Dehydrogenative Condensation of (*o*-Borylphenyl)hydrosilane with Alcohols and Amines

Atsushi Kawachi,* Masatoshi Zaima, Atsushi Tani, and Yohsuke Yamamoto
Department of Chemistry, Graduate School of Science, Hiroshima University,
1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526

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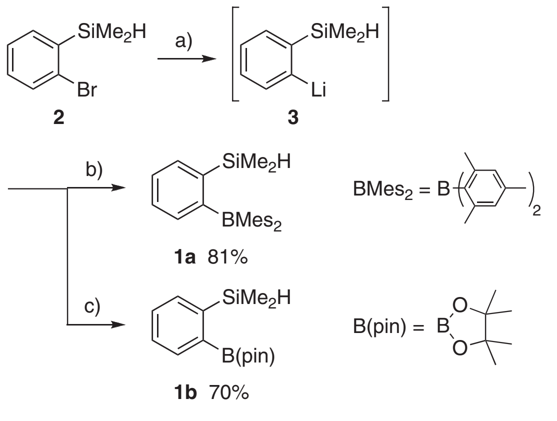
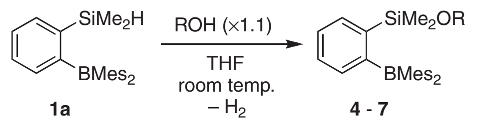
o-[(Dimesitylboryl)phenyl]dimethylsilane (**1a**) undergoes dehydrogenative condensation with alcohols and amines, giving the corresponding alkoxysilanes **4**–**7** and aminosilanes **8** and **9** in moderate to high yields. It is plausible that the *ortho*-boryl group in **1a** electrophilically activates the Si–H bond.

Dehydrogenative condensation of hydrosilanes with alcohols[1] is a facile and clean reaction for the synthesis of alkoxysilanes because only dihydrogen is formed as the by-product of the reaction. This reaction has received much attention in organic synthesis in terms of protection of alcohols by silyl groups. Since the Si–H bond is rather inert toward nucleophilic attack by alcohols, its activation is generally required. There are mainly three modes of Si–H bond activation reported so far. The first one is transition-metal-catalyzed reaction.[2] Transition-metal catalysts activate the Si–H bond via oxidative addition or formation of a σ-complex. The second one is hypercoordination of hydrosilanes.[3] Inter- or intramolecular coordination of a ligand to the silicon produces a pentacoordinate silicon species, in which the Si–H bond is polarized and the silicon center is sufficiently electrophilic to receive the alcohols. The third one is electrophilic activation of the Si–H bond by a strong Lewis acid such as $B(C_6F_5)_3$.[4] The highly electrophilic boron center interacts with the hydrogen on the silicon, which renders the Si–H bond polarized and the silicon center susceptible to nucleophilic attack by the alcohols. We disclose here the first example of the intramolecular electrophilic activation of a Si–H bond by an *ortho*-boryl group in arylhydrosilane **1a**, which leads to its dehydrogenative condensation with alcohols and amines.

(*o*-Borylphenyl)hydrosilanes **1** were prepared as follows (Scheme 1). The halogen–lithium exchange reaction of (*o*-bromophenyl)hydrosilane **2** with *tert*-BuLi (2 molar amounts) in Et_2O at −78 °C produced ortho lithiated product **3**, which was reacted with fluorodimesitylborane to give **1a** in 81% yield.[5] The reaction of **3** with (isopropoxy)pinacolborane also afforded pinacolborane derivative **1b** as a colorless oil in 70% yield.[5]



Scheme 1. (a) *tert*-BuLi (×2)/Et_2O/−78 °C, 2 h. (b) Mes_2BF (×1.5)/0 °C–r.t., 12 h. (c) (i) *i*-PrOB(pin) (×1.5)/−78 °C. (ii) Me_3SiCl (×2), 0 °C–r.t., 17.5 h.



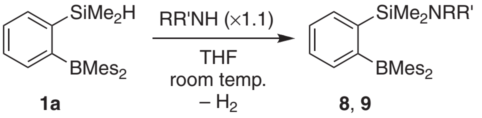
ROH	Time	Product	Yield ^{1}H NMR[a]	 Isolated[b]
MeOH	10 min	**4**	94%	63%
EtOH	20 min	**5**	94%	69%
i-PrOH	4 h	**6**	87%	49%
t-BuOH	42 h	**7**	59%	30%[c]

[a]Estimated by use of anisole as an internal standard. [b]Precipitated from CH_3CN. [c]Obtained by HPLC.

Scheme 2.

Upon treatment of **1a** with MeOH in THF at room temperature, gas evolution occurred immediately. After 10 min, methoxysilane **4** was formed in 94% yield (^{1}H NMR) (Scheme 2). ^{1}H NMR analysis demonstrated that the septet at δ 4.54 (*H*–Si) disappeared and the singlet at δ 3.15 (*Me*–O) appeared. The reaction of **1a** with EtOH and *i*-PrOH also produced corresponding alkoxysilanes **5** in 94% yield (^{1}H NMR) and **6** in 87% yield (^{1}H NMR), respectively, within a few hours. Precipitation of the obtained alkoxysilanes from CH_3CN gave their pure form in good yields (Scheme 2).[6] The reaction of **1a** with *tert*-BuOH took a longer time, affording *tert*-butoxy derivative **7** in 59% yield (^{1}H NMR).[6] In contrast to the high reactivity of **1a**, pinacolborane derivative **1b** did not react with even MeOH for 24 h.

The dehydrogenative condensation of **1a** with amines was also successful.[7] The reaction of **1a** with a secondary amine (Et_2NH) and a primary amine ($PhNH_2$) at room temperature afforded corresponding aminosilanes **8** in 98% yield and **9** in 82% yield, respectively (^{1}H NMR) (Scheme 3). The products were isolated by precipitation from CH_3CN in good yields.[6]



RR'NH	Time	Product	Yield ^{1}H NMR[a]	 Isolated[b]
Et_2NH	20 min	**8**	98%	63%
$PhNH_2$	30 min	**9**	82%	73%

[a]Estimated by use of anisole as an internal standard. [b]Precipitated from CH_3CN.

Scheme 3.

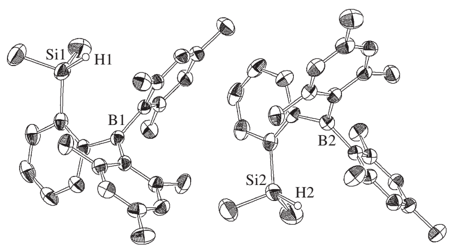


Figure 1. Crystal structure of **1a** with 30% probability level. H atoms except for those on Si are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–H1, 1.47(2); Si2–H2, 1.55(2); H1···B1, 3.22(2); H2···B2, 3.25(2); Σ(∠C–B1–C), 359.9; Σ(∠C–B2–C), 359.8.

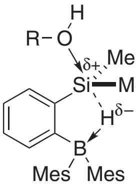


Figure 2. Intramolecular electrophilic activation of the Si–H bond by the *ortho*-boryl group.

The reaction time required to consume **1a** increased with increasing steric bulkiness of the alcohols (Scheme 2). This is in clear contrast to the trend observed by Piers et al. in the $B(C_6F_5)_3$-catalyzed system:[4a] primary alcohols react with hydrosilanes more slowly than secondary or tertiary ones because the less bulky alcohols more readily form adducts with $B(C_6F_5)_3$ in situ, which inhibits the electrophilic Si–H activation by $B(C_6F_5)_3$. In our system, interactions of the boron site in **1a** with alcohols are less likely because of steric congestion around the boron bearing the two mesityl groups and the *ortho*-silylphenyl group. Thus, the primary alcohol reacts with **1a** faster than secondary or tertiary ones.

It is plausible that the electrophilic activation of the Si–H bond by the *ortho*-boryl group renders the silicon center in **1a** susceptible to nucleophilic attack by the alcohols. Actually, less acidic pinacolborane derivative **1b** did not react with MeOH. The physical properties of the Si–H bond in **1a**[5] including $^1J_{\text{Si–H}}$ (193 Hz), $\nu_{\text{Si–H}}$ (2148 and 2167 cm^{-1}), and the Si–H bond lengths (1.47(2) and 1.55(2) Å) in the crystal structure[8] (Figure 1) are within normal values of tetracoordinate Si–H bonds. In addition, the H···B atomic distances (3.22(2) and 3.25(2) Å) are almost equal to the sum of the van der Waals radii of hydrogen atom and boron atom (3.28 Å). Although these data suggest that there is no remarkable Si–H···B interaction[9] in **1a** itself, activation of the Si–H bond may be facilitated in a push–pull manner with the aid of the attacking alcohol, as shown in Figure 2.

In summary, the *ortho*-boryl group in arylhydrosilane **1a** electrophilically activates the Si–H bond in a intramolecular manner, which leads to the dehydrogenative condensation with alcohols and amines. Details of the reaction mechanism are under study in our laboratory.

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References and Notes

1 "Dehydrogenative silylation of alcohols" may be a more common designation in the field of organic synthesis.

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5 Compound **1a**: colorless crystals (from hexane). mp 134–136 °C. ^{1}H NMR (benzene-d_6, δ) −0.09 (br, 3H), 0.24 (br, 3H), 1.75–2.44 (br, 12H), 2.19 (s, 6H), 4.54 (sept, $^3J = 4$ Hz, 1H), 6.79 (br, 4H), 7.17 (ddd, $^3J = 7$ Hz, $^3J = 7$ Hz, $^4J = 2$ Hz, 1H), 7.24 (ddd, $^3J = 7$ Hz, $^3J = 7$ Hz, $^4J = 2$ Hz, 1H), 7.47 (d, $^3J = 7$ Hz, 1H), 7.56 (d, $^3J = 7$ Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ) −2.9 (br), 21.25, 22.0–24.0 (br), 127.5–129.5 (br), 128.56, 128.97, 133.22, 134.31, 137.0–145.0 (br), 142.59, 156.7 (br). ^{11}B NMR (THF-d_8, δ) 75 (br). ^{29}Si NMR (toluene-d_8, δ) −18.0 (d of sept, $^1J_{\text{Si–H}} = 193$ Hz, $^2J_{\text{Si–H}} = 7$ Hz). MS(EI): m/z 384 (M^+, 34), 369 ($M^+ -$ Me, 99), 204 (100). IR (KBr, cm^{-1}) 2148 ($\nu_{\text{Si–H}}$), 2167 ($\nu_{\text{Si–H}}$). Anal. Calcd for $C_{26}H_{33}BSi$: C, 81.23; H, 8.65%. Found: C, 81.51; H, 8.50%. Compound **1b**: colorless oil. bp 80–84 °C/0.4 mmHg. ^{1}H NMR ($CDCl_3$, δ) 0.38 (d, $^3J = 4$ Hz, 6H), 1.35 (s, 6H), 4.52 (sept, $^3J = 4$ Hz, 1H), 7.36 (ddd, $^3J = 7$ Hz, $^3J = 7$ Hz, $^4J = 2$ Hz, 1H), 7.41 (ddd, $^3J = 7$ Hz, $^3J = 7$ Hz, $^4J = 2$ Hz, 1H), 7.65 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 1H), 7.87 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ) −2.14, 24.96, 83.88, 128.09, 129.76, 135.00, 135.41, 144.51. ^{11}B NMR ($CDCl_3$, δ) 31 (br). ^{29}Si NMR ($CDCl_3$, δ) −13.8 (d of sept, $^1J_{\text{Si–H}} = 193$ Hz, $^2J_{\text{Si–H}} = 7$ Hz). MS(EI): m/z 261 ($M^+ -$ H, 34), 247 ($M^+ -$ Me, 48), 84 (100). IR (KBr, cm^{-1}) 2105 ($\nu_{\text{Si–H}}$), 2138 ($\nu_{\text{Si–H}}$). Anal. Calcd for $C_{14}H_{23}BO_2Si$: C, 64.12; H, 8.84%. Found: C, 64.28; H, 9.04%.

6 The high solubility of the prepared alkoxy- and aminosilanes in common organic solvents lowered their isolated yields by recrystallization or precipitation. Precipitation from CH_3CN was found to suppress loss of the products to as little as possible. However, the precipitate of **7** from CH_3CN was contaminated with a small amount of by-products, which are under characterization. Pure **7** was obtained by recycling preparative HPLC in 30% yield.

7 Some recent examples of transition-metal-catalyzed reactions: a) A. Iida, A. Horii, T. Misaki, Y. Tanabe, *Synthesis* **2005**, 2677. b) K. Takaki, K. Komeyama, K. Takehira, *Tetrahedron* **2003**, *59*, 10381. c) K. Takaki, T. Kamata, Y. Miura, T. Shishido, K. Takehira, *J. Org. Chem.* **1999**, *64*, 3891.

8 Crystal data for **1a**: $C_{26}H_{33}BSi$, fw 384.42, orthorhombic, *Pbca* (No. 61), $a = 17.6410(6)$, $b = 27.6290(8)$, $c = 19.7830(8)$ Å, $V = 9642.3(6)$ Å^3, $Z = 16$, $D_{\text{calcd}} = 1.059$ g cm^{-3}, $R(I > 2\sigma(I)) = 0.0792$, R_w(all data) $= 0.2514$, GOF $= 1.065$, $T = 173$ K (CCDC No. 632074).

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