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AN EFFICIENT AND EXPEDITIOUS ROUTE TO STANNYLALLENES

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Summary: *(Triphenylstannyl)allenes (**2**) are formed in excellent yield by reacting 3-chloro-1-triphenylstannyl-1-propynes (**1**) with several alkylcopper(I) species RCu. An 1-alkynyl group could be introduced by using instead of RCu the zinc reagent and* $Pd[PPh_3]_4$ *as catalyst.*

Reports on the synthesis of tin-containing allenes are rather rare. Nevertheless such functionalized allenes are of interest, for instance, because of their easy and selective transmetallation into the more reactive allenyllithium compounds.[1] Until recently, stannylallenes were prepared through triorganotin lithium induced substitution of propargylic bromides and the inversed route involving reaction of allenylmagnesium reagents with triorganotin halides.[2] Both approaches suffer from a low regioselectivity and disappointing yields. Much better results were reported for the reaction of allenylsilver(I) species with triorganotin halides,[3] while also the stannylcuprate induced conversion of 2-propynylic esters is a promising method.[4]

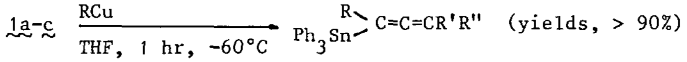
In view of the well known ability of organocopper(I) reagents to induce S_N2' reactions in 2-propynylic esters and halides, we wondered whether it would be possible to use this fruitful principle for the preparation of stannylallenes from 1-alkynylstannanes bearing in the 3-position a leaving group, $R_3Sn{-}C{\equiv}C{-}\overset{|}{\underset{|}{C}}{-}X$. We had our doubts on the feasibility of this strategy as we had learned from other experiments that 1-alkynylstannanes, *e.g.* $Ph_3SnC{\equiv}CH$, are very susceptible to transmetallation when treated with RCu compounds.

For our study, appropriately substituted 1-alkynylstannanes were required. It was found that such substrates are easily accessible by reacting propargylic chlorides subsequently with BuLi in tetrahydrofuran (THF) at -100°C and triphenyltin chloride at -60°C (reaction time, 0.5 hr) followed by allowing the temperature of the resulting mixture to rise to room temperature.

$$HC{\equiv}C{-}CR'R''{-}Cl \xrightarrow[2)\,Ph_3SnCl]{1)\,BuLi/THF} Ph_3Sn{-}C{\equiv}C{-}CR'R''{-}Cl \quad \text{(yields 90\%)} \qquad (1)$$

1a: R',R"= H, H
1b: R',R"= Me, H
1c: R',R"= Me, Me

Compounds **1** proved to be excellent substrates for the preparation of α-alkyl substituted allenyltin compounds, **2** (eqn. 2). Thus, treatment of **1** with RCu reagents[5] (R ≠ Me) during 1 hr at -60°C in THF gave pure allenes **2** in over 90% yield. On the other hand, an almost exclusive transmetallation of **1** was observed when MeCu, $H_2C{=}CHCu$ and Ph-Cu were used indicating that there is a delicate balance between the desired 1,3-substitution and attack by R on Sn in **1**.



$$\mathbf{1a\text{-}c} \xrightarrow[\text{THF, 1 hr, }-60^\circ\text{C}]{\text{RCu}} \overset{\text{R}}{\text{Ph}_3\text{Sn}}\!\!>\text{C=C=CR'R''} \quad \text{(yields, > 90\%)} \tag{2}$$

2a: R = Et, Pr, i-Pr, Bu, *t*-Bu
2b: R = Et, *t*-Bu
2c: R = *t*-Bu

Allenes **2** show the characteristic allene absorption in the IR spectrum at 1920-1940 cm^{-1}. In the ^{13}C NMR spectrum ($CDCl_3$, Me_4Si) the signals for the C*sp*-atom are found in the region 202-207 ppm. In the ^1H NMR spectrum ($CDCl_3$, Me_4Si) the allenic hydrogen atom(s) appear in the region 4.28-4.35 ppm in case of compounds **2a** and at 4.70-4.73 ppm in case of compounds **2b**.

Similar to MeCu, H_2C=CHCu and Ph-Cu, (trimethylsilyl)ethynylcopper(I) appeared to be unable of inducing the 1,3-substitution reaction. We were therefore very pleased to find that the interesting allenyne **2** in which R is $Me_3SiC{\equiv}C$ could be prepared in 98% yield by using instead of the copper(I) compound RCu the corresponding zinc reagent, $Me_3SiC{\equiv}C$-ZnCl, and 4 mol % of the complex $Pd[PPh_3]_4$ (studied for **1c**).[6] Apparently, transmetallation of **1** by the zinc reagent is so slow that the palladium(0)-catalyzed allene formation can compete effectively. This approach will undoubtedly be suited to introduce other unsaturated groups R too, and will be elaborated on further.

Preliminary experiments with $Me_3SiC{\equiv}C$-$C(SnPh_3)$=C=CMe_2 (**2c**, R = $Me_3SiC{\equiv}C$) revealed that this allenyne undergoes a quantitative transmetallation into the lithium derivative $Me_3SiC{\equiv}C$-C(Li)==C=CMe_2 upon treatment with methyllithium at -80°C in THF. The chemistry of this interesting lithium species will be investigated.

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References and notes

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(5) Prepared by stirring RMgCl with an equimolar amount of $LiCuBr_2$ during 30 min at -60 - -50°C in THF.
(6) This principle was recently applied to the synthesis of allenes from HC≡C-CR'R''-X: Ruitenberg, K.; Kleijn, H.; Westmijze, H.; Meijer, J.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas 101 (1982) 405.*

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