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Facile Synthesis of Alkenylsilanes from Organic Halides and Vinylsilanes in the Presence of Triethylamine and Palladium Catalysts

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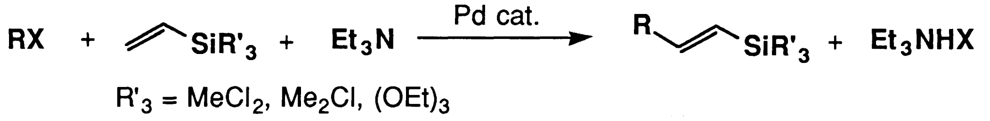
Organic halides such as PhI, ArBr, and β-bromostyrene reacted with di- or monochlorovinylsilanes or triethoxyvinylsilane in the presence of triethylamine and palladium catalysts to give β-substituted vinylsilanes in excellent to moderate yields.

Alkenylsilanes are useful reagents which allow numerous synthetic applications.1) Hallberg et al. previously reported palladium-catalyzed Heck reactions of organic iodides (RI) with trimethylvinylsilane affording β-substituted vinylsilanes ($RCH=CHSiMe_3$).2a,b) However, the necessity of one equivalent of silver nitrate per mole of an organic iodide is the major drawback of the method; the absence of silver nitrate causes extensive desilylation leading to simple vinylated products ($RCH=CH_2$).2c) We have now found unexpectedly that the Heck type reaction normally proceeds in the absence of the silver salt when the starting vinylsilane has electronegative substituents attached to the silicon.

A typical reaction procedure is as follows. A mixture of 1-bromonaphthalene (50 mmol), dichloromethylvinylsilane (55 mmol), triethylamine (30 cm^3) and $PdCl_2(PPh_3)_2$ (0.14 mmol) was heated in a sealed glass vessel at 120 °C for 24 h. The precipitate formed in the reaction was removed by filtration and washed by hexane (80 cm^3). The filtrate and the hexane washing were combined and concentrated under reduced pressure. Distillation of the residue afforded trans-1-[β-(dichloromethylsilyl)vinyl]naphthalene (40.2 mmol, 80.3%). Anal. Found: C, 58.55; H, 4.60%. Calcd for $C_{13}H_{12}SiCl_2$: C, 58.42; H, 4.54%.

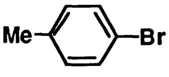
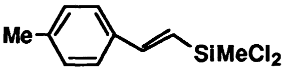
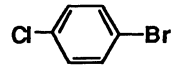
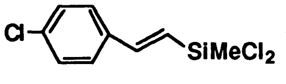
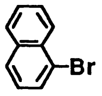
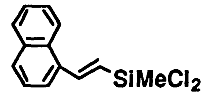
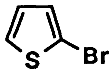
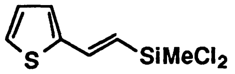
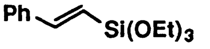
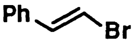
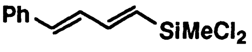
Likewise, other β-substituted vinylsilanes with trans geometry are produced from various organic halides in excellent to moderate yields (Eq. 1, Table 1). In these reactions small amounts of simple vinylated compounds were also formed. Although the mechanism of simple vinylation is ambiguous, the electronegative substituents in vinylsilanes significantly inhibit the desilylation process; the reaction of bromobenzene with dichrolomethylvinylsilane gave much smaller amount of styrene (1.1%) than with chlorodimethylvinylsilane (19.4%) as estimated by GC analysis. In the present reactions both $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ were effective catalysts except for the case of bromothiophene which hardly reacted with dichloromethylvinylsilane in the presence of $Pd(PPh_3)_4$.



(1)

In conclusion, palladium-catalyzed Heck reactions of organic halides efficiently proceeded by using di- or monochlorovinylsilanes or triethoxyvinylsilane affording alkenylsilanes. Since the products contain reactive

Table 1. Reactions of Organic Halides with Vinylsilanes in the Presence of Triethylamine and Palladium Catalysts [a]

Halides	Vinylsilanes	Products[b]	Bp θ_b/°C (mmHg)	Yields[c] / %
PhI[d]			84 (1.0)	76.7
PhBr			84 (1.0)	76.0 (97.2)
		 [f]	89 (0.6)	59.4 (76.7)
		 [f]	120 (1.0)	70.2 (93.6)
		 [f]	137 (0.6)	80.3
		 [f]	75 (0.7)	40.9
PhBr			82 (0.9)	34.4 (59.7)
PhBr		 [f]	132 (0.5)	30.7 (79.6)
PhBr[e]			110 (0.6)	69.1
		 [f]	108 (0.3)	66.1

a) Reaction conditions: halide (50 mmol), vinylsilane (55 mmol), triethylamine (30 cm^3), $PdCl_2(PPh_3)_2$ (0.14 mmol), 120 °C, 22-100 h. b) trans/cis = >98/2. c) Isolated yields. Figures in parentheses are GC yields obtained in the reactions of aryl halides (0.5 mmol) with vinylsilanes (0.55 mmol) in the presence of triethylamine (0.3 cm^3) and $PdCl_2(PPh_3)_2$ (0.005 mmol) at 120 °C for 17 h. d) PhI (45 mmol), CH_2=$CHSiMeCl_2$ (100 mmol), $PdCl_2(PPh_3)_2$ (0.37 mmol), 100 °C, 20 h. e) $Pd(PPh_3)_4$ (0.14 mmol) was used. f) All new compounds gave satisfactory spectral data.

chlorine atoms or ethoxy groups, they are useful not only as synthetic reagents but also as monomers for functional organosilicon polymers.[3] Further extension to the synthesis of bis[β-(chlorosilyl)vinyl]arenes and relevant polymers is under way.

References

1) For instance, see W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer-Verlag, Berlin (1983).

2) a) K. Karabelas and A. Hallberg, *J. Org. Chem.*, **51**, 5286 (1986); b) K. Karabelas and A. Hallberg, *ibid.*, **53**, 4909 (1988); c) A. Hallberg and C. Westerlund, *Chem. Lett.*, **1982,** 1993.

3) J. Oshita, D. Kanaya, M. Ishikawa, and T. Yamanaka, *J. Organomet. Chem.*, **369**, C18 (1989), and references cited therein.

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