J. Am. Chem. Soc. **1993,** *115,* 10414–10415

Palladium-Catalyzed Decarbonylative Coupling of Acid Chlorides, Organodisilanes, and 1,3-Dienes

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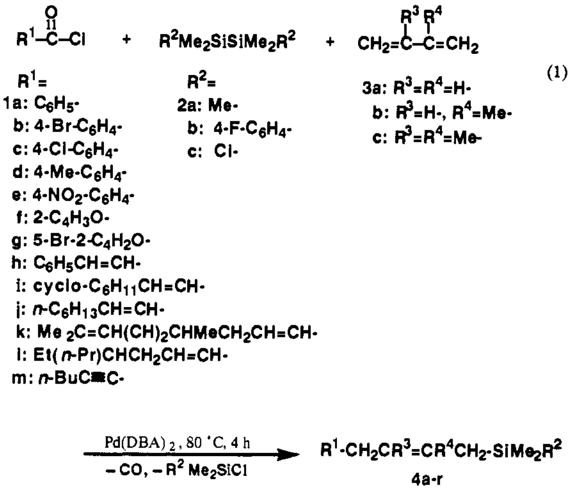
Received July 26, 1993

Silicon–carbon bonds are prepared by a wide variety of methods such as hydrosilylation[1] and reactions with Grignard reagents.[2] On the other hand, addition of C–Si bonds to unsaturated substrates, carbosilylation, might be far more beneficial. However, it seems exceedingly difficult to activate C–Si bonds directly toward the reaction, since most C–Si bonds are inert under usual reaction conditions.[3] Alternatively, when both carbon and silicon substituents can be introduced into unsaturated substrates from different sources, the reaction may provide the same products as the carbosilylation reaction. Recently, Murai and co-workers successfully added trimethylsilyl and alkynyl units to acetylenes with aid of a palladium catalyst.[4]

In this communication, we report decarbonylative coupling of acid chlorides **1**, organodisilanes **2**, and 1,3-dienes **3** to afford allylic silanes selectively as products (eq 1). The reaction involves activation of Si–Si σ-bonds of **2**[5] and decarbonylation[6] of **1**. Allylic silanes are highly versatile synthetic intermediates and have a large number of applications in organic synthesis.[7] The present reaction will provide a new useful synthetic method for allylic silanes with easily accessible substrates.



$$R^1\text{–}C(=O)\text{–}Cl + R^2Me_2SiSiMe_2R^2 + CH_2{=}C(R^3)\text{–}C(R^4){=}CH_2 \quad (1)$$

R^1=
1a: C_6H_5-
b: 4-Br-C_6H_4-
c: 4-Cl-C_6H_4-
d: 4-Me-C_6H_4-
e: 4-NO_2-C_6H_4-
f: 2-C_4H_3O-
g: 5-Br-2-C_4H_2O-
h: $C_6H_5CH{=}CH$-
i: cyclo-$C_6H_{11}CH{=}CH$-
j: *n*-$C_6H_{13}CH{=}CH$-
k: $Me_2C{=}CH(CH)_2CHMeCH_2CH{=}CH$-
l: Et(*n*-Pr)$CHCH_2CH{=}CH$-
m: *n*-BuC≡C-

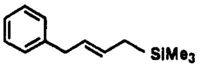
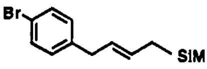
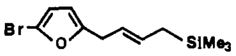
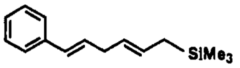
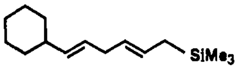
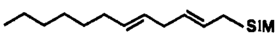
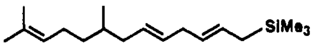
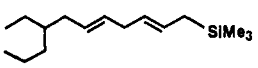
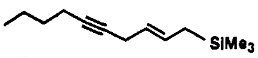
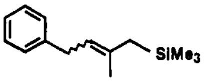
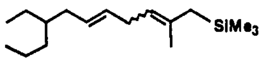
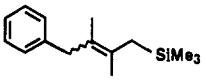
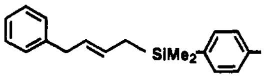
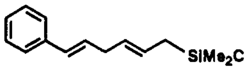
R^2=
2a: Me-
b: 4-F-C_6H_4-
c: Cl-

3a: $R^3{=}R^4{=}H$-
b: $R^3{=}H$-, $R^4{=}Me$-
c: $R^3{=}R^4{=}Me$-

$$\xrightarrow[-CO,\ -R^2Me_2SiCl]{Pd(DBA)_2,\ 80\ ^\circ C,\ 4\ h} R^1\text{-}CH_2CR^3{=}CR^4CH_2\text{-}SiMe_2R^2 \quad \mathbf{4a\text{-}r}$$

The results are summarized in Table I. When benzoyl chloride (**1a**) was allowed to react with hexamethyldisilane (**2a**) and 1,3-butadiene (**3a**) in the presence of a catalytic amount (5 mol %) of Pd(DBA)$_2$[8] (DBA = dibenzylideneacetone), the 1,4-addition product with the silyl group at the 1-position and the phenyl group at the 4-position (**4a**) was isolated in high yield (entry 1). The reaction is highly regio- and stereoselective to afford the (*E*)-1,4-isomer. The reaction also proceeds with several substituted benzoyl chloride derivatives (**1b–e**) and the corresponding products (**4b–e**) were isolated in 90% (**4b**; entry 2), 80% (**4c**), 77% (**4d**), and 51% (**4e**) yields. 2-Furoyl chloride (**1f**) and 5-bromo-2-furoyl chloride (**1g**) afforded (*E*)-1,4-adducts in 60% (**4f**) and 63% (**4g**; entry 3) yields. Furthermore, various (*E*)-alkenoyl chlorides (**1h–l**) as well as an alkynoyl chloride (**1m**) afforded the corresponding (*E*)-1,4 adducts regio- and stereoselectively (entries 4–9). As 1,3-dienes, isoprene (**3b**) and 2,3-dimethyl-1,3-diene (**3c**) can be employed and gave the products **4n–p** regioselectively (entries 10–12), but stereoselectivity was modest in some cases. Substituted disilanes (**2b** and **2c**) also

Table I. Decarbonylative Coupling of Acid Chlorides, Disilanes, and 1,3-Dienes[a]

entry	1	product 4		yield/ %[b]
1	**1a**		**4a**	86(93)
2	**1b**		**4b**	90
3	**1g**		**4g**	63
4	**1h**[c]		**4h**	94
5	**1i**[c]		**4i**	78
6	**1j**[c]		**4j**	72
7	**1k**[c]		**4k**	57
8	**1l**[c]		**4l**	81
9	**1m**		**4m**	75
10[d]	**1a**		**4n**[e]	82(91)
11[d]	**1l**[c]		**4o**[f]	80
12[g]	**1a**		**4p**[h]	47
13[i]	**1a**		**4q**	71
14[j]	**1h**[c]		**4r**	61

[a] Conditions: acid chloride (**1**; 0.50 mmol), Me$_3$SiSiMe$_3$ (**2a**; 0.50 mmol), 1,3-butadiene (**3a**; 1.5 mmol), Pd(DBA)$_2$ (0.025 mmol; 5 mol %), and toluene (2.0 mL) at 80 °C for 4 h. [b] Isolated yields. Numbers in a parentheses show GLC yields. [c] (*E*) isomer. [d] Isoprene (**3b**) as the 1,3-diene. [e] (*E*)/(*Z*) = 75/25. [f] (*E*)/(*Z*) = 91/9. [g] 2,3-Dimethyl-1,3-butadiene (**3c**) as the 1,3-diene. [h] (*E*)/(*Z*) = 65/35. [i] **2b** as the disilane. [j] **2c** as the disilane.

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(1) (a) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, 1989; Chapter 25. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 564–568.

(2) Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 2, p 20.

(3) For C–Si bond cleavages within a transition metal complex, see: (a) Lin, W.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1993,** *115,* 3022. (b) Horton, A. D.; Orpen, A. G. *Organometallics* **1992,** *11,* 1193. (c) Chang, L. S.; Johnson, M. P.; Fink, M. J. *Organometallics* **1991,** *10,* 1219 and references cited therein.

(4) Chatani, N.; Amishiro, N.; Murai, S. *J. Am. Chem. Soc.* **1991,** *113,* 7778.

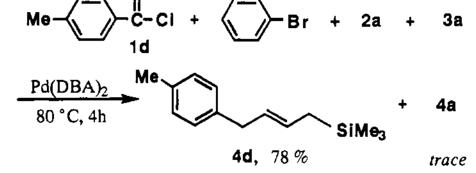
(5) For silylation with organodisilanes, see: (a) Tsuji, Y.; Lago, R. M.; Tomohiro, S.; Tsuneishi, H. *Organometallics* **1992,** *11,* 2353. (b) Tsuji, Y.; Kajita, S.; Isobe, S.; Funato, M. *J. Org. Chem.* **1993,** *58,* 3607. (c) Obora, Y.; Tsuji, Y.; Kawamura, T. *Organometallics* **1993,** *12,* 2853 and references cited therein.

0002-7863/93/1515-10414$04.00/0

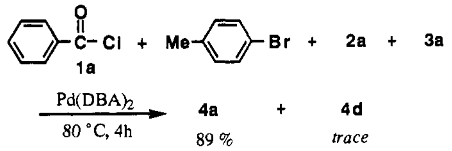
afforded the corresponding products (**4q** and **4r**) with high regio- and stereoselectivity (entries 13 and 14).

In the present reaction, decarbonylation[6] from the acid chlorides **1** took place completely.[9] Under carbon monoxide pressure (10 kg/cm^2), consumption of acid chlorides was low (<10%) and no allylic silanes **4** were formed. As the catalyst precursor, Pd(DBA)$_2$,[10] a naked Pd(0) complex without donating ligand, is most effective. Addition of AsPh$_3$ (As/Pd = 4) or P(OEt)$_3$ (P/Pd = 4) to the reaction mixture under the same reaction conditions as in entry 1 reduced the yield of **4a** to 41% or 13%, respectively, while the addition of PPh$_3$ or PBu$_3$ (P/Pd = 4) totally suppressed the formation of **4a**. Other selected transition metal precursors (5 mol %) such as Pd(PPh$_3$)$_4$, PdCl$_2$(PPh$_3$)$_2$, and Pt(DBA)$_2$ lowered the conversion of **1**, and no allylic silanes **4** were formed.

Acid chlorides **1** provide the products **4** smoothly *via* decarbonylation. Aryl and alkenyl bromides also afforded the 1,4-adducts, although yields of the products decrease considerably. Thus, bromobenzene in place of **1a** gave **4a** in 40% yield[11] under the same reaction conditions as in entry 1, and β-bromo styrene provided **4h** in 32% yield (cf. entry 4). Aromatic bromide functionality, which can participate in the reaction as mentioned above, remained intact in entries 2 and 3. The reaction at the acid chloride site seems to be faster than that at the aromatic bromide site. This rate difference was confirmed in a competitive reaction between 4-methylbenzoyl chloride (**1d**; 1.0 equiv) and bromobenzene (1.0 equiv) with Me$_3$SiSiMe$_3$ (**2a**; 0.50 equiv) and 1,3-butadiene (**3a**; 3.0 equiv) under the standard reaction conditions (eq 2). The product **4d** came almost entirely from the acid chloride, and most of the bromobenzene was recovered. The same results were observed with benzoyl chloride (**1a**; 1.0 equiv), 4-bromotoluene (1.0 equiv), **2a** (0.50 equiv), and **3a** (3.0 equiv) (eq 3), showing the that p-methyl substituents have virtually no effect on the reactivity.



(2)



(3)

The fate of the trimethylsilyl moiety of Me$_3$SiSiMe$_3$ (**2a**) in the reactions was determined by ^{29}Si NMR in toluene (locked with C$_6$D$_6$). After the reaction, the expected amount of Me$_3$SiCl (30.31 ppm; lit.[12a] 30.27 ppm) was found along with excess **2a** (−20.51 ppm; lit.[12b] −20.50 ppm), indicating that one of the silyl groups of the disilane was trapped as the silyl chloride. A possible catalytic cycle for the present reaction would be as follows. Oxidative addition of acid chloride **1** to a Pd(0) center initiates the catalytic cycle. After the decarbonylation, the 1,3-diene **2** inserts into a resulting C–Pd bond to generate an allylpalladium species. Transmetalation with disilane **2**, which provides a silyl–metal species and the silyl chloride, followed by reductive elimination then affords the allylic silane **4** as the product and regenerates the active catalyst species.

Acknowledgment. This work was supported by a Grant-in-Aid for scientific research from the Ministry of Education, Science and Culture, Japan (No. 04650753). Financial support from the Sumitomo Foundation (No. 92-103-103) is also gratefully acknowledged.

Supplementary Material Available: Experimental details and spectroscopic and analytical characterization of the products (6 pages). Ordering information is given on any current masthead page.

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[6] (a) Rich, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 5886. (b) Krafft, T. E.; Rich, J. D.; McDermott, P. J. *J. Org. Chem.* **1990**, *55*, 5430.

[7] (a) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic: London, 1988; pp 25–37. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer: Berlin, 1983; pp 173–205. (c) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981; pp 97–124.

[8] (a) Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065. (b) Rettig, M. F.; Maitlis, P. M. *Inorg. Synth.* **1977**, *17*, 134.

[9] (a) Yamamoto *et al.* reported reaction of acid chlorides **1** with Me$_3$SiSiMe$_3$ (**2a**) to afford acyl silanes (RCO–SiMe$_3$) with suppression of the decarbonylation of **1** in the presence of catalytic amounts of [PdCl(η^3-C$_3$H$_5$)]$_2$ and P(OEt)$_3$.[9b] We tried the same catalyst system in entry 1. However, conversion of **1a** was low (<10%), and yield of **4a** was 7% with formation of PhCOSiMe$_3$ in a trace amount. (b) Yamamoto, K.; Hayashi, A.; Suzuki, S.; Tsuji, J. *Organometallics* **1987**, *6*, 974.

[10] (a) Pd$_2$(DBA)$_3$·CHCl$_3$[10b] showed similar catalytic activity. (b) Ukai, T.; Kawazuka, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.

[11] When iodobenzene was employed under the same reaction conditions, **4a** was obtained in only 8% yield with a low conversion of the iodide. Phenyl trifluoromethanesulfonate (PhOTf) was totally inert under the same reaction conditions.

[12] (a) Van Den Berghe, E. V.; Van Der Kelen, G. P. *J. Organomet. Chem.* **1973**, *59*, 175. (b) Hunter, B. K.; Reewes, L. W. *Can. J. Chem.* **1967**, *46*, 1399.