PALLADIUM-CATALYZED CROSS-COUPLING REACTION
OF ALKENYLALKOXYSILANES WITH ARYL AND ALKENYL HALIDES
IN THE PRESENCE OF A FLUORIDE ION[1]

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Summary: Alkenyl-monoalkoxydimethylsilanes, dialkoxymethylsilanes, and trialkoxysilanes undergo palladium-catalyzed cross-coupling reaction with alkenyl and aryl halides in the presence of tetra-*n*-butylammonium fluoride. A one-pot transformation of a homopropargyl alcohol to regio- and stereo-defined trisubstituted homoallyl alcohols has been achieved by a sequence of intramolecular hydrosilation and the palladium-catalyzed coupling reaction.

   Transition metal-catalyzed cross-coupling reactions between organometallic reagents and organic halides and related compounds have now become one of the most efficient methods for the carbon-carbon σ-bond formation.[2] Among a variety of alkenyl organometallic reagents, alkenyl-silicon compounds have also been examined as promising candidates for palladium-catalyzed coupling reactions, but the reactions so far developed have not necessarily been synthetically useful with respect to generality, efficiency and selectivity.[3] In 1988, Hatanaka and Hiyama have reported an efficient method for the palladium-catalyzed coupling of alkenyl-trimethylsilanes and -fluorodimethylsilanes with C(sp2)-halides in the presence of a fluoride ion as an accelerating additive, raising the reaction to a synthetically useful level.[4]
   In the course of our study on the synthetic applications of silafunctional silicon compounds, we have been interested in the feasibility of alkenylalkoxysilanes for the Pd-catalyzed coupling reaction, since several new methodologies for the synthesis of various types of alkenylalkoxysilanes have recently been developed.[1,5] We now report that the coupling reaction indeed proceeds smoothly under essentially the same condition as that described by Hatanaka and Hiyama;[4b] tetra-*n*-butylammonium fluoride (TBAF) can be used conveniently as a fluoride ion source in all cases (eq 1).
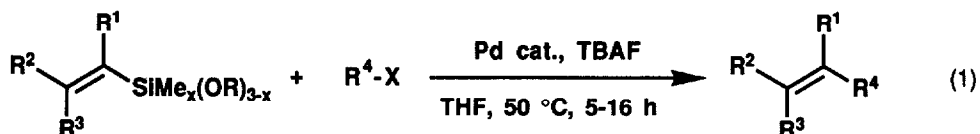
$$R^2\!\!\diagdown\!\!\underset{R^3}{\overset{R^1}{\diagup}}\!\!\diagdown SIMe_x(OR)_{3-x} \; + \; R^4\text{-}X \quad \xrightarrow[\textbf{THF, 50 °C, 5-16 h}]{\textbf{Pd cat., TBAF}} \quad R^2\!\!\diagdown\!\!\underset{R^3}{\overset{R^1}{\diagup}}\!\!\diagdown R^4 \qquad (1)$$

Table 1. Palladium-catalyzed cross-coupling of alkenylalkoxysilanes with C(sp^2)-halides[a]

entry	alkenylalkoxysilane	halide	reaction time (h)	coupling product	yield (%)[b]
		1-Np-I[c]			
1	SIX$_3$ = SiMe$_2$(OEt)		5		95
2	SIX$_3$ = SiMe(OEt)$_2$		5		96
3	SIX$_3$ = Si(OEt)$_3$		5		54
4	SiMe(OEt)$_2$	Ph-I	5		90
5		I-C$_6$H$_4$-COMe	5		77
6		Br-CH=CH-Ph	16		73
7		I-CH=CH-C$_4$H$_9$	6		45
8	SiMe(O-i-Pr)$_2$	Br-CH=CH-Ph	16		71
9		1-Np-I[c]	5		91
10		Br-C(=CH$_2$)-CH$_2$Ph	12		31
11	SiMe(OEt)$_2$	Br-CH=CH-Ph	16		63
12	SiMe$_2$(O-i-Pr)	1-Np-I[c]	7		79 (Z/E = 95/5)
13	SiMe(OEt)$_2$	I-thiophene	7		77 (Z/E = 91/9)

[a] A mixture of an alkenylsilane, a halide (1.1 equiv), TBAF (1.5 equiv), [PdCl(η^3-C$_3$H$_5$)]$_2$ (2.5 mol%), and P(OEt)$_3$ (5 mol%) in THF was heated at 50 °C under nitrogen. [b] Isolated yield. E or E,E > 99%, unless otherwise stated. [c] 1-Iodonaphthalene.

Representative results are listed in Table 1. A general procedure is given for the coupling of (*E*)-5-(diethoxymethylsilyl)-5-decene with 1-iodonaphthalene (entry 2). To a mixture of [PdCl(η^3-C$_3$H$_5$)]$_2$ (4.6 mg; 0.0125 mmol), P(OEt)$_3$ (4.3 μL; 0.025 mmol), and dry THF (1 mL) were added successively 1-iodonaphthalene (140 mg; 0.55 mmol), TBAF (1.0 M THF solution, 0.75 mL), and the alkenylsilane (136 mg; 0.5 mmol) at 0 °C. The mixture was stirred at 50 °C for 5 h under nitrogen. After cooling to room temperature, the mixture was diluted with ether, stirred under air for 15 min, and filtered through a thin Celite/SiO$_2$ pad. The filtrate was concentrated and subjected to preparative TLC (SiO$_2$, hexane, R$_f$ 0.58) to give 128 mg (96% yield) of (*E*)-5-(1-naphthyl)-5-decene.[6]

Several points deserve comment. (1) Alkenyl-monoalkoxy, dialkoxy and trialkoxy silanes all undergo coupling smoothly (entries 1-3). A considerable reactivity of alkenyl*trialkoxysilanes* makes a sharp contrast to inertness of alkenyl*trifluorosilanes* as reported previously.[4b] (2) In addition to linear internal and terminal alkenylalkoxysilanes (entries 4-10), a cyclic alkenylsilane (entry 11) and *Z* exocyclic silyldienes[1a] (entries 12 and 13) can undergo coupling. (3) Alkenyl bromides, as well as alkenyl and aryl iodides, can be used, although prolonged reaction times are required. (4) Olefin geometry is highly retained in all cases except the *Z* silyldienes in which some loss of stereochemistry is observed (entries 12 and 13). (5) Catalytic activities are not largely dependent upon the nature of palladium complexes; comparable activities have been observed with [PdCl(η^3-C$_3$H$_5$)]$_2$ alone or together with P(OEt)$_3$ or PPh$_3$, with Pd(OAc)$_2$/P(OEt)$_3$, and with Pd$_2$(dba)$_3$·CHCl$_3$/ Ph$_2$P(CH$_2$)$_4$PPh$_2$.

Scheme 1
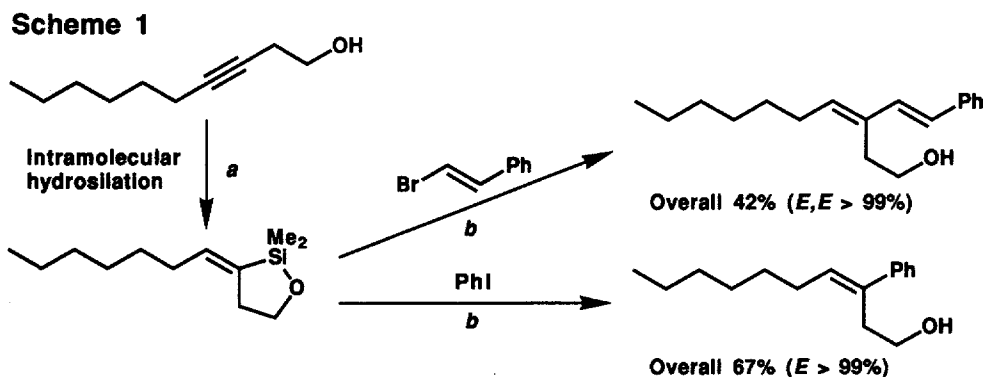
^{a} (1) (HMe$_2$Si)$_2$NH, (2) H$_2$PtCl$_6$·6H$_2$O (cat.), CH$_2$Cl$_2$, room. temp.
^{b} TBAF (x1.5), [PdCl(η^3-C$_3$H$_5$)]$_2$ (2.5 mol%), P(OEt)$_3$ (5 mol%), THF, 50 °C, 12-16 h.

The synthetic utility of the present coupling reaction of alkenylalkoxysilanes may further be well demonstrated by the one-pot transformation of a homopropargyl alcohol to regio- and stereo-defined trisubstituted homoallyl alcohols, as shown in Scheme 1. Thus, the homopropargyl alcohol can be converted to a cyclic alkenylalkoxysilane by the platinum-catalyzed intramolecular hydrosilation,[5a] which is directly subjected to the present palladium-

catalyzed cross-coupling reaction. Obviously, such an efficient transformation is impossible with alkenyl-trimethylsilanes or fluorosilanes.[7]

The present development may thus enhance the synthetic utility of the palladium-catalyzed coupling reaction of alkenyl-silicon compounds.

References and Notes

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6. ^{1}H NMR (200 MHz, CDCl3) δ ppm: 0.85 (t, J = 6.7 Hz, 3H), 0.99 (t, J = 6.7 Hz, 3H), 1.24~1.35 (m, 4H), 1.42~1.55 (m, 4H), 2.32 (q, J = 7.3 Hz, 2H), 2.54 (t, J = 7.0 Hz, 2H), 5.47 (t, J = 7.3 Hz, 1H), 7.21~7.29 (m, 1H), 7.34~7.52 (m, 3H), 7.69~7.78 (m, 1H), 7.80~7.91 (m, 1H), 7.95~8.07 (m, 1H).

7. The procedure may be compared with one-pot procedures for coupling of alkenyl-boron or aluminum reagents derivable from acetylenes by hydroboration, hydroalumination or carbometalation.[2c,2g] Negishi, E. *Acc. Chem. Res.* **1987**, *20*, 65.