

Palladium-catalysed Addition of the Silicon–Tin Bond to Alk-1-yne and 1,1-Dimethylallene

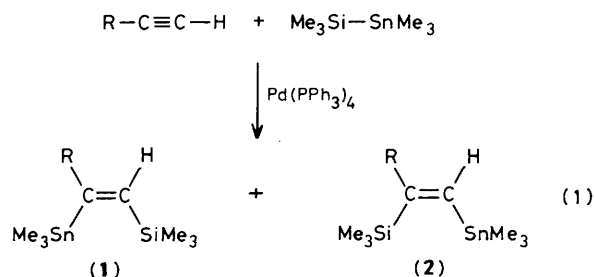
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(Trimethylsilyl)trimethylstannane adds regio- and stereo-specifically to alk-1-yne in the presence of tetrakis(triphenylphosphine)palladium(0); regiospecific addition to 1,1-dimethylallene is also observed.

The increasing importance of organosilicon compounds in organic synthesis has led to considerable interest in the formation of vinylsilanes¹ which are extremely useful synthetic intermediates. One method of preparing such compounds is the addition of silicon–metal(loid) bonds to alkynes; such reactions, which often require the presence of transition metal catalysts, lead to functionally-substituted vinylsilanes. Apart from silicon itself,² the metals used include copper,³ magnesium, zinc, and aluminium.⁴

Our recent observations that hexa-alkyldistannanes add to allenes⁵ and stereospecifically to alk-1-yne⁶ in the presence of



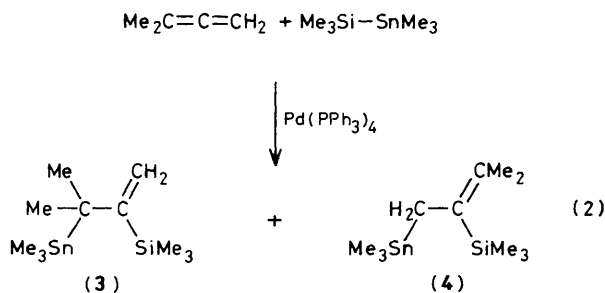
R = Buⁿ, Ph, PhCH₂, Me₂NCH₂, MeOCH₂, HOCH₂, HOCHMe, HOCHMe₂, and HOCH₂CH₂.

Pd(PPh₃)₄ led us to investigate whether similar reactions are possible using (trimethylsilyl)trimethylstannane.⁷

We find that a number of alk-1-yne readily undergo a clean regio- and stereo-specific addition with formation of (1), equation (1). An exception is provided by methyl propiolate which at reaction temperatures between 25 and 115 °C gives a 1 : 1 mixture of (1) and its regioisomer (2). The proportion of (1) in the mixture can be increased to ca. 90% by carrying out the reaction at 0 °C for 48 h. In general, the reactions are carried out without the addition of solvent in the presence of up to 1 mol% Pd(PPh₃)₄ and require 48 h at 60–70 °C. Isolated yields (10 mmol Me₃SiSnMe₃ were taken in each case) range from 28% for R = CO₂Me (incomplete reaction) to 65%.

Structural proof of adduct formation is provided by the ¹H (and additionally ²⁹Si) n.m.r. spectra: the values of ³J(SnH) for the vinyl proton lie between 165 and 211 Hz and are thus typical for a *trans*-coupling.⁸ The coupling ³J(²⁹Si–¹¹⁹Sn) lies between 29 and 40 Hz. Partial photochemical isomerisation to *E*-(1) has been carried out in several cases: ³J(Sn–H) decreases to 56–60 Hz and ³J(SiSn) increases to 67–88 Hz. The corresponding values for (2), R = CO₂Me, are 66 Hz for

† Isomerisation occurs in each case only to 50–60%.



$^2J(\text{SnH})$ and 29 Hz for $^3J(\text{SiSn})$; in this compound $^3J(\text{SnC})$ is 106 Hz, typical for a *trans*-coupling.⁸

1,1-Dimethylallene reacts with $\text{Me}_3\text{SiSnMe}_3$ in 48 h in refluxing tetrahydrofuran to give (in 67% isolated yield) a 1 : 1 mixture of (3) and (4), equation (2). The proportion of (4) can be increased to *ca.* 80% (based on n.m.r. spectra) by adding 1 mol% $\text{Pd}(\text{PPh}_3)_4$ to the distilled product mixture and heating at 90 °C for 15 h.

The structures of (3) and (4) are also determined by n.m.r. spectroscopy. The vinylic protons of (3) show no coupling to tin, while $^3J(\text{SiSn})$ is approximately equal in both compounds (13 and 14 Hz respectively). The ^{13}C n.m.r. data closely parallel those for the adducts between Me_6Sn_2 and 1,1-dimethylallene. Thus the addition of $\text{Me}_3\text{SiSnMe}_3$ is regio-

specific with respect to silicon. The specificity with respect to the allene can be shifted towards the thermodynamic product by the use of appropriate reaction conditions.

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