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Palladium-Catalyzed Silylation of Allylic Acetates with Hexamethyldisilane or (Trimethylsilyl)tributylstannane

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Summary: Various allylic acetates (**1a-j**) are silylated with hexamethyldisilane ($Me_3SiSiMe_3$, **2**) in the presence of a catalytic amount of $Pd(DBA)_2$ and LiCl at 100 °C to afford the corresponding allylic silanes in high yields. In addition, (trimethylsilyl)tributylstannane ($Me_3SiSnBu_3$, **3**) can be used for the silylation of aromatic allylic acetates **1g-j** at room temperature.

Allylic silanes are highly versatile synthetic intermediates and have a large number of applications in organic synthesis.[1] Therefore, much attention has been paid to methods for the synthesis of allylic silanes, which include allylic Grignard reactions,[2] hydrosilylations of 1,3-dienes,[3] and Wittig reactions with β-silylethylidenephosphorane.[4]

Allylic acetates are now recognized as potent allylic sources, particularly in the presence of transition-metal catalysts.[5] Many studies have focused on synthetic uses of allylic acetates and on the mechanism of the allylation reaction. Silylation of allylic acetates is expected to be a promising method for the preparation of allylic silanes. To date, a few silylation reactions have been attempted with allylic acetates. Fleming and his colleagues employed dimethylphenylsilyl cuprates with tertiary[6a] and secondary[6b] allylic acetates to obtain the corresponding allylic silanes. Trost and co-workers explored palladium- and molybdenum-catalyzed silylations of allylic acetates with tris(trimethylsilyl)aluminum (($(Me_3Si)_3Al$·etherate) as the silylating reagent.[7] However, the former reaction[6] did not utilize trimethylsilyl cuprate or primary allylic acetates, and the latter one[7] often suffered from low regioselectivity. Hexamethyldisilane ($Me_3SiSiMe_3$, **2**) may be one of the most accessible alternative silylation reagents. Suzuki *et al.* used **2** in the palladium ($Pd(PPh_3)_4$)-catalyzed silylation of allylic acetates.[8] Unfortunately, this potentially useful reaction is not applicable to allylic acetates that have a primary or secondary alkyl group at the γ- or α-position of the allylic moiety. The failure of the reaction with these substrates indicates that the π-allyl palladium intermediates[5] readily decomposed by β-hydrogen elimination.

We have recently developed novel transition metal-catalyzed silylation and stannation reactions that proceed via activation of Si–Sn,[9a] Sn–Sn,[9b] and Si–Si[9c,d] σ-bonds. During the course of these studies, we found a new reactivity for $Me_3SiSiMe_3$ (**2**). In this paper, we wish to report the first general method for the silylation of allylic acetates (**1**) with $Me_3SiSiMe_3$ (**2**).[10] By carefully tuning the catalyst system, we were able to silylate various allylic acetates by using **2**. Furthermore, with the same catalyst system used for **2**, (trimethylsilyl)tributylstannane ($Me_3SiSnBu_3$, **3**) was found to be a reactive silylating reagent for **1** even at room temperature. Although the synthetic utility of organosilylstannanes is of current interest,[9a,12] there is no precedent for silylation of **1** with the organosilylstannanes, including **3**.

The results obtained with $Me_3SiSiMe_3$ (**2**) are listed in Table I. Two equiv of **2** smoothly reacted with allylic acetates (**1**) in the presence of $Pd(DBA)_2$ (DBA = dibenzylideneacetone)[13] and LiCl at 100 °C. No reaction occurred at room temperature. Notably, aliphatic and alicyclic allylic acetates such as **1a-f** were readily silylated to give the corresponding allylic silanes (**4**) in high isolated yields with good regioselectivity (entries 1-6). Under the conditions used by Suzuki *et al.*,[8] these substrates could not be used because of the β-hydrogen elimination of the π-allyl palladium intermediates (vide supra). Thus, the present reaction is the first general method for the silylation of the allylic acetates with **2** and provides a new method for the synthesis of allylic silanes. Aromatic allylic acetates (**1g-j**) also afforded the corresponding allylic silanes in high yields.

The added chloride salt, LiCl, was necessary for the reaction. Without the salt, no reaction occurred. Varying the amount of LiCl had only a small effect; yields of **4f** from **1g** were 92% with 0.5 equiv of LiCl (entry 7), 86% with 1.0 equiv, and 83% with 5.0 equiv. Other salts (4 equiv) could replace LiCl; yields of **4f** from **1g** were 92%

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(10) There were precedents for the synthesis of allylic silanes using $Me_3SiSiMe_3$ (**2**). Matsumoto *et al.* reported the palladium-catalyzed silylation of allylic halides with **2**.[11a] However, they employed only substrates that gave π-allyl palladium intermediates that were unable to undergo the β-hydrogen elimination. Hwu and co-workers used **2** and a stoichiometric amount of MeLi for the silylation of allylic alcohols.[11b]

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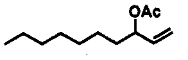
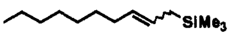
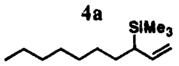
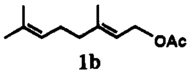
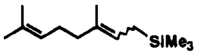
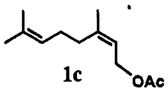
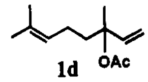
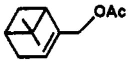
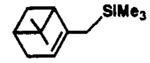
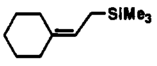
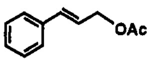
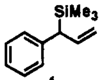
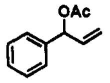
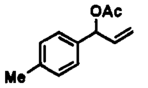
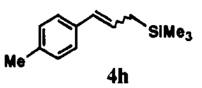
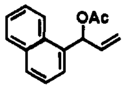
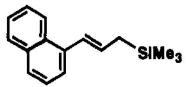
Table I. Silylation of Allylic Acetates (1) with $Me_3SiSiMe_3$ (2)[a]

entry	allylic acetate (1)	product (4)	yield[b]/ %	*E/Z* ratio
1	 1a	 4a	81	95/5
		 4b	3	-
2	 1b	 4c	78	56/44
3	 1c	4c	74	55/45
4	 1d	4c	97	53/47
5[c]	 1e	 4d	79	-
6[d]	 1f	 4e	62	-
7	 1g	 4f	(92)	96/4
		 4g	(4)	-
8	 1h	4f	(81)	96/4
		4g	(3)	-
9	 1i	 4h	77	95/5
10	 1j	 4i	80	-

[a] Conditions: 1 (1.0 mmol), 2 (2.0 mmol), LiCl (0.50 mmol), $Pd(DBA)_2$ (0.040 mmol), DMF (3.8 mL), at 100 °C, for 40 h. [b] Isolated yields. Numbers in parentheses show GLC yields determined by an internal standard method. [c] At 120 °C. [d] For 8 h.

with NaCl, 90% with KCl, 47% with KBr, and 15% with LiI. No allylic silanes were obtained with fluoride salts such as LiF, KF, and CsF. The reaction also proceeded similarly in diglyme, but no reaction took place in toluene.

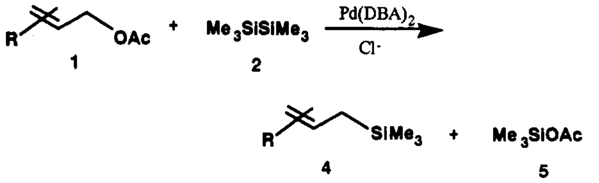
The fate of the trimethylsilyl group in the reaction was determined by ^{29}Si-NMR in DMF (locked with C_6D_6). After the reaction, the expected amount of trimethylsilyl acetate (5) (21.5 ppm (lit.[14a] 22.0 ppm)) was found along with the excess $Me_3SiSiMe_3$ (2) (−20.5 ppm (lit.[14b] −20.5 ppm)).

Table II. Silylation of Allylic Acetates (1) with $Me_3SiSnBu_3$ (3)[a]

entry	allylic acetates (1)	product (4)	yield[b]/%	*E/Z* ratio
1	1g	4f	81 (84)	97/3
2[c]	1g	4f	(67)	97/3
3[d]	1g	4f	(30)	97/3
4	1h	4f	82	92/8
5	1i	4h	70	99/1
6	1j	4i	91	>99

[a] Conditions: 1 (0.5 mmol), 3 (2.0 mmol), LiCl (2.0 mmol), $Pd(DBA)_2$ (0.025 mmol), DMF (3.5 mL), at rt, for 12 h. [b] Isolated yields. Figures in parentheses show GLC yields determined by an internal standard method. [c] 3 (1.0 mmol). [d] 3 (0.50 mmol).

However, no trace of Me_3SiCl (lit.[14c] 30.2 ppm) was detected in the reaction mixture, even in the reaction with 5.0 equiv of LiCl. These observations indicated that stoichiometry of the reaction is that shown in eq 1 and that the added chloride anion does not scavenge a trimethylsilyl group from 2.[15]



(1)

With the same catalyst system used for 2, $Me_3SiSnBu_3$ (3)[9a,12] also could be used as the silylating reagent (Table II).[17] From aromatic allylic acetates (1g-j), the corresponding allylic silanes were obtained in high yields. The silylation reaction proceeded readily and highly regioselectively at room temperature. Again, LiCl was necessary for the catalytic activity. Excess 3 increased the yields (entries 1-3 in Table II), and all the excess 3 was completely converted into hexabutyldistannane ($Bu_3SnSnBu_3$, 6) and 2 after the reaction. It is noteworthy that the reaction gave only the corresponding allylic silanes. No allylic tributylstannanes, which would be obtained by stannation of 1, were detected in the reaction mixtures. The aliphatic allylic acetates (1a-f), by contrast, remained intact under the same reaction conditions, and all the 3 was converted to 6 and 2. The silylation of these aliphatic substrates is slow compared to the matathesis of 3.

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Supplementary Material Available: Experimental details and ^{1}H and ^{13}C NMR and MS spectral data for the products (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(15) It is possible that the added chloride salt reacts with the palladium complex to give a chloropalladate species as shown by eq i. A similar palladate catalyst species has been postulated in the palladium-catalyzed cross-coupling reaction of enol triflates with organostannanes;[16] in this reaction, as in ours, LiCl is required for the catalytic activity.

$$PdL_n + LiCl \xrightarrow{-L} Li^+ [PdL_{n-1}Cl]^- \qquad (i)$$

(16) Scott, W. J.; McMurry, J. E. *Acc. Chem. Res.* **1988**, *21*, 47.

(17) For palladium-catalyzed alkylations of allylic acetates with organostannanes, see: (a) Trost, B. M.; Keinan, E. *Tetrahedron Lett.* **1980**, *21*, 2595. (b) Valle, L. D.; Stille, J. K.; Hegedus, L. S. *J. Org. Chem.* **1990**, *55*, 3019.