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# Palladium/$Me_3SiOTf$-Catalyzed Bis-silylation of α,*β*-Unsaturated Carbonyl Compounds without Involving Oxidative Addition of Disilane

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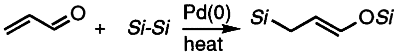
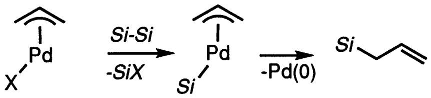
The conjugate silylation of enone has been studied well, which can be classified into two reactions. One is the stoichiometric conjugate addition of silyl anion to enones,[1] and the other is the palladium-catalyzed reaction of disilane with enones to give $\gamma$-siloxyallylsilane (Scheme 1).[2,3] Oxidative addition of disilanes is suggested to be a crucial process in the palladium-catalyzed bis-silylation of the unsaturated bond.[4] The requirement of the reactive disilanes and heating conditions in Scheme 1 would be due to the hardness of the oxidative addition. Thus, the construction of catalytic bis-silylation of α,*β*-unsaturated carbonyl compounds, which does not proceed via oxidative addition of disilane, would expand the scope of bis-silylation of the unsaturated bond. As a new method to this goal, we envisaged the silylation of the $\eta^3$-siloxyallylpalladium complex with disilane to give the desired product under milder conditions, because the reaction of the $\eta^3$-allylpalladium intermediate with disilane has been known to give allylsilanes rather facilely (Scheme 2).[5] Efficient generation of $\eta^3$-siloxyallylpalladium is then the key to the new catalytic conjugate silylation. We searched for suitable conditions to generate $\eta^3$-siloxyallylpalladium by referring to the reaction of Lewis acid with $\eta^2$-enonepalladium complex leading to the formation of zwitterionic $\eta^3$-metalloxyallylpalladium complexes.[6,7] Here, we report the palladium/$Me_3SiOTf$-catalyzed addition of disilane to α,*β*-unsaturated carbonyl compounds via $\eta^3$-siloxyallylpalladium generated by the reaction of enone, enal, or aromatic aldehyde with palladium and $Me_3SiOTf$.

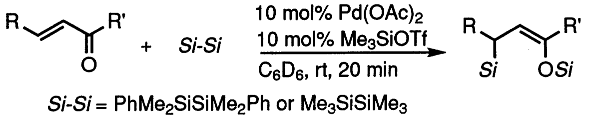
**Scheme 1**



**Scheme 2**

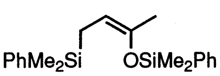


In the presence of 10 mol % of $Me_3SiOTf$ and $Pd(OAc)_2$, the reaction of methyl vinyl ketone with diphenyltetramethyldisilane proceeded very rapidly and cleanly in 20 min to give the expected 1,4-bis-silylation product quantitatively (eq 1).[8,9] In the absence of Pd catalyst or $Me_3SiOTf$, the reaction did not occur at all. Other enones and enals also reacted with disilane under the same condition to give the corresponding conjugate addition products. The hydrolysis of the conjugate silylation products gave *β*-silyl ketones, of which structures were confirmed by the comparison of the NMR spectra with those of the authentic samples.[3] An alternative precursor ($\eta^3$-allyl)PdCp in 3 mol % was also effective for the isolation of the *β*-silylcarbonyl compound.[10] As compared with the reported transition metal-catalyzed conjugate silylation,[2,3] this reaction proceeds much more rapidly under very mild conditions. Thus, the conjugate addition product of methyl vinyl ketone or acrolein (**1**, **2**) was obtained quantitatively, which had previously been prepared in poor to modest yields. Furthermore, both diphenyltetramethyldisilane and even hexamethyldisilane can be employed in this reaction, while the reported palladium-catalyzed reaction of disilanes with enones required more active halogenated disilanes.

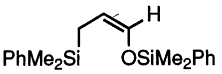


(1)

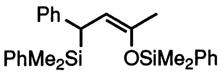
*Si-Si* = $PhMe_2SiSiMe_2Ph$ or $Me_3SiSiMe_3$



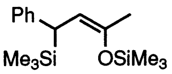
**1** 99% (95%)
(E/Z = 69/31)



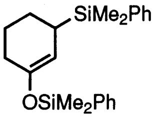
**2** 99%
(E/Z = 58/42)



**3** 40%
(E/Z = 30/70)



**4** 99% (95%)
(E/Z = 18/82)

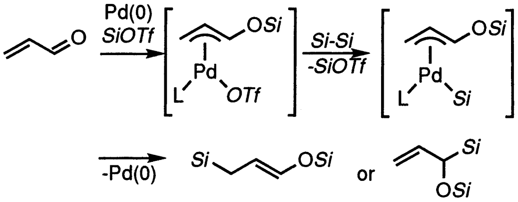


**5**
99% (85%)

The reaction would proceed as shown in Scheme 3. The electrophilic addition of $Me_3SiOTf$ to $\eta^2$-enonepalladium leads to the formation of $\eta^3$-siloxyallylpalladium intermediates followed by transmetalation of disilane with $\eta^3$-siloxyallylpalladium intermediates to regenerate $Me_3SiOTf$.[11] Thus, only a catalytic amount of $Me_3SiOTf$ was required. The reductive elimination then occurs to give the conjugate addition products and regenerate palladium(0) species. In this reaction, even symmetrical disilanes can be employed, which is similar to the formation of allylsilanes via $\eta^3$-allylpalladium(II) species as depicted in Scheme 2.

The addition of $PPh_3$ suppressed the reaction completely possibly due to the formation of unreactive complex.[12] In fact, a stoichiometric reaction of $Pd(\eta^2\text{-}RCH{=}CHCHO)(PPh_3)_2$ (R = H or Ph) with $Me_3SiOTf$ gave ($\eta^3$-1-siloxyallyl)palladium complex (**6**, **7**) quantitatively, which did not react with disilane at room temperature (eq 2).[13] In the absence of $PPh_3$, more reactive $\eta^3$-siloxyallylpalladium would be generated.

**Scheme 3**



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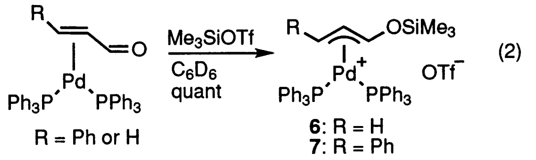
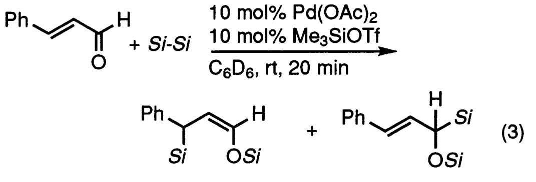


R = Ph or H

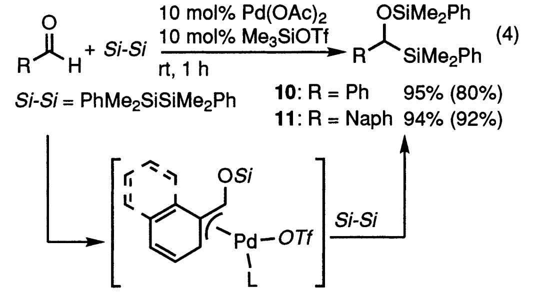
**6**: R = H
**7**: R = Ph

The reaction of cinnamaldehyde gave a mixture of 1,4- and 1,2-addition products (**8**, **9**) (eq 3), which is consistent with the reaction path via the $\eta^3$-allylpalladium intermediate in Scheme 3. Moreover, this reaction leading to **9** could be extended to benzaldehyde or naphthaldehyde to give the 1,2-addition product (**10**,[14] **11**[15]) in excellent yield where the $\eta^3$-siloxybenzylpalladium intermediate may be generated (eq 4). Equation 4 is the first example of the addition of the Si−Si bond of acyclic disilanes across the carbon−oxygen double bond. So far, only the reaction of strained four-membered cyclic disilanes with the carbonyl compound in the presence of Ni, Pd, or Pt catalyst had been reported.[16]



**8** **9**

*Si-Si* = $PhMe_2SiSiMe_2Ph$
9% (E/Z = 0/100) 65% (E/Z = 100/0)
*Si-Si* = $Me_3SiSiMe_3$
40% (E/Z = 52/48) 52% (E/Z = 100/0)



*Si-Si* = $PhMe_2SiSiMe_2Ph$

**10**: R = Ph 95% (80%)
**11**: R = Naph 94% (92%)

Yield including the trimethylsiloxy product
Isolated yield of β-silylketone in parenthesis

In summary, we demonstrated that the $Me_3SiOTf$/palladium catalyst system is very efficient for the addition of disilanes to enones and enals including aryl aldehydes via the $\eta^3$-siloxyallylpalladium intermediate, which allows us to employ methyl vinyl ketone and acrolein as a substrate and unreactive disilanes as a silylation reagent. The present reaction without involving the oxidative addition of disilane is a very new method to introduce two silyl groups into the unsaturated bond. Further studies of this theme are ongoing in our group.

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(8) Typical procedure for **4**: To a solution of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), benzalacetone (36.6 mg, 0.25 mmol), hexamethyldisilane (43.9 mg, 0.30 mmol), and toluene (internal standard) (23.0 mg, 0.25 mmol) in 0.5 mL of $C_6D_6$ was added $Me_3SiOTf$ (5.6 mg, 0.025 mmol). The reaction was followed by NMR.

(9) The reaction was not catalyzed by $Ni(cod)_2$ in the presence of $Me_3SiOTf$, although $Ni(cod)_2$ catalyzed the conjugate addition of organotin compounds to enone in the presence of a stoichiometric amount of $Me_3SiCl$.[7]

(10) Isolation of hydrolysis product of **4**: To a solution of ($\eta^3$-allyl)PdCp (6.4 mg, 0.03 mmol (3 mol %)), benzalacetone (146.2 mg, 1.0 mmol), and hexamethyldisilane (175.7 mg, 1.2 mmol) in 0.5 mL of benzene was added $Me_3SiOTf$ (6.7 mg, 0.03 mmol). The reaction mixture was stirred for 1 h and concentrated in vacuo. The residue was separated by column (silica gel) to give the corresponding $\beta$-silyl ketone (209.9 mg, 95%).[3]

(11) The reaction of enone with $Me_3SnSnMe_3$ under the same condition did not occur.

(12) The stoichiometric reaction of $\eta^3$-allylpalladium with disilanes had been reported, in which the addition of $PPh_3$ suppressed the transmetalation with disilanes. Macsári, I.; Hupe, E.; Szabó, K. J. *J. Org. Chem.* **1999**, *64*, 9547.

(13) Selected spectral data for **6**: $^1H$ NMR (270 MHz, $C_6D_6$) $\delta$ −0.19 (s, 9H), 3.08 (ddd, $J_{HH}$ = 7.5, 2.5 Hz, $J_{HP}$ = 7.7 Hz, 1H), 3.72 (ddd, $J_{HH}$ = 12.5, 2.5 Hz, $J_{HP}$ = 9.5 Hz, 1H), 4.95 (ddd, $J_{HH}$ = 7.7, 12.5, 10.5 Hz, 1H), 6.90−7.56 (m, 30H), 7.96 (dd, $J_{HH}$ = 10.5 Hz, $J_{HP}$ = 9.5 Hz).$^{13}C$ NMR (67.9 MHz, $CDCl_3$) $\delta$ 62.7 (dd, $J_{CP}$ = 1.6, 26.9 Hz), 104.8 (dd, $J_{CP}$ = 4.4, 5.6 Hz). The resonance of the other allyl carbon is hidden by the resonance of Ph groups. $^{31}P$ NMR (109 MHz, $C_6D_6$) $\delta$ 25.63 (d, $J_{PP}$ = 35.6 Hz), 26.59 (d, $J_{PP}$ = 35.6 Hz). **7**: $^1H$ NMR (270 MHz, $C_6D_6$) $\delta$ −0.13 (s, 9H), 5.39 (dd, $J_{HH}$ = 11.5 Hz, $J_{HP}$ = 10.4 Hz, 1H), 5.51 (dd, $J_{HH}$ = 11.5, 9.7 Hz, 1H), 6.62−7.42 (m, 35H), 8.47 (dd, $J_{HH}$ = 9.7 Hz, $J_{HP}$ = 8.9 Hz).$^{13}C$ NMR (67.9 MHz, $C_6D_6$) $\delta$ 77.4 (dd, $J_{CP}$ = 5.5, 27.5 Hz), 102.4 (dd, $J_{CP}$ = 4.7, 6.9 Hz), 136.8 (dd, $J_{CP}$ = 3.4, 7.0 Hz). $^{31}P$ NMR (109 MHz, $C_6D_6$) $\delta$ 25.33 (d, $J_{PP}$ = 42.8 Hz), 27.53 (d, $J_{PP}$ = 42.8 Hz).

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(15) Isolation of hydrolysis product of **11**: To a solution of $Pd(OAc)_2$ (22.4 mg, 0.1 mmol), naphthaldehyde (156.2 mg, 1.0 mmol), and diphenyltetramethyldisilane (324.6 mg, 1.2 mmol) in 0.5 mL of benzene was added $Me_3SiOTf$ (22.2 mg, 0.1 mmol). The reaction mixture was stirred for 1 h. The reaction mixture was added to 0.01 N HCl solution in 2 mL of EtOH(95%), and the mixture was stirred for 12 h. To the mixture was added 50 mg of $NaHCO_3$, and the solvent was removed in vacuo. The concentrate was stirred for 18 h and separated by column (silica gel, EtOAc/hexane = 1/20) to give the corresponding alcohol (267.7 mg, 92%). Spectral data for the hydrolysis product of **11**: $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 0.21 (s, 3H), 0.31 (s, 3H), 1.75 (s, 1H), 5.62 (s, 1H), 7.28−7.86 (m, 12H). $^{13}C$ NMR (67.9 MHz, $CDCl_3$): $\delta$ −5.8, −4.4, 65.9, 122.9, 123.6, 125.1, 125.4, 125.6, 126.3, 127.8, 128.7, 129.5, 130.0, 133.5, 134.4, 136.3, 140.0.

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