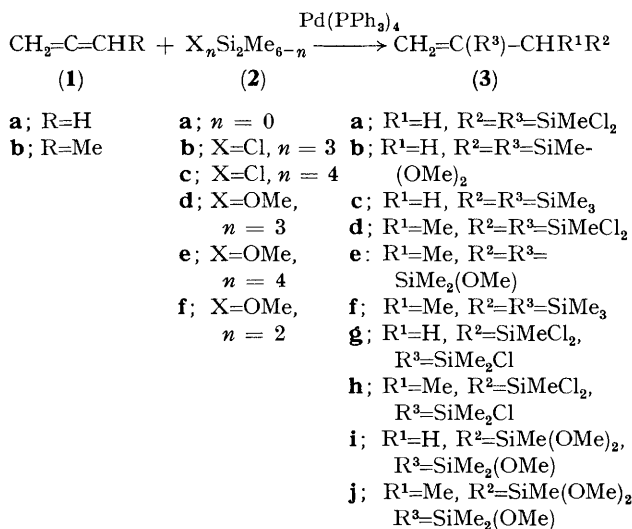


## Double Silylation of Allene and Buta-1,2-diene: Formation of New Organosilicon Compounds containing both Vinylsilane and Allylsilane Units

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**Summary** Addition of chloromethyl- and methoxymethyl-disilanes, as well as hexamethyldisilane, to allene and buta-1,2-diene in the presence of a Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst gave, regioselectively, new functionalized organosilicon compounds, 2,3-bis(organosilyl)prop-1-enes and 2,3-bis(organosilyl)but-1-enes, respectively.

ALTHOUGH several studies on the addition of disilanes to acetylenes<sup>1</sup> and conjugated dienes<sup>2</sup> have been reported, the double silylation of allenic compounds using disilanes has not yet been described. We now report that the addition of allenic compounds such as allene and buta-1,2-diene with chloromethyl- and methoxymethyl-disilanes, as well as hexamethyldisilane, in the presence of a Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst gave, regioselectively, the corresponding 1:1 adducts 2,3-bis(organosilyl)prop-1-enes and 2,3-bis(organosilyl)but-1-enes, respectively.



The reactions were carried out at 100–120 °C for 5–20 h to give compounds (**3**) in moderate to good yields. A typical procedure is outlined. To a mixture of *sym*-dimethoxytetramethyldisilane (10 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.1 mmol; 1.0 mol% relative to the disilane used) in an evacuated stainless-steel vessel was introduced buta-1,2-diene [10 mmol, condensed in a calibrated tube at 0 °C (ice-water-bath) and then distilled into the vessel] and the mixture was heated at 120 °C (oil-bath) for 15 h with magnetic stirring. G.l.c. analysis showed that the resultant mixture contained a single product in 97% yield which was the 1:1 adduct (**3e**), identified by the usual means. Distillation afforded the product (**3e**) (2.0 g, 88%), b.p. 103 °C/30 mmHg, which gave satisfactory elemental analyses {*n*<sub>D</sub><sup>25</sup> 1.4395; <sup>1</sup>H n.m.r. δ[CCl<sub>4</sub>, tetramethylsilane (TMS)] 0.02 (s), 0.09 (s) (12 H, SiMe), 1.07 (d, 3 H, CH-Me), 1.81 (q, 1 H, CH), 3.37 (s, 6 H, O-Me), 5.38 (d), and 5.55 (d, =CH<sub>2</sub>)}. The i.r. spectrum of compound (**3e**) (liquid film, sandwich) was also

TABLE. Addition of disilanes to allene<sup>a</sup> and buta-1,2-diene.<sup>b</sup>

Allene	Disilane	Reaction T/°C (t/h)	Yield of ( <b>3</b> ) <sup>c</sup> /%	B.p./°C (mmHg)
(1a)	(2b)	120 (15)	77(53)	100(35)
(1a)	(2c)	120 (15)	85(67)	105(30)
(1a)	(2d)	120 (20)	64(55)	75(5)
(1a)	(2e)	120 (20)	50(40)	102(20)
(1a) <sup>e</sup>	(2a)	120 (20)	29	63(60)
(1b)	(2b)	100 (15)	81(59)	99(30)
(1b) <sup>f</sup>	(2c) <sup>f</sup>	100 (5)	(84)	141(20)
(1b)	(2f)	120 (15)	97(88)	103(30)
(1b)	(2d)	120 (16)	57	105(30)
(1b)	(2a)	120 (15)	83(73)	67(30)

<sup>a</sup> Allene-disilane-Pd(PPh<sub>3</sub>)<sub>4</sub> = 20:10:0.1 (mmol). <sup>b</sup> A 50:50 mixture of buta-1,2-diene and but-2-ene which is commercially available; allene-disilane-Pd(PPh<sub>3</sub>)<sub>4</sub> = 10:10:0.1 (mmol). <sup>c</sup> Satisfactory elemental analyses and i.r. and n.m.r. (<sup>1</sup>H and <sup>13</sup>C) spectra were obtained for all compounds. <sup>d</sup> G.l.c. yield based on the disilane used; isolated yield is given in parentheses. <sup>e</sup> Benzene (1.2 ml) was used as solvent. <sup>f</sup> Allene-disilane-Pd(PPh<sub>3</sub>)<sub>4</sub> = 100:100:1.0 (mmol).

consistent with the structure (**3e**) and exhibited characteristic bands at 3050 ( $=\text{CH}_2$ ), 1590 (C=C), 1252 (Si-Me), and 1095  $\text{cm}^{-1}$  (Si-O-C).

It was shown that the addition reactions of unsymmetrical disilanes proceeded with complete regioselectivity to give, in each case, only one product, which we believe to have the structures (**3g**)—(**3j**) shown. Thus, the  $^{13}\text{C}$  n.m.r. spectrum for (**3g**) (in  $\text{CDCl}_3$ ; TMS) showed signals at  $\delta$  141.2 ( $=\text{C}$ ), 129.8 ( $=\text{CH}_2$ ), 28.0 ( $\text{CH}_2$ ), 5.2 ( $\text{CH}_2\text{SiMe}$ ), and 1.6 p.p.m. ( $=\text{C}-\text{SiMe}$ ), and for (**3h**) at  $\delta$  148.7 ( $=\text{C}$ ), 128.3 ( $=\text{CH}_2$ ), 29.3 ( $\text{CH}_2$ ), 16.6 ( $\text{CH}-\text{Me}$ ), 4.1 ( $\text{CH}-\text{SiMe}$ ), and 1.6 and 1.5 p.p.m. ( $=\text{C}-\text{SiMe}$ ).

Actually, the double silylation occurred on a larger scale in high yield, as evidenced by the preparation of compound

(**3d**) from *sym*-tetrachlorodimethyldisilane and buta-1,2-diene (see the Table).

The present reaction may provide not only a novel and convenient route to the selective synthesis of new, functionalized organosilicon compounds which are potentially useful precursors for polysiloxanes and intermediate chemicals in organic syntheses, but also a way to utilize various disilanes which are readily available in large amounts.<sup>3</sup>

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