The Synthesis of Allylstannanes and Vinylstannanes by the Stannyl-cupration of Allenes

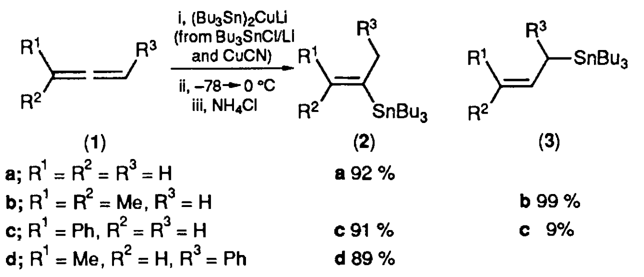
Asunción Barbero,[a] Purificación Cuadrado,[a] Ian Fleming,[b] Ana M. González,[a] and Francisco J. Pulido*[a]

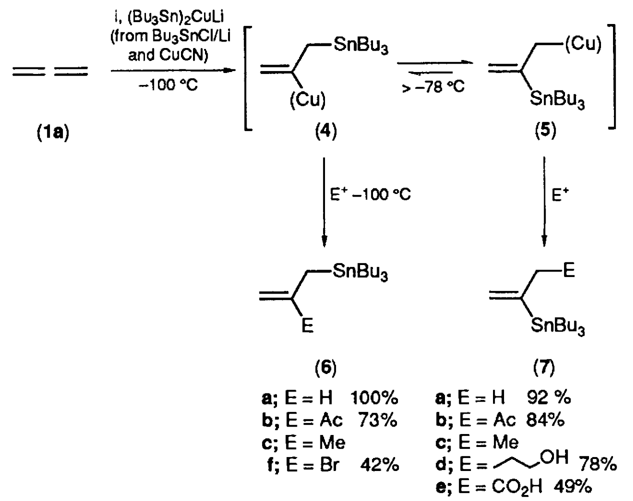
[a] *Departamento de Química Orgánica, Universidad de Valladolid, 47011-Valladolid, Spain*
[b] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK*

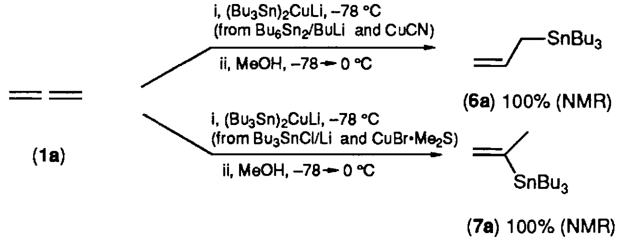
Stannyl-cupration of allenes followed by electrophilic attack gives allyl- and vinylstannanes with a variety of substitution patterns; the regiochemistry of the reaction depends upon the temperature and the nature of the stannyl-cuprate reagent.

In earlier papers,[1—3] we reported the synthesis of allylsilanes and vinylsilanes by silyl-cupration of allenes. The reactions usually proceed with a high degree of regiocontrol, which depends upon the substitution pattern of the allene. Other metallo-metallations of unactivated allenes are also known, such as the addition of silicon–magnesium, silicon–aluminium, and silicon–zinc to allenes catalysed by copper(I) or palladium.[4] We have also reported briefly the stannyl-cupration of allenes,[3] in which we used Piers' stannyl-cuprate reagent, a lower-order cuprate.[5] We now report further work, in which we find that the regiochemistry of the stannyl-cupration of allenes depends upon the nature of the stannyl-cuprate and on the temperature.

Bis(tributylstannyl)cuprate, prepared at −78 °C from two equivalents of tributylstannyl-lithium (itself prepared from tributyltin chloride and metallic lithium)[6] and one of copper(I) cyanide, and therefore a higher-order cuprate,[5] reacts with allenes (**1a—d**) [tetrahydrofuran (THF); −78 to 0 °C; 1 h] giving, after protonation, either vinylstannanes (**2a,c,d**) or allylstannanes (**3b,c**) in good yields. The stereochemistry of the vinylstannanes (**2c**) and (**2d**) is cleanly *E* (transmetallation with butyl-lithium followed by protonation gives the *Z*-

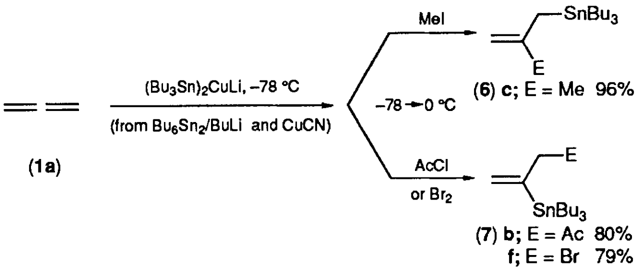


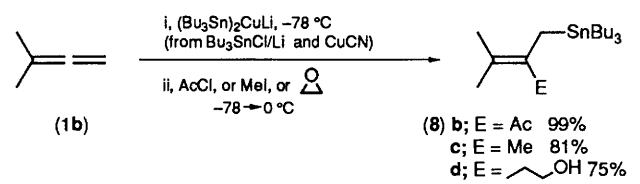




alkenes), presumably as a result of the stannyl-cuprate's attacking the less-hindered face of the allene. Phenylallene (**1c**) gives a mixture of regioisomers, favouring the vinylstannane over the allylstannane (10 : 1). The formation of (**3b**) and (**3c**) shows that the stannyl-cuprate attaches the tin atom to the less-substituted end of the allene. Trisubstituted allenes fail to react with this cuprate.†

The regiochemistry strongly depends upon the reaction temperature: when we treated allene itself (**1a**) with the same stannyl-cuprate reagent at −100 °C, instead of at −78 °C, and quenched the intermediate with methanol at −100 °C instead of at 0 °C, we got only the allylstannane (**6a**) instead of the vinylstannane [(**7a**) = (**2a**)]. When we treated allene with the stannyl-cuprate at −100 °C for 1 h, allowed the mixture to warm to 0 °C over 1 h, and quenched it at −100 °C, we got only the vinylstannane (**7a**); when we repeated the experiment, warming the mixture from −100 °C only to −78 °C, and then quenched it at that temperature, we got a mixture of (**6a**) and (**7a**) (1 : 4.5; 98%). Thus it appears that the intermediate (**4**) is the kinetic product of stannylcupration, and the intermediate (**5**) is the thermodynamic product. Because of the low temperature at which the kinetic intermediate (**4**) starts to rearrange to the thermodynamic intermediate (**5**), there is a very limited range of electrophiles that can react with the kinetic product. Bromine was effective, giving the allylstannane (**6f**), but amongst carbon electrophiles, only acetyl chloride straightforwardly gave the ketone (**6b**). The thermodynamic intermediate (**5**), however, reacts with a range of carbon electrophiles (acetyl chloride, ethylene oxide, and carbon dioxide), giving the products (**7b**), (**7d**), and (**7e**), respectively. Methyl iodide, however, is anomalous: we always obtained mixtures of the allylstannane (**6c**) and the vinylstannane (**7c**), with the latter the major product, but to an unreproducible degree (1 : 4 to 1 : 1.5), as we have already reported[3] for the reaction using Piers' reagent. This result indicates, perhaps, that our simple analysis of kinetic and thermodynamic intermediates is at least incomplete.





We have also prepared a similar but halide-free stannylcuprate (hexabutylditin and butyl-lithium, CuCN),[7] which reacts with allene at −78 °C. Quenching it (MeOH; −78 °C) gives only the allylstannane (**6a**), in contrast to the mixture of (**6a**) and (**7a**) obtained in the experiment described above, and with our earlier result[3] using Piers' stannyl-cuprate reagent (Bu_3SnLi, $CuBr·SMe_2$), in which we got only the vinylstannane (**7a**). This would seem to indicate that the equilibrium (**4**) $\rightleftharpoons$ (**5**) is faster in the presence of halide ion (and/or dimethyl sulphide). However, when the intermediate in the halide-free series is quenched with other electrophiles, no simple pattern emerges. With methyl iodide at −78 °C, we get only the allylstannane (**6c**), and with acetyl chloride at −78 °C or bromine at −78 °C, only the vinylstannanes (**7b**) and (**7f**).

The reaction of dimethylallene (**1b**) with the higher-order cuprate, quenching at −78 °C with methyl iodide, acetyl chloride, or ethylene oxide, gave only the allylstannanes (**8**), just as we had found using Piers' reagent.[3]

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† The results with allene itself (**1a**) and the dimethylallene (**1b**) are the same as we had observed earlier using Piers' stannyl-cuprate.[3]