

The Palladium-catalysed Reaction of Disilanylstannanes with Alkynes

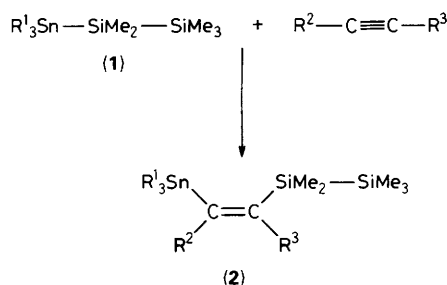
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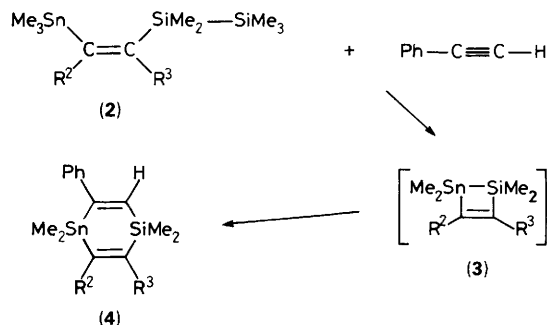
Palladium-catalysed reaction of disilanylstannanes with alkynes afforded (β -disilanylalkenyl)stannanes, which underwent subsequent reaction with phenylethyne in the presence of palladium catalyst giving the corresponding 1-sila-4-stannacyclohexa-2,5-dienes.

Much interest has been focused on the reaction of bimetallic compounds having Si-Si or Si-Sn bonds with unsaturated organic compounds, in order to develop new syntheses of silicon- and tin-containing materials. Recently, we have found that organodisilanes¹ and silylstannanes² undergo palladium-catalysed α -addition to isocyanides to give the corresponding imine derivatives. The reaction of organodisilanes and silylstannanes with alkynes was studied by several groups.³ Now, we report the palladium-catalysed reaction of disilanylstannanes, possessing both Si-Si and Si-Sn bonds in the same molecule, with alkynes.

Alkynes underwent selective insertion into the Si-Sn bond of disilanylstannanes (1)† in the presence of palladium catalyst to afford the corresponding (β -disilanylalkenyl)stannanes (2). The reaction was regio- and stereo-selective as observed in the reaction of organosilylstannanes with alkynes;^{3a,b} the (β -disilanylalkenyl)stannane (2) arose from *cis*-addition of the Si-Sn to the carbon-carbon triple bond. With terminal alkynes, the stannyl group added regioselectively to the internal carbon atom (entries 1,3, Table 1). Structures were assigned on the basis of ³J_{Sn-H} values and ¹H NMR NOE



Scheme 1. Reagents: Pd(PPh₃)₄ (catalyst), toluene (see Table 1 for conditions).



Scheme 2. Reagents: Pd(PPh₃)₄ (catalyst), toluene (see Table 2).

experiments.‡ In general, tetrakis(triphenylphosphine)-palladium was the catalyst of choice. Aliphatic alkynes did not react with (1) under the present reaction conditions.

The (β -disilanylalkenyl)stannane (2) was synthesized by heating a mixture of the alkyne (0.3 mmol), disilanylstannane (0.2 mmol), and Pd(PPh₃)₄ (0.006 mmol) in toluene (2 ml). The (β -disilanylalkenyl)stannane (2) was isolated by preparative TLC on silica gel and/or HPLC on polystyrene gel, and characterized by ¹H NMR, IR, and mass spectrometry.§

In entry 3 of Table 1, the cyclized product, 1-sila-4-stannacyclohexa-2,5-diene (4c), was produced in 13% yield along with (β -disilanylalkenyl)stannane (2c). Compound (4c) might be produced by a subsequent reaction of (2c) with phenylethyne. Indeed, the regioselective cyclization reaction of compounds (2) (0.1 mmol) with phenylethyne (0.5 mmol) in the presence of tetrakis(triphenylphosphine)palladium (0.003 mmol) in toluene (2 ml) afforded the silastannacyclohexadienes (4) as single isomers in high yields (Table 2). The 1-sila-2-stannacyclobutene (3), formed *via* oxidative addition of the Si-Si bond of (2) to palladium(0) followed by elimination of tetra-alkylsilane, might be an intermediate in the cyclization.¶ 1-Sila-4-stannacyclohexa-2,5-dienes have been prepared previously by hydrostannation of dialkynylsilanes with dialkylstannanes in moderate yields.⁴ The present reaction provides a novel and efficient method for the synthesis of 1-sila-4-stannacyclohexa-2,5-dienes.

The (β -disilanylalkenyl)stannanes (2), formed by insertion of alkynes into (1), may be versatile synthetic units for

Table 1. Synthesis of (β -disilanylalkenyl)stannanes (2).

Entry	R ¹	R ²	R ³	Conditions	Product	% Yield
1	Me	EtO ₂ C	H	43 °C; 2 h	(2a)	63
2	Me	MeO ₂ C	MeO ₂ C	50 °C; 3 h	(2b)	63
3	Me	Ph	H	60 °C; 5 h	(2c)	42
4	Bu ⁿ	MeO ₂ C	MeO ₂ C	55 °C; 24 h	(2d)	55 ^a

^a Pd(OAc)₂ (0.03 equiv.) and 2,6-xylyl isocyanide (0.26 equiv.) were used as a catalyst instead of Pd(PPh₃)₄.

Table 2. Synthesis of 1-sila-4-stannacyclohexa-2,5-dienes (4) from (2).

Entry	R ²	R ³	Temp./°C	Product	% Yield
1	EtO ₂ C	H	80	(4a)	100
2	MeO ₂ C	MeO ₂ C	60	(4b)	87
3	Ph	H	80	(4c)	82

‡ The Sn-H coupling constant with the vinyl proton of (2) was in the range 156–189 Hz, suggesting a *trans*-geometry. In addition, an NOE between C=C-H and C=C-SiMe₂ was observed.

§ (2a): Satisfactory elemental analysis; ¹H NMR (200 MHz; CDCl₃): δ 0.09 (s, 9H), 0.21 (s, 6H), 0.24 (s, 9H), 1.28 (t, 3H, *J* 7 Hz), 4.16 (q, 2H, *J* 7 Hz), 7.69 (s, 1H); IR (neat) 1714, 1692, 1248 cm⁻¹; *m/z* 379 (*M* - Me), 321 (*M* - CO₂Et).

¶ It was reported that 1,2-disilacyclobutene reacts with alkynes to afford 1,4-disilacyclohexa-2,5-dienes.⁵

† Disilanylstannanes (1) were prepared by the coupling reaction of organostannyl-lithium reagents with chlorodisilanes in tetrahydrofuran.

synthesis of organosilicon and organotin compounds. Synthetic reactions using (2) are being developed in our laboratory.

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