Hydrosilylation

International Edition: DOI: 10.1002/anie.201508669
German Edition: DOI: 10.1002/ange.201508669

Borane-Catalyzed Reductive α-Silylation of Conjugated Esters and Amides Leaving Carbonyl Groups Intact

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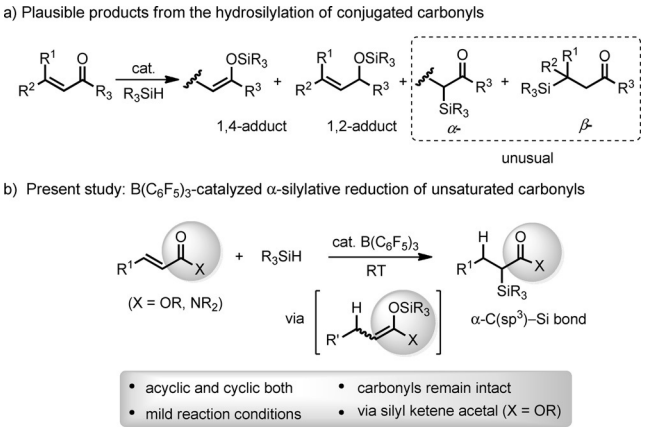
Abstract: *Described herein is the development of the $B(C_6F_5)_3$-catalyzed hydrosilylation of α,β-unsaturated esters and amides to afford synthetically valuable α-silyl carbonyl products. The α-silylation occurs chemoselectively, thus leaving the labile carbonyl groups intact. The reaction features a broad scope of both acyclic and cyclic substrates, and the synthetic utility of the obtained α-silyl carbonyl products is also demonstrated. Mechanistic studies revealed two operative steps: fast 1,4-hydrosilylation of conjugated carbonyls and then slow silyl group migration of a silyl ether intermediate.*

Hydrosilylation of unsaturated bonds with silanes is a straightforward approach to organosilicon compounds, which are widely utilized in organic synthesis as well as medicinal, polymer, and materials chemistry.[1] This method takes advantage of the labile Si–H bond of silanes, bonds which can be activated by either Lewis acids,[2] radical mediators,[3] or transition-metal species.[4] Alkenes and alkynes are representative unsaturated hydrocarbon substrates which react with silanes and lead to the corresponding alkyl- or alkenylsilicon products.[5] Hydrosilylation of unsaturated polar bonds, such as carbonyls, imines, nitriles, or heteroaromatics has been shown to yield heteroatom-containing silyl compounds.[6] The α,β-unsaturated carbonyl compounds containing these two types of functional groups connected, that is an olefin and carbonyl, can bring out an interesting selectivity issue in the hydrosilylation reaction. Indeed, reaction of α,β-unsaturated carbonyls with silanes may lead to four types of silylated molecules: *O*-silyl enol ether (1,4-addition adduct), *O*-silyl allyl ether (1,2-), α-*C*-silyl carbonyl, and β-*C*-silyl carbonyl products (Scheme 1 a). Although there have been efforts made to achieve chemoselective hydrosilylation of α,β-unsaturated esters, only a few examples of α-*C*-silylation are known, and transition-metal catalysts such as Ni, Rh, Pd, or Pt were employed with limited scope and unsatisfactory selectivity.[7] Moreover, no report has been published on the chemoselective hydrosilylation of α,β-unsaturated amides, to the best of our knowledge.



Scheme 1. Selective hydrosilylation of α,β-unsaturated carbonyls.

Piers et al. reported that tris(pentafluorophenyl)borane $B(C_6F_5)_3$ is an efficient catalyst for the hydrosilylation of aryl aldehydes, ketones, and esters.[8] Its applicability to additional types of important substrates such as imines, olefins, carboxylic acids, or nitriles was elegantly demonstrated by several groups.[9] Mechanistic studies illuminated the activation mode of silanes by Lewis-acidic boranes to disclose that a key borane-silane adduct reacts with Lewis-basic substrates.[10] Based on the mechanistic consideration that $B(C_6F_5)_3$-catalyzed hydrosilylation of polar C=X bonds furnishes exclusively a H–CX–[Si] connectivity, reaction of α,β-unsaturated carbonyls is predicted to give O-silylated products, rather than *C*-silylated ones under the borane catalyst system (Scheme 1 a).[11]

Herein, we report the first example of $B(C_6F_5)_3$-catalyzed hydrosilylation of α,β-unsaturated esters and amides to form a valuable α-C(sp^3)–Si bond, thus leaving the labile carbonyl groups intact (Scheme 1 b).[12] Mechanistic studies revealed that the reaction proceeds by two stepwise processes: fast 1,4-hydrosilylation of conjugated carbonyls and a subsequent slow silyl-group migration of a silyl ketene acetal intermediate in the case of ester substrates. The substrate scope is broad and includes both acyclic and cyclic conjugated esters and amides to afford synthetically versatile α-silyl carbonyl compounds.[13]

At the beginning of our study, we wondered if any notable selectivity could be attained from the treatment of ethyl cinnamate (**1b**) with triethylsilane (1.0 equiv) in the presence of the $B(C_6F_5)_3$ catalyst [Eq. (1)]. To our surprise, an α-silyl ester (**2a**) was obtained, with the carbonyl group left intact, after 12 hours at room temperature, albeit in moderate yield.[14] To get some preliminary insight into this interesting chemoselectivity, the reaction progress was briefly monitored

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201508669.

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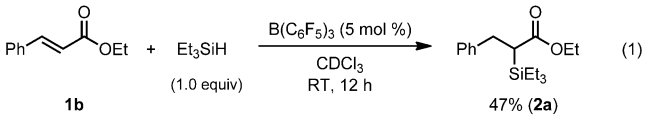
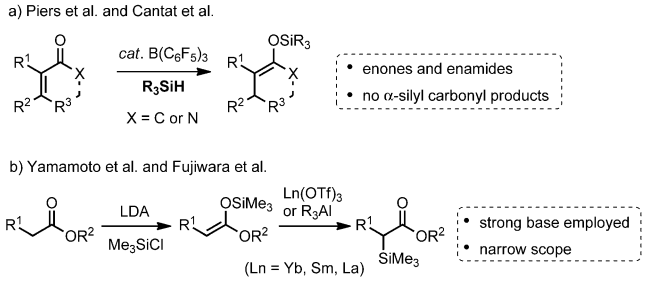


by ^{1}H NMR spectroscopy. This analysis revealed that a silyl ketene acetal intermediate was formed immediately at 25 °C and that the intermediate was observed to convert gradually into **2a** at the same temperature. This result was noteworthy for several reasons: 1) the formation of a new C(sp^3)–Si bond was regio- and chemoselective, thus leaving a labile ester group intact, 2) the $B(C_6F_5)_3$-catalyzed silyl-group migration from a silyl ketene acetal intermediate is unprecedented, and 3) a synthetically valuable α-silyl ester was produced.

Although there are two relevant transformations known, our present result is distinct from such precedents. The groups of Piers and Cantat independently reported that $B(C_6F_5)_3$-catalyzed hydrosilylation of enones and enamides leads to *O*-silyl ethers, but without giving α-*C*-silyl carbonyls, which can be formed by silyl group migration (Scheme 2a).[11] In



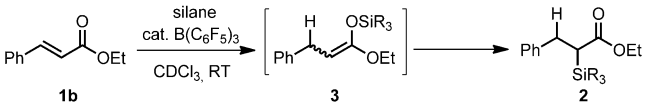
Scheme 2. Relevant previous studies. Tf = trifluoromethanesulfonyl.

addition, although the groups of Yamamoto and Fujiwara independently showed that either lanthanide metals or aluminum can facilitate the silyl group migration, the silyl ketene acetals need to be prepared from the corresponding alkyl esters using a strong base, such as LDA (Scheme 2b).[15] Moreover, the scope of this approach was narrow and no mechanistic details were reported.

The above initial observation prompted us to examine the factors that control the selectivity in the present hydrosilylation of conjugated carbonyls. The influence of silanes on the reaction efficiency was first examined. The initial 1,4-hydrosilylation step to form a silyl ketene acetal intermediate (**3**) was observed to be fast, largely irrespective of silanes tested, while the subsequent silyl group migration was highly dependent upon the silanes (Table 1, and see also the Supporting Information for details). On the basis of the screening experiments, the reactivity trend of silanes examined in the present transformation of ethyl cinnamate (**1b**) into α-silyl esters can be summarized as follows: $Me_2PhSiH \approx MePh_2SiH \gg BnMe_2SiH \approx EtMe_2SiH > Et_3SiH$.

With the above optimized reaction conditions and mechanistic insights in hand, the generality of the present α-silylative conversion was next investigated. A wide range of α,β-unsaturated esters were successfully transformed into the

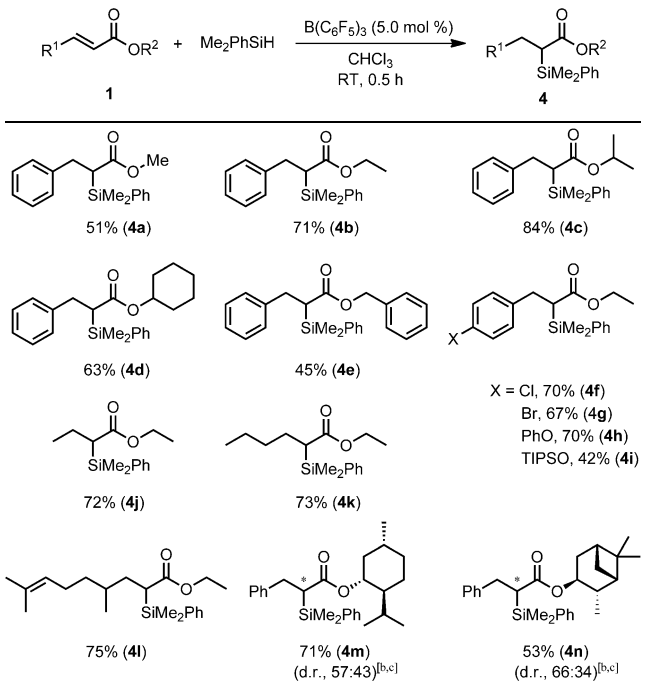
Table 1: Screening of silanes in the silylative reduction.[a]



Entry	Silane	*t*	**3** Yield [%][b]	**2** Yield [%][b]
1	Et_3SiH	5 min	80	6
2		12 h	41	48
3	$EtMe_2SiH$	5 min	67	32
4		12 h	19	79
5	$BnMe_2SiH$	5 min	83	14
6		12 h	18	78
7	$MePh_2SiH$	5 min	18	79
8	**Me_2PhSiH**	**5 min**	**12**	**82**

[a] **1b** (0.20 mmol), silane (0.22 mmol), and catalyst (5 mol%) in $CDCl_3$ (0.5 mL) at 25 °C. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture (internal standard: mesitylene).

Table 2: Substrate scope of α,β-unsaturated esters.[a]



[a] **1** (0.20 mmol), dimethylphenylsilane (0.22 mmol), and catalyst in $CHCl_3$ (0.5 mL) at 25 °C for 0.5 h. Yields are those of the isolated products. [b] Diastereomeric ratio determined by ^{1}H NMR analysis of the crude reaction mixture. [c] For 12 h at 25 °C.

corresponding α-silyl esters in reaction with dimethylphenylsilane (Table 2). The alkoxy moiety of the substrates turned out to be flexible in use, and methyl (**4a**), ethyl (**4b**), isopropyl (**4c**), cyclohexyl (**4d**), and benzyl (**4e**) cinnamates were all smoothly reacted by the action of the $B(C_6F_5)_3$ catalyst (5 mol%) in a short period of time (30 min, 25 °C).[16] The

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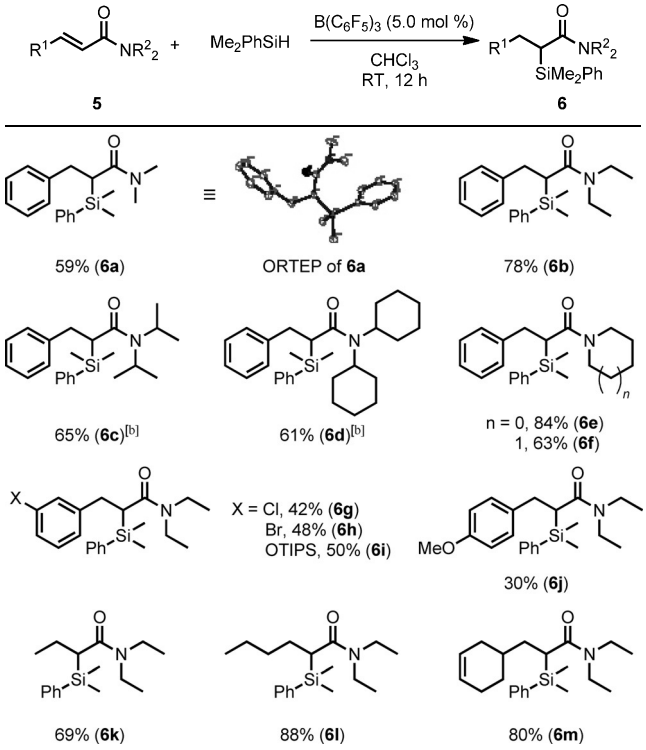
reaction conditions were compatible with various functional groups, including halides (**4f** and **4g**), phenyloxy (**4h**), and silyl ether (**4i**). In addition, the procedure was readily applied to alkyl-substituted α,β-unsaturated esters to furnish the desired α-silyl alkyl carboxylate esters in high yields (**4j** and **4k**). A substrate bearing a remote double bond underwent the desired chemoselective hydrosilylation in good yield without reacting at the isolated olefin (**4l**). When conjugated esters having a chiral alkoxy group were subjected to the reaction conditions, only a moderate level of diastereoselectivity was observed (**4m** and **4n**), although the product yields were still satisfactory.

Subsequently, our attention turned to an important type of substrate: enamides (Table 3). We were pleased to see that

Table 3: Substrate scope of enamides.[a]

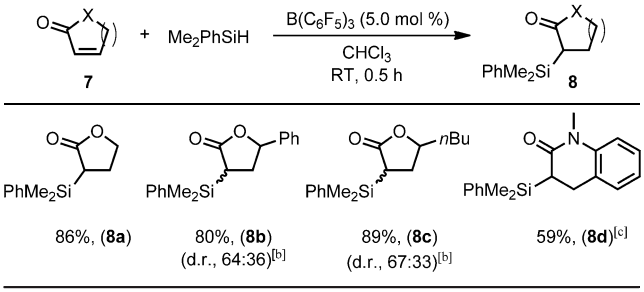


[a] **5** (0.20 mmol), dimethylphenylsilane (0.22 mmol), and catalyst in $CHCl_3$ (0.5 mL) at 25 °C for 12 h. Yields are those of isolated products. [b] For 48 h at 25 °C. Thermal ellipsoids shown at 50% probability.[24]

the same reaction conditions were also successfully applied to enamide substrates to afford α-silyl amides in high to moderate yields, although the reaction was slower than α,β-unsaturated esters. Alternation of the N,N-dialkylamido group did not change the reaction efficiency much, as demonstrated in the reactions of *N*,*N*-dimethyl (**6a**), *N*,*N*-diethyl (**6b**), *N*,*N*-diisopropyl (**6c**), and *N*,*N*-dicyclohexyl (**6d**) amides. The structure of one α-silyl amide product (**6a**) was confirmed by its solid-state X-ray crystallographic analysis. In addition, pyrrolidinyl and piperidinyl enamides were readily hydrosilylated to give the corresponding α-silyl amides (**6e** and **6f**). Functional-group tolerance was observed to be satisfactory as shown in the reaction of α,β-unsaturated amides bearing various labile groups (**6g–j**). Moreover, the same reaction conditions were also adaptable to the α-silylation of alkyl enamides (**6k** and **6l**). Also, an isolated double bond was completely tolerated (**6m**)

We were pleased to see that the present procedure could be applicable to the α-silylation of conjugated lactones and lactams with similar efficiency (Table 4). α-Silyl-γ-butyrolac-

Table 4: α-Silylation of lactones and lactams.[a]

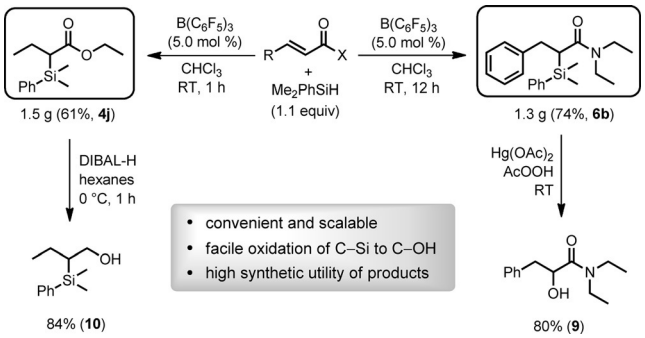


[a] **7** (0.20 mmol), dimethylphenylsilane (0.22 mmol), and catalyst in $CHCl_3$ (0.5 mL) at 25 °C for 0.5 h. Yields are those of isolated products. [b] Diastereomeric ratio determined by ^{1}H NMR analysis of the crude reaction mixture. [c] For 12 h at 25 °C.

tones were obtained from 2-furanones in excellent yields after 30 minutes (**8a–c**). In cases where substituents are present in lactones, the reaction proceeded with moderate diastereoselectivity under the present reaction conditions. In addition, 1-methyl-2(1*H*)-quinolinone was readily converted into its α-silyl lactam in acceptable yield (**8d**).

The present reaction procedure was conveniently performed on large scale, and α,β-unsaturated esters and amides were transformed into their corresponding α-silyl carbonyls adducts in gram quantities (Scheme 3; **4j** and **6b**). Moreover, the silyl group was readily oxidized, according to a known method,[17] to the α-hydroxy amide **9** in good yield.[18] A post-transformation of the obtained α-silyl ester was also successfully demonstrated in the facile reduction of the α-silyl ester **4j** into 1,2-silylalcohol **10**, which has a versatile synthetic utility.[19]

To shed light on the details of the reaction pathway, a series of mechanistic studies were designed (Scheme 4). When a separately prepared silyl ketene acetal (**3a**)[20] was



Scheme 3. Gram-scale reaction with subsequent transformations. DIBAL-H = diisobutylaluminum hydride.

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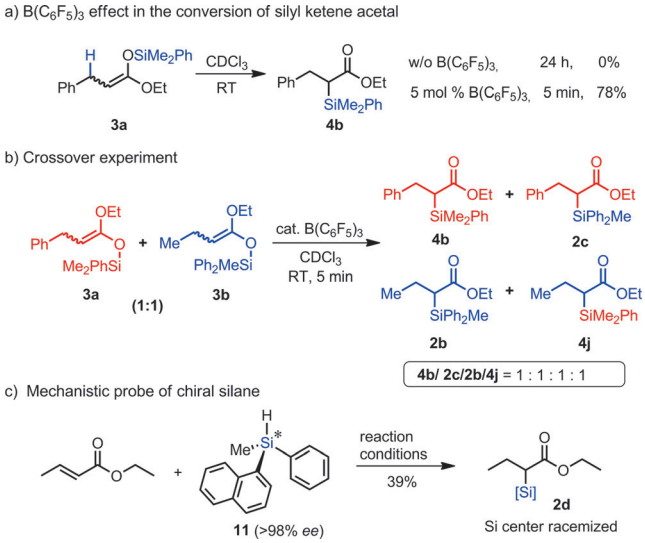

Scheme 4. Mechanistic investigations.

subjected to the reaction conditions, the silyl group migration occurred smoothly only in the presence of the $B(C_6F_5)_3$ catalyst, whereas no conversion was observed without the borane species (Scheme 4a). This result indicates that the borane catalyst is essential in the second stage of the silyl group migration, as well as in the initial 1,4-hydrosilylation step.

When an equimolar mixture of two silyl ketene acetals (**3a** and **3b**) was treated with the $B(C_6F_5)_3$ catalyst, four scrambled α-silyl ester compounds (**4b**, **2c**, **2b**, and **4j**) were obtained with the same ratio within 5 minutes at room temperature (Scheme 4b). This complete crossover outcome implies that the silyl group migration more likely occurs in an intermolecular manner rather than intramolecularly.

A stereochemical outcome can often be used as a mechanistic probe when optically active substrates or reactants are employed under the reaction conditions of interest. Indeed, Oestreich et al. elegantly proved that $B(C_6F_5)_3$-catalyzed hydrosilylation proceeds via a concerted S_N2-type transition state by observing an inversion of the silicon center with the use of an optically active silane.[10b] In our case, when an optically active silane **11** (>98% *ee*), prepared according to the reported procedure,[21] was subjected to the current borane-catalyzed conditions in a reaction with ethyl crotonate, the silicon center of **2d** was determined, by HPLC analysis, to be completely racemized (Scheme 4c). This stereochemical outcome can be interpreted to mean that a silylium ion (R_3Si^+) may be formed during the conversion of the silyl ketene acetal intermediate into the α-silyl ester product since the first step of the silyl ketene acetal formation proceeds by an inversion of the chiral silicon center.[22] However, as recently reported by Oestreich et al.,[23] a pathway via a pentacoordinate silicon cation intermediate cannot be ruled out at the present stage.

On the basis of the initial observation and the above mechanistic studies, a reaction pathway consisting of two tandem processes is proposed. Initially, $B(C_6F_5)_3$-catalyzed 1,4-hydrosilylation leads to a silyl ketene acetal intermediate in cases of conjugated esters. Subsequently, an intermolecular silyl-group migration of this intermediate yields α-silyl carbonyl products, and is assumed to be facilitated by the $B(C_6F_5)_3$ catalyst, presumably either by silylium ion (R_3Si^+) extrusion or through a pentacoordinate silicon cation intermediate.

In summary, we have developed the $B(C_6F_5)_3$-catalyzed silylative reduction of α,β-unsaturated esters and amides to afford synthetically valuable α-silyl carbonyls. Especially significant is the regio- and chemoselective introduction of a $C(sp^3)$–Si bond with the labile carbonyl groups intact. Mechanistic investigations revealed that the reaction takes place by distinct cascade steps mediated by the borane catalyst: fast 1,4-hydrosilylation of α,β-unsaturated carbonyls and a subsequent rate-limiting silyl-group migration of an *O*-silyl ether intermediate.

Acknowledgements

This research was supported by the Institute for Basic Science (IBS-R010-D1). We thank Dr. Jaesung Kwak, Dr. Seewon Joung, Dr. Jeung Gon Kim, and Mr. Yoonsu Park for helpful discussions and Mr. Jinseong Gwak for the XRD analysis.

Keywords: boron · chemoselectivity · conjugation · hydrosilylation · reaction mechanisms

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 218–222
Angew. Chem. **2016**, *128*, 226–230

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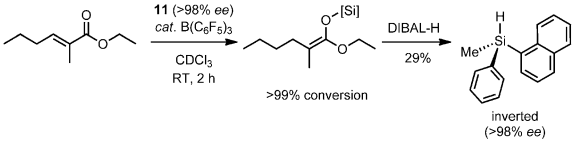
[22] When a silyl ketene acetal intermediate, generated from an optically active silane (**11**), was reduced by DIBAL-H, the silicon center of the recovered silane was completely inverted as determined by HPLC analysis using a chiral stationary phase (see the Supporting Information for details of this experiment).



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[24] CCDC 1424740 (**6a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Received: September 16, 2015
Published online: November 9, 2015

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