

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*

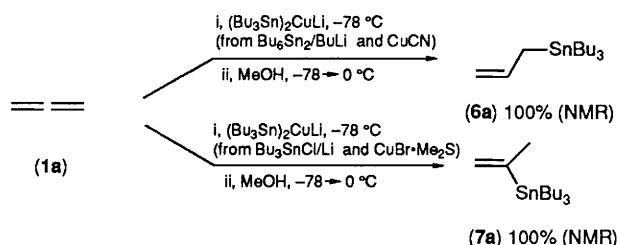
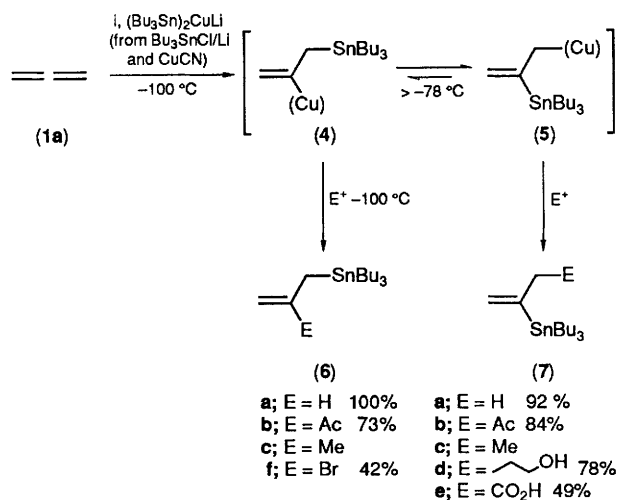
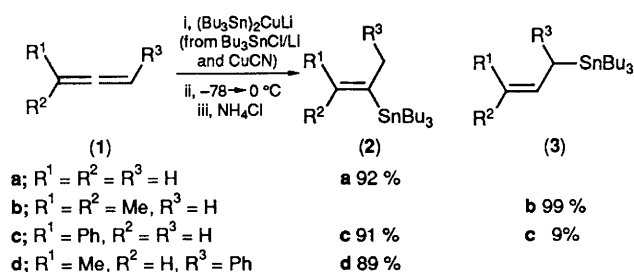
^b *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK*

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

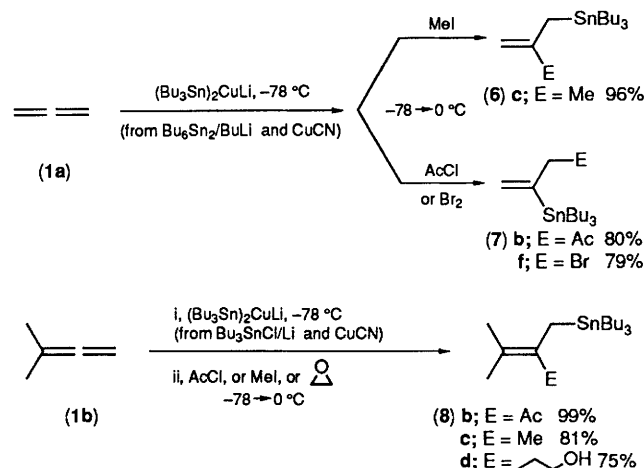
allenes depends upon the nature of the stannyl-cuprate and on the temperature.

Bis(tributylstannyl)cuprate, prepared at $-78\text{ }^{\circ}\text{C}$ 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 $0\text{ }^{\circ}\text{C}$; 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 reported³ 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 stannyl-cuprate (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 result³ using Piers' stannyl-cuprate reagent (Bu₃SnLi, CuBr·SMe₂), 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

Received, 9th April 1990; Com. 0/01596B

References

- I. Fleming and F. J. Pulido, *J. Chem. Soc., Chem. Commun.*, 1986, 1010.
- P. Cuadrado, A. M. Gonzalez, F. J. Pulido, and I. Fleming, *Tetrahedron Lett.*, 1988, **29**, 1825.
- I. Fleming, M. Rowley, P. Cuadrado, A. M. González-Nogal, and F. J. Pulido, *Tetrahedron*, 1989, **45**, 413.
- Y. Morizawa, H. Oda, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, 1984, **25**, 1163; see also T. N. Mitchell, H. Dilling, R. Dicke, and R. Wickenkamp, *J. Chem. Soc., Chem. Commun.*, 1985, 354.
- E. Piers, H. E. Morton, and J. M. Chong, *Can. J. Chem.*, 1987, **65**, 78; S. Sharma and A. C. Oehlschlager have characterised this and other stannyl-cuprates, *J. Org. Chem.*, accepted for publication.
- C. Tamborski, F. E. Ford, and E. J. Sotoski, *J. Org. Chem.*, 1963, **28**, 237.
- W. C. Still, *J. Am. Chem. Soc.*, 1977, **99**, 4836.

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