examples include 1,4-additions, substitutions on aryl, benzylic, and vinylic centers, as well as an S_N2' addition to an allylic epoxide. One case of stannylcupration was also examined. All substrates reacted fairly rapidly and yields tend to be good to excellent.

Scheme 2. Reactions of mixed trimethylstannylcyanocuprates **1**.



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[a] Products were fully characterized by IR, NMR, MS, & HRMS data; [b] Isolated yields, (%); [c] 1, R = Me, 1.1 equiv of the reagent was used; [d] 1, R = *n*-Bu, 1.5 equiv of the cuprate was used; [e] -78°, 0.5 -1h; [f] -78° to rt, 1h; [g] A mixture of 92 : 8, trans : cis isomers; [h] A mixture of 86 : 14 *trans* : *cis* isomers; [i] The other regioisomer (8%) is also obtained. The reaction was conducted in the presence of MeOH.

The following procedure for stannylcupration of 3-butyne-1-ol illustrates the preparation and use of *in situ* generated $Me_3Sn(Bu)Cu(CN)Li_2$:

Ethereal methyllithium (6.6 mL, 1.5 M, Aldrich) was added to a solution of hexamethyldisilane (2.0 mL, 10.0 mmol, obtained from Aldrich) in 24 mL of THF/HMPA (3:1 by volume) at -78° C under argon. The resulting deep red solution was stirred for 1h while allowing it to warm to -30°C. The reaction was cooled to -78°C after which Me_3SnCl^1 (1.99g, 10.0 mmol, available commercially from Aldrich) in 2 mL of THF was added. The reaction mixture was further stirred for 1.5h while warming to -50°C. In a separate flask, $Bu_2Cu(CN)Li_2$ (10.0 mmol, prepared from 8.7 mL of 2.3 M *n*-BuLi and 0.89g of CuCN) in 10 mL of THF was prepared at -45°C. After stirring for 0.5h, this solution was transferred *via* cannula to a solution of $Me_3SnSiMe_3$ maintained at -78°C. The resulting lemon yellow solution was warmed to -50°C and stirred for 1h to ensure complete transmetallation. 3-Butyn-1-ol (0.63g, 9.0 mmol) was then added neat *via* syringe followed by 5 mL of MeOH. The reaction immediately turned red in color. After 30 min the bath was removed and the solution warmed to room temperature. Usual workup followed by chromatography on silica gel (hexanes:ethyl acetate, 8:1 as eluant) gave 1.56g (74%) of 4-hydroxy-2-trimethylstannyl-1-butene and 0.17g (8.0%) of 4-hydroxy-1-trimethylstannyl-1-butene. GC analysis revealed a purity of > 95% for both isomers; 4-hydroxy-2-trimethylstannyl-1-butene: IR (neat, cm^{-1}) 3350; NMR (500 MHz, $CDCl_3$) δ 0.14 (s, 9H, $\underline{Me}_3Sn$, $^2J_{Sn\text{-}H}$ = 54 Hz), 1.34 (t, 1H, $O\underline{H}$), 2.5 (t, 2H, $C\underline{H}_2C{=}C$), 3.6 (q, 2H, $OC\underline{H}_2$), 5.3 (d, 1H, $C{=}C\underline{H}_2$, J = 2 Hz, $^3J_{Sn\text{-}H}$ = 69 Hz), 5.7 (d, 1H, $C{=}C\underline{H}_2$, J = 2 Hz, $^3J_{Sn\text{-}H}$ = 147 Hz); MS (EI) *m/z* 219 (M^+ - 15); HRMS calcd for $C_6H_{13}SnO$ (M^+ - 15) 219.9895; found 219.9960; 4-hydroxy-1-trimethylstannyl-1-butene: IR (neat, cm^{-1}) 3350; NMR (500 MHz, $CDCl_3$) δ 0.10 (s, 9H, $\underline{Me}_3Sn$, $^2J_{Sn\text{-}H}$ = 55 Hz), 1.36 (t, 1H, $O\underline{H}$), 2.4 (t, 2H, $C\underline{H}_2C{=}C$), 3.7 (q, 2H, $OC\underline{H}_2$), 5.9 (dt, 1H, $C{=}C\underline{H}_2$, J = 19, 6 Hz, $^2J_{Sn\text{-}H}$ = 60 Hz), 6.1 (d, 1H, $C{=}C\underline{H}_2$, J = 19 Hz, $^3J_{Sn\text{-}H}$ = 32 Hz); MS (EI) *m/z* 219 (M^+ - 15); HRMS calcd for $C_6H_{13}SnO$ (M^+ - 15) 219.9895; found 219.9971.

In summary, Me_3Sn-containing cuprates (**1**) can be formed, in particular for small scale experiments, from the commercially available elements of $Me_3Si\text{-}SiMe_3$ and Me_3SnCl and utilize 100% of the Me_3Sn committed to reagent formation.

Acknowledgement. Financial support provided by the NSF and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We warmly thank Mr. Otto Loeffler (Argus Chemical Co.) for generously supplying the Me_2SnCl_2 used to prepare Me_3SnCl.

References and Notes

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(4) For compositional studies on $Me_3Sn(Me)Cu(CN)Li_2$, see Sharma, S.; Oehlschlager, A.C. *J. Org. Chem.*, in press.

(5) **(a)** Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063. It has been recently reported that pentamethyldisilyl anion is also formed in the cleavage reaction of hexamethyldisilane and MeLi in THF/HMPA.[5b] We did not observe any formation $Me_3SnMe_2SiSiMe_3$ in our system as judged by ^1H NMR of **2**; **(b)** Nadler, E.B.; Rappoport, Z. *Tetrahedron Lett.*, **1990**, *31*, 555.

(6) Solutions of **2** can be stored at room temperature for months without loss of reactivity toward transmetallations with cuprates **3**.

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(Received in USA 23 May 1990)