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The regiochemistry of the stannylcupration of allenes: synthesis of allylstannanes using the lower order cuprate $(Bu_3Sn)CuCNLi$

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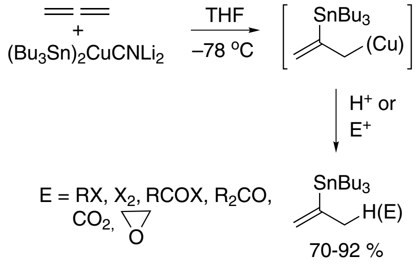
Abstract—The lower order cuprate $(Bu_3Sn)CuCNLi$, prepared by mixing 1 equiv of tributylstannyllithium and 1 equiv of copper(I) cyanide, reacts with allenes showing a regiochemistry opposite to that previously reported for higher order stannylcuprates. Capture of the intermediate allylstannane–vinylcuprate species with different electrophiles allows the selective formation of allylstannanes with different substitution pattern. Reaction with acetylenes was also checked.

Metallocupration of multiple bonds is one of the most powerful methods for the formation of C–metal bonds.[1] In particular, silylcupration and stannylcupration of alkenes and alkynes are efficient procedures for introducing silicon or tin into organic molecules, giving raise to a great variety of small silicon or tin synthons of much applicability in organic synthesis.[2] In the past years, our group[3] and others[4] have been very much involved in the study of the silyl and stannylcupration of allenes and acetylenes and their synthetic scope. The silylcupration of allenes is a high yielding reaction, which leads to allyl or vinylsilanes depending on different factors as the structure of the allene, the nature of the silyl group or the temperature.[5] We observed that the order of the silylcuprate could also modify the regiochemistry. Higher order silylcuprates $(PhMe_2Si)_2CuCNLi_2$ give vinylsilanes whereas the lower order ones $(PhMe_2Si)CuCNLi$ afford selectively allylsilanes.[6,7] By this way, selective formation of one or the other can be easily accomplished varying the stoichiometry of the cuprate.

The stannylcupration of allenes and acetylenes was also studied.[8] We noted[8a] that the higher order cuprate $(Bu_3Sn)_2CuCNLi_2$ reacts with allene itself (1,2-propadiene) at −78 °C leading exclusively to 2-tributylstannylpropene after protonation (Scheme 1). Formation of the vinylstannane takes place by *syn* addition of the Sn–Cu pair to the double bond of the allene, with tin in the middle and copper at the end. This regiochemistry is the same as that observed for the silylcupration of allene with the higher order cuprate $(PhMe_2Si)_2CuCNLi_2$.[5a] The intermediate allylcuprate reacts with electrophiles other than proton affording vinylstannanes with different substitution pattern (Scheme 1). To our knowledge, this is one of the best methods for the regioselective preparation of functionalised vinylstannanes.[8a]



Scheme 1.

The regiochemistry of the stannylcupration of allene can also be greatly influenced by the temperature of the reaction.[8a] As it was observed for silylcupration,[5] the stannylcupration of allenes is also a reversible process, which final outcome strongly depends on the equilibrium temperature. Thus, when we treated 1,2-propadiene with the $(Bu_3Sn)_2CuCNLi_2$ reagent at −100 °C instead of at −78 °C, and quenched the intermediate with methanol at −100 °C, we obtained only the allyltributylstannane (Scheme 2). Accordingly, one should

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Keywords: Allenes; Stannylcupration; Allylstannanes; Cuprates; Regiochemistry.

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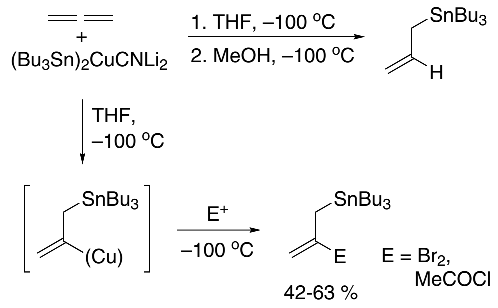


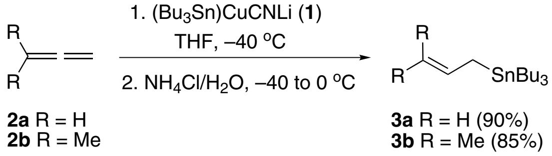
Scheme 2.

expect that control of the regiochemistry (and hence selective formation of allyl or vinylstannanes) could be easily achieved by choosing properly the temperature conditions. However, owing to the low temperature (−100 °C) at which the kinetic allylstannane is formed, there is a very limited range of electrophiles that can react with the intermediate vinylcuprate (Scheme 2). In fact, apart from proton only bromine and acetyl chloride are reactive enough to give allylstannanes in acceptable yield.

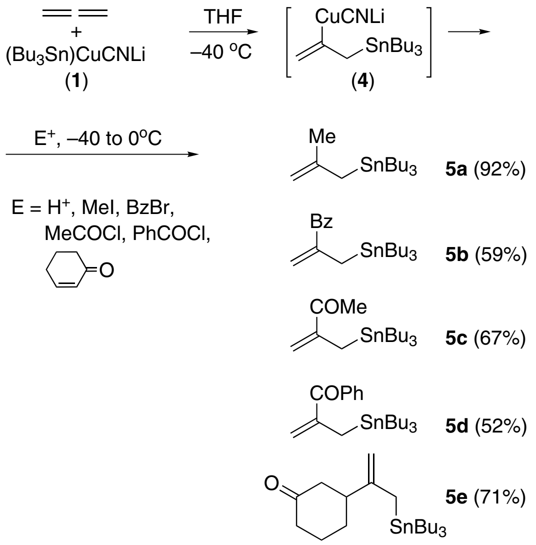
From previous observations, it seems evident that the synthesis of allylstannanes by stannylcupration of allenes is still an unresolved question. Obviously, due to the synthetic interest of allylstannanes as allylic nucleophilic species,[9] the search of efficient methods for their synthesis is an attractive goal. At this point, we wondered if using a lower order cuprate as $(Bu_3Sn)CuCNLi$ would not make any difference in the regiochemistry of the reaction, as we previously observed for the silylcupration.[6,7] Effectively, lithium tributylstannylcyanocuprate **1**, prepared by the first time, inverts the regiochemistry of the addition leading selectively to allylstannanes. We now describe in preliminary form the results obtained from this study.

$(Bu_3Sn)CuCNLi$ (**1**), prepared by stirring 1 equiv of tributylstannyllithium[10] and copper(I) cyanide at −20 °C in THF for 30 min, and formally a low order cuprate, reacts with allenes **2a**,**b** at −40 °C in THF for 1 h to give, after hydrolysis, vinylstannanes **3a**,**b** in high yield (Scheme 3). The protocol[10] used for the preparation of Bu_3SnLi does not change appreciably the final result.

We checked whether the process is temperature dependent or not, quenching the reaction mixture from **2a** at different temperatures. At any temperature between −78 and −40 °C we obtained almost exclusively allylstannane **3a**. At temperatures above −40 °C, allylstannane **3a** is still the major product although formation of the regioisomeric vinylstannane is also observed (5:1, NMR). Near 0 °C the reaction results in formation of dirty mixtures, probably due to cuprate decomposition.



Scheme 3.

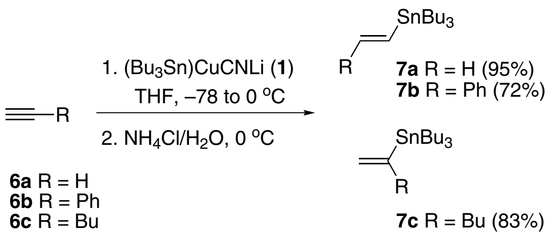


Scheme 4.

The intermediate allylstannane–vinylcuprate **4** resulting from addition of **1** to allene **2a** reacts with electrophiles (alkyl halides, acyl chlorides or conjugate enones) at −40 °C in THF for 1 h leading selectively to the allylstannanes **5a**–**e** (Scheme 4).[11] In some cases, addition of the electrophile at −70 °C and warming up to −40 °C results in better yield. When conjugate enones are used, activation with BF_3 improves the final output. This route provides an easy entry to functionalised allylstannanes that could not be prepared by our standard procedures.

It should be noted that the regiochemistry found in these reactions is opposite to that showed by the higher order tin-cuprate $(Bu_3Sn)_2CuCNLi_2$, which led selectively to vinylstannanes. In this manner, the overall regiochemistry in the stannylcupration of allene can be easily controlled in either sense just managing adequately the nature of the cuprate reagent.

We extended the reaction to acetylenes. Addition of **1** to acetylenes **6a**–**c** (THF, −78 °C to 0 °C, 2 h) affords vinylstannanes **7a**–**c** (Scheme 5). These results are essentially the same as those obtained with the higher order cuprate.[8b]



Scheme 5.

In conclusion, the lower order cuprate **1**, although less reactive than $(Bu_3Sn)_2CuCNLi_2$, requiring temperatures around −40 °C for optimum reactivity with allenes, shows the opposite regiochemistry to that of the higher order cuprate, thus providing an useful method for the synthesis of allylstannanes whose rich chemistry is well known.

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11. General procedure: Typically, 4 mmol of Bu_3SnLi[10a] were added by syringe to a suspension of CuCN (4 mmol) in THF (10 mL) at −20 °C and the mixture was stirred for 30 min under argon. The resulting dark red solution was cooled at −40 °C and a slight excess of allene (1,2-propadiene) was added from a balloon. The mixture was stirred for 1 h, then 4.4 mmol of the corresponding electrophile (Scheme 4) were added at −40 °C and the mixture stirred at this temperature for an additional hour. After warming up to 0 °C, the mixture was hydrolysed with saturated ammonium chloride solution, extracted with Et_2O, dried with $MgSO_4$ and evaporated. The crude was chromatographed (EtOAc–hexanes) on silica gel (230–400 mesh) previously deactivated with Et_3N (5%), yielding the allylstannanes **5a**–**e** (Scheme 4). Compound **5e**: ^1H NMR (300 MHz, $CDCl_3$) 4.63 (s, 1H, $J_{Sn-H} = 10$ Hz), 4.52 (s, 1H, $J_{Sn-H} = 10$ Hz), 2.55–2.25 (m, 5H), 2.15 (m, 2H), 1.97 (m, 2H), 1.79 (s, 2H), 1.45–0.9 (m, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) 211.7, 142.1, 104.1, 47.2, 46.5, 41.2, 31.6, 30.6, 29.1, 27.4, 25.2, 13.7, 9.6; IR (film): 1722, 1627 cm^{-1}; m/z (%) 428 (3), 371 (20).