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Nickel-Catalyzed Regio- and Stereoselective Silylation of Terminal Alkenes with Silacyclobutanes: Facile Access to Vinylsilanes from Alkenes

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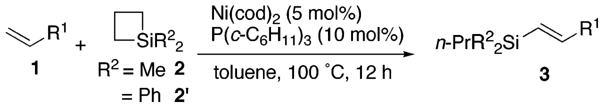
Vinylsilanes constitute an important class of compounds in organosilicon chemistry and in organic synthesis. Transition-metal-catalyzed hydrosilylation[1] and silylmetalation[2] are common routes to vinylsilanes from alkynes. However, the reactions of terminal alkynes often encounter difficulty in controlling regio- and stereoselectivity of the reaction.[3] On the other hand, dehydrogenative silylation of alkenes with hydrosilanes is an attractive alternative to the reactions mentioned above since vinylsilanes can be synthesized from alkenes in a highly regio- and stereoselective fashion. Although iron,[4] ruthenium,[5] cobalt,[6] and rhodium[7] complexes are known to catalyze the dehydrogenative silylation of alkenes with hydrosilanes, the substrates were still limited to activated alkenes such as α,β-unsaturated esters, styrenes, and 1,5-dienes. Moreover, the dehydrogenative silylations required a large excess of alkenes because the alkenes were hydrogen acceptors as well as substrates to be silylated.

Silacyclobutanes are interesting compounds that have unique reactivity based on their ring strain and Lewis acidity.[8] Therefore, our group[9] and others[10] have developed their synthetic utilities. During the course of our recent studies on the reactivity of silacyclobutanes under nickel catalysis,[11] we have now found nickel-catalyzed silylation of alkenes with silacyclobutanes. The silylation provides a new and efficient protocol for regio- and stereoselective synthesis of (*E*)-vinylsilanes from a variety of terminal alkenes.

Treatment of benzyl acrylate (**1a**) and 1,1-dimethylsilacyclobutane (**2**) in the presence of 5 mol % of Ni(cod)$_2$ and 10 mol % of P(c-C_6H_{11})$_3$ in toluene at 100 °C provided benzyl (*E*)-3-(dimethylpropylsilyl)acrylate (**3a**) in 95% yield with high regio- and stereoselectivities (Table 1, entry 1).[12] The reaction of **1a** with 1,1-diphenylsilacyclobutane (**2′**) proceeded without any difficulties to give **3a′** in 95% yield despite its increased steric hindrance (entry 2). Sterically demanding ester **1b** smoothly underwent the silylation (entry 3). The silylation of α,β-unsaturated amide **1c** resulted in good yield, albeit the product was obtained as a mixture of stereoisomers (entry 4). Styrene derivatives were converted to the corresponding silylated products in high yields with high regio- and stereoselectivity except for electron-deficient **1g** (entries 5−8). A pyridine ring did not prevent the reaction (entry 9). It is worth noting that simple aliphatic terminal alkenes **1i**−**l** participated in the reaction (entries 10−13). Moreover, silyl, siloxy, and ester moieties were tolerated under the reaction conditions.

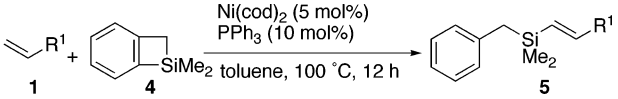
Table 1. Silylation with Dimethyl- or Diphenylsilacyclobutane[a]



entry	1	R^1	3	yield (%), *E*/*Z*[b]
1	**1a**	CO_2CH_2Ph	**3a**	95, >99:1
2[c]	**1a**	CO_2CH_2Ph	**3a′**	95, >99:1
3[c]	**1b**	CO_2*t*-Bu	**3b′**	95, >99:1
4[d,e]	**1c**	$CONEt_2$	**3c**	82, 88:12
5	**1d**	Ph	**3d**	98, >99:1
6	**1e**	2-MeC_6H_4	**3e**	99, >99:1
7	**1f**	4-MeOC_6H_4	**3f**	93, >99:1
8	**1g**	4-$CF_3C_6H_4$	**3g**	trace
9[d]	**1h**	2-pyridyl	**3h**	71, >99:1
10	**1i**	n-$C_{12}H_{25}$	**3i**	93, >99:1
11[d,f]	**1j**	CH_2SiMe_2Ph	**3j**	82, >99:1
12[d]	**1k**	$(CH_2)_9OSi$*t*-$BuMe_2$	**3k**	93, >99:1
13[d]	**1l**	$(CH_2)_9OCO$*t*-Bu	**3l**	81, >99:1

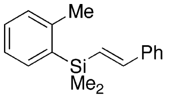
[a] A mixture of Ni(cod)$_2$ (0.025 mmol), P(c-C_6H_{11})$_3$ (0.050 mmol), **1** (0.50 mmol), and **2** (0.60 mmol) was heated at 100 °C in toluene (5.1 mL) for 12 h. [b] Isolated yields. *E*/*Z* ratios were determined by ^{1}H NMR. [c] Silacyclobutane **2′** was used instead of **2**. [d] With 1.0 mmol of **2**. [e] Reaction time was 15 h. [f] Reaction time was 8 h.

Table 2. Silylation with Benzene-Fused Silacyclobutane **4**[a]

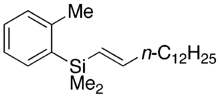


entry	1	R^1	5	yield (%), *E*/*Z*[b]
1	**1d**	Ph	**5d**	64, >99:1[c,d]
2[e,f]	**1i**	n-$C_{12}H_{25}$	**5i**	80, 70:30[c,g]
3	**1m**	(*E*)-(CH═CH)Ph	**5m**	70, 83:17
4	**1n**	(*E*)-(CH═CH)(1-Np)	**5n**	88, 94:6

[a] A mixture of Ni(cod)$_2$ (0.025 mmol), PPh_3 (0.050 mmol), **1** (0.50 mmol), and **4** (0.60 mmol) was heated at 100 °C in toluene (5.1 mL) for 12 h. [b] Isolated yields. *E*/*Z* ratios were determined by ^{1}H NMR. [c] ^{1}H NMR yield. [d] Dimethyl(2-methylphenyl)[(*E*)-2-phenylethenyl]silane (**6d**) was also obtained in 8% yield. [e] P(c-C_6H_{11})$_3$ was used instead of PPh_3. [f] With 1.0 mmol of **4**. [g] Dimethyl(2-methylphenyl)[(*E*)-1-tetradecenyl]silane (**6i**) was also obtained in 12% yield.



6d

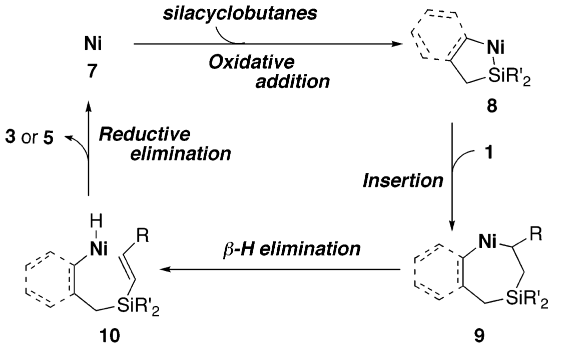


6i

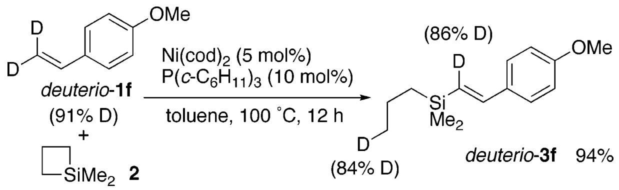
Notably, the benzene-fused silacyclobutane **4** was also the suitable silylating agent (Table 2). In the reaction with **4**, Ni(cod)$_2$/2PPh$_3$ catalyst system generally gave the better results. Styrene (**1d**) reacted with **4** to furnish the benzyldimethylsilyl-substituted styrene **5d** regio- and stereoselectively (entry 1). The palladium-catalyzed Hiyama cross-coupling reaction of **5d** with aryl halides would be available according to the reported procedures.[13] Unfortunately, the reaction of **1i** with **4** furnished the silylated product **5i** with moderate stereoselectivity (entry 2). Conjugated 1,3-dienes also took part in the reaction. While the silylation of (*E*)-1-phenyl-1,3-butadiene (**1m**) took place to produce the corresponding silane **5m** in good yield, **5m** comprised an 83:17 mixture of (*E*) and (*Z*) isomers (entry 3). A 1-naphthyl (1-Np) substitution led to the improvement of stereoselectivity (entry 4). As described above, the dienes obtained could be further converted to the corresponding asymmetrical 1,4-diaryl-1,3-dienes under palladium catalysis.[13]

10.1021/ja070938t CCC: $37.00

Scheme 1. Plausible Mechanism



Scheme 2



We are tempted to assume the reaction mechanism for the silylation of alkenes with silacyclobutanes as follows (Scheme 1). Initial oxidative addition of silacyclobutanes to zerovalent nickel species **7** followed by insertion of alkene **1** to the Si−Ni bond of **8** gives the nickelasilacycle **9**.[14] In the case of the benzene-fused silacyclobutane **4**, the oxidative addition of sp^{2}C−Si bond to Ni(0) is preferable to that of the benzylic sp^{3}C−Si bond.[15] Subsequent β-H elimination[16] followed by reductive elimination produces **3** or **5** along with the starting zerovalent nickel complex to complete the catalytic cycle. The result of the silylation of deuterio-**1f** was consistent with our plausible mechanism (Scheme 2).

In conclusion, we have found the efficient nickel catalyst system for silylation of terminal alkenes with silacyclobutanes. The reaction provides a facile and straightforward access to vinylsilanes from terminal alkenes in a highly regio- and stereoselective fashion. Further studies to improve the catalytic turnover and frequency parameter are currently underway.

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Supporting Information Available: Experimental details, characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The oxidative addition of the benzylic sp^3 C−Si bond to Ni(0) would cause the formations of **6d** and **6i** (Table 2, entries 1 and 2) (see Supporting Information for details).

(16) The β-H elimination in a similar seven-membered palladasilacycle was suggested (see ref 9d).

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