Coupling of (amino)alkylchlorosilanes with lithium: new access to symmetrical di- and tetrafunctional alkyldisilanes

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Coupling of (Amino)alkylchlorosilanes with Lithium: New Access to Symmetrical Di- and Tetrafunctional Alkyldisilanes

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Summary: Homocoupling reactions of amino- and diaminoalkylchlorosilanes with lithium metal proceed readily in THF at room temperature to form the corresponding symmetrical diamino- and tetraaminoalkyldisilanes, respectively, in high yields, which are transformed into chloro- and alkoxyalkyldisilanes under mild conditions.

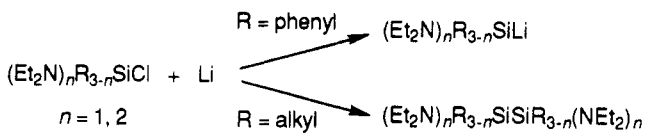
We have recently reported the synthesis of (amino)phenylsilyl anions as the first stable functional silyl anions by the reaction of (amino)*phenyl*silyl chlorides with lithium.[1] We now find that the action of lithium on (amino)*alkyl*silyl chlorides results in the formation of not the silyl anions but the corresponding coupling products, symmetrical polyfunctional disilanes, as shown in Scheme I.

There have been only two methodologies for the synthesis of polyfunctional alkyldisilanes:[2] (1) functional group transformation of the "disilane fraction" $Si_2Me_{6-n}Cl_n$ (n = 3, 4) in the industrial direct synthesis of methylchlorosilanes[3] and (2) demethylation of hexamethyldisilane or dephenylation of phenylalkyldisilanes by the action of strong electrophilic agents such as sulfuric acid (followed by treatment with ammonium halide),[3,4] trifluoromethanesulfonic acid,[5] $HCl/AlCl_3$,[6-8] and $MeCOCl/AlCl_3$.[7] The present coupling reaction provides the third method, which should be more convenient and versatile for the synthesis of symmetrical functional disilanes containing a variety of alkyl groups in view of the ready availability of (amino)alkylsilyl chlorides[9] and facile functional group transformations under mild conditions.

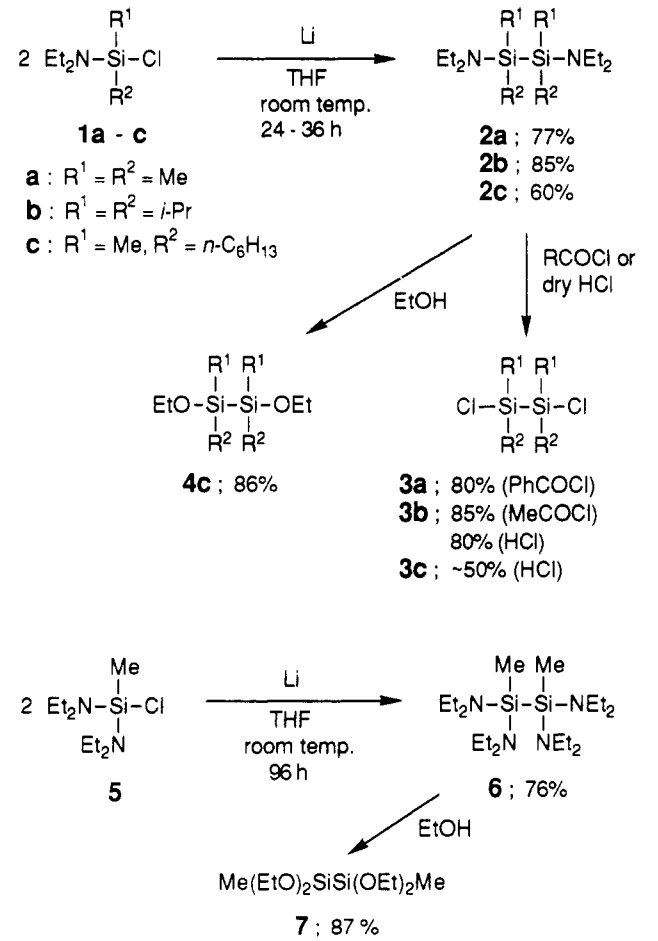
Results and Discussion

Several representative results are summarized in Scheme II. Aminochlorosilanes **1** and **5** are readily prepared by treatment of the corresponding dichloro- and trichlorosilanes with 1 equiv and 2 equiv of diethylamine, respectively, in the presence of a slightly excess amount of triethylamine in ether, followed by filtration and distillation.[9] The coupling reaction of **1** with lithium dispersion in THF proceeded smoothly at room temperature in 1-1.5 days under nitrogen atmosphere to afford diaminodisilanes **2**. Alkyl groups on silicon may be not only methyl (**2a**) but also sterically crowded isopropyl (**2b**) and long alkyl chains such as the *n*-hexyl group (**2c**). In the last case an almost 1:1 mixture of *meso* and *dl* stereoisomers was formed. Diaminochlorosilane **5** was considerably less reactive than **1** and required a longer period of time to give tetraaminodimethyldisilane **6** in moderate yields. These re-

Scheme I



Scheme II



(1) Tamao, K.; Kawachi, A.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 3898.
(2) Reviews: (a) Kumada, M.; Tamao, K. *Adv. Organomet. Chem.* **1968**, *6*, 19. (b) West, R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1989; Vol. 2, p 365.
(3) Kumada, M.; Yamaguchi, M.; Yamamoto, M.; Nakajima, N.; Shiina, K. *J. Org. Chem.* **1956**, *21*, 1264.
(4) Kumada, M.; Ishikawa, M. *J. Organomet. Chem.* **1963**, *1*, 153.
(5) (a) Uhlig, W.; Tzschach, A. *J. Organomet. Chem.* **1989**, *378*, C1. (b) Uhlig, W. *J. Organomet. Chem.* **1991**, *421*, 189.
(6) Kumada, M.; Ishikawa, M.; Maeda, S. *J. Organomet. Chem.* **1964**, *2*, 478.
(7) (a) Sakurai, H.; Tominaga, K.; Watanabe, T.; Kumada, M. *Tetrahedron Lett.* **1966**, 5493. (b) Kumada, M.; Watanabe, T.; Sakurai, H. *J. Organomet. Chem.* **1967**, *7*, P15.
(8) Tamao, K.; Kumada, M. *J. Organomet. Chem.* **1971**, *30*, 329 and 339.
(9) E.g., Tamao, K.; Nakajo, E.; Ito, Y. *Tetrahedron* **1988**, *44*, 3997.
(10) Gilman, H.; Shiina, K.; Aoki, D.; Gaj, B. J.; Wittenberg, D.; Brennan, T. *J. Organomet. Chem.* **1968**, *13*, 323.

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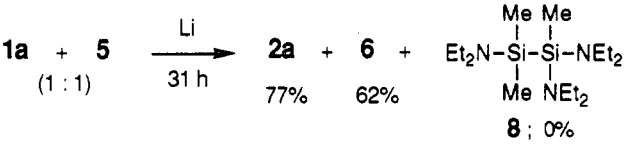
Scheme III



action conditions are similar to those for the coupling of trimethylchlorosilane with lithium.[10] *Caution*! In the isolation step, filtration of the excess lithium metal in the air may cause ignition of the lithium-containing filter cake. The following two-step filtration is recommended: The remaining lithium dispersion is filtered briefly first through glass wool under nitrogen and the filtrate that contains the salt is then filtered safely in the air. The clear filtrate is concentrated and distilled under reduced pressure to give pure **2** and **6**.

Although the coupling reactions proceeded faster under reflux conditions in THF, satisfactory results were obtained in only one case. Thus, the reaction of **1a** with lithium under THF reflux was completed in 6 h, much faster than 1 day at room temperature, to give **2a** of high purity in comparable yield (74%). In other cases, however, the coupling products were obtained only in much lower yields and in lower purities. Reactions were also considerably accelerated by ultrasonication,[11] but the yields and purities were decreased greatly. Refluxing and sonication are thus *not* recommended for the present disilane synthesis.

The resulting aminodisilanes are converted into the corresponding chlorodisilanes or alkoxydisilanes,[12] as shown in Scheme II. Thus, **2a** and **2b** were treated with 2 equiv of benzoyl chloride and with excess acetyl chloride, respectively, to afford the corresponding dichlorodisilanes **3a** and **3b**. The latter was also obtained by the action of dry hydrogen chloride[13] on **2b** in THF. We have encountered, however, some problems in transformations of **2c** and **6** under similar conditions. Thus, while with hydrogen chloride **2c** afforded dichlorodisilane **3c** in about 50% yield together with uncharacterizable nonvolatile byproducts, only a complex mixture of product was formed from **2c** and **6** with acetyl chloride; the reason remains to be clarified. Ethanolysis of these aminodisilanes, however, proceeded readily to form the corresponding ethoxydisilanes cleanly. Thus, **2c** and **6** afforded **4c** and **7**, respectively, in high yields.

In order to get unsymmetrical functional disilanes and oligosilanes by cross-coupling of two different chlorosilanes, we have attempted a variety of combinations without success so far. For example, as shown in Scheme III, a 1:1 mixture of **1a** and **5** afforded a mixture of homocoupling products **2a** and **6** in high yields, without formation of the cross-coupling product, triaminodisilane **8**.[14] We have obtained no appreciable amounts of cross-coupling products in other combinations such as **1a**/Me_3SiCl, **1a**/$MeSiCl_3$, and **5**/Me_3SiCl, suggesting a rather unusual behavior of aminochlorosilanes toward lithium coupling.

Experimental Section

General Comments. ^1H NMR (200 MHz) spectra were recorded on a Varian VXR-200 spectrometer equipped with a VX-4000 computer. The elemental analyses were performed at the Microanalysis Center of Department of Pharmaceutical Sciences, Kyoto University: analytical samples were purified by preparative GLC. Ether and THF were distilled under nitrogen from sodium/benzophenone. Hexane was dried over sodium wire and distilled under nitrogen. Diethylamine and triethylamine were distilled from calcium hydride. Diisopropyldichlorosilane was commercially available. Lithium dispersion (25 wt. % in mineral oil) was purchased from Aldrich.

Preparation of Aminochlorosilanes 1 and 4. The known compounds **1a**[9,15] and **4**[16] were prepared by essentially the same method as described below.

Diisopropyl(diethylamino)chlorosilane (1b). To a mixture of diisopropyldichlorosilane (12.6 mL; 70 mmol), triethylamine (10.8 mL; 77 mmol), and dry THF (70 mL) was added slowly a solution of diethylamine (7.4 mL; 70 mmol) in THF (10 mL) at 0 °C over 30 min. The white mixture was warmed to room temperature, stirred for 24 h, diluted with hexane, and filtered with suction. The filtrate was evaporated, and the residue was distilled under reduced pressure to give 11.0 g (71% yield) of **1b**: bp 51–53 °C/0.9 mmHg. ^1H NMR (C_6D_6): δ 0.97 (t, J = 7.0 Hz, 6H), 1.05–1.20 (m, 14H), 2.81 (q, J = 7.0 Hz, 4H). Anal. Calcd for $C_{10}H_{24}NSiCl$: C, 54.14; H, 10.90. Found: C, 53.98; H, 10.91.

***n*-Hexylmethyl(diethylamino)chlorosilane (1c).** This compound was obtained in 72% yield in a similar manner from *n*-hexylmethyldichlorosilane, readily available by platinum-catalyzed hydrosilation of 1-hexene with methyldichlorosilane: bp 74–75 °C/1.0 mmHg. ^1H NMR (C_6D_6): δ 0.40 (s, 3H), 0.85–1.02 (m, 5H), 0.98 (t, J = 7.0 Hz, 6H), 1.20–1.65 (m, 8H), 2.80 (q, J = 7.0 Hz, 4H). Anal. Calcd for $C_{11}H_{26}NSiCl$: C, 56.01; H, 11.11. Found: C, 55.79; H, 11.38.

Preparation of Aminodisilanes 2 and 6. 1,2-Bis(diethylamino)tetramethyldisilane (2a). A solution of **1a** (1.57 g; 9.46 mmol) in dry THF (3 mL) was added to a suspension of lithium dispersion (41.8 mmol) in THF (5 mL) at room temperature under an inert atmosphere. The mixture was stirred for 24 h at room temperature. The complete disappearance of **1a** was confirmed by GLC analysis. The mixture was then filtered through a short pad of glass wool under a nitrogen atmosphere. After concentration of the filtrate under reduced pressure, the residue was diluted with dry hexane and filtered through a glass fiber pad safely in the air. The filtrate was concentrated, and the residue was purified by bulb-to-bulb distillation under reduced pressure to give 1.07 g (77% yield) of **2a** as a colorless liquid: bp 110–130 °C/1.1 mmHg (bath temperature). ^1H NMR (C_6D_6): δ 0.30 (s, 12H), 1.04 (t, J = 7.0 Hz, 12H), 2.87 (q, J = 7.0 Hz, 8H). Anal. Calcd for $C_{12}H_{32}N_2Si_2$: C, 55.31; H, 12.38. Found: C, 55.08; H, 12.49.

When the reaction mixture was refluxed, the coupling reaction was completed in 6 h, as monitored by the disappearance of the starting material by GLC. A similar workup gave pure **2a** in 74% yield. Alternatively, when the reaction flask was immersed in a ultrasound cleaning bath (Iwaki Glass Co., Ltd., 120 W, 38 kHz) filled with water, the coupling reaction was completed in 13 h, during which time the bath temperature rose to 50 °C. The product **2a** was obtained in rather low yield (40–50%) and in low purity (70–80%) contaminated with several unknown impurities, leaving substantial amounts of nonvolatile distillation residue.

Other disilanes were prepared in essentially the same manner as described for the synthesis of **2a** at room temperature. Note:

(11) Wurtz-type coupling reactions of chlorosilanes have been known to be accelerated by ultrasound. E.g.: (a) Price, G. J. *J. Chem. Soc., Chem. Commun.* **1992**, 1209. (b) Kim, H. K.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1988**, *110*, 3321 and references cited therein.

(12) Bazant, V.; Chvalovsky, V.; Rathousky, J. *Organosilicon Compounds*; Academic Press: New York and London, 1965; Vol. 1, 76–89.

(13) Bailey, D. L.; Sommer, L. H.; Whitmore, F. C. *J. Am. Chem. Soc.* **1948**, *70*, 435.

(14) A referee suggested a possibility for disproportionation of the initially formed **8** into **2a** and **6** under the reaction condition. We attempted preparation of **8** by other route, amination of 1,1,2-trichlorotrimethyldisilane, but obtained a complex mixture of products only. We will confirm the referee's interesting suggestion when we can obtain **8** in due course. The dimethylamino analog of **8** has been prepared in low yield by Hengge: Hengge, E.; Pletka, H. D.; Höfler, F. *Monatsh. Chem.* **1970**, *101*, 325.

(15) Hundeck, J. *Z. Anorg. Allgem. Chem.* **1966**, *345*, 23.

(16) Tansjo, L. *Acta Chem. Scand.* **1959**, *13*, 35.

under reflux conditions, **2b**, **2c**, and **6** were obtained only in low yields (<50%) and in low purities.

1,2-Bis(diethylamino)tetraisopropyldisilane (2b). This compound was obtained in 85% yield from **1b** by stirring with lithium at room temperature for 24 h: bp 120–160 °C/0.50 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 1.08 (t, J = 7.0 Hz, 12H), 1.16–1.38 (m, 28H), 3.00 (q, J = 7.0 Hz, 8H). Anal. Calcd for $C_{20}H_{48}N_2Si_2$: C, 64.44; H, 12.98. Found: C, 64.14; H, 13.22.

1,2-Bis(diethylamino)-1,2-di-*n*-hexyl-1,2-dimethyldisilane (2c). This compound was obtained in 60% yield from **1c** by stirring with lithium at room temperature for 36 h as a nearly 1:1 mixture of *meso* and *dl* stereoisomers: bp 130–135 °C/0.80 mmHg. ^{1}H NMR (C_6D_6): δ 0.37 (s, 6H), 0.38 (s, 6H), 0.70–1.02 (m, 10H), 1.09 (t, J = 7.0 Hz, 12H), 2.93 (q, J = 7.0 Hz, 8H), 1.30–1.70 (m, 16H). Anal. Calcd for $C_{22}H_{52}N_2Si_2$: C, 65.92; H, 13.08. Found: C, 65.79; H, 13.35.

1,1,2,2-Tetrakis(diethylamino)dimethyldisilane (6). This compound was obtained from **5** in 76% yield after 96-h stirring: bp 110–130 °C/1.0 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 0.39 (s, 6H), 1.10 (t, J = 7.0 Hz, 24H), 3.00 and 3.01 (dq, J = 7.0 Hz, 16H). Anal. Calcd for $C_{18}H_{46}N_4Si_2$: C, 57.69; H, 12.37. Found: C, 57.76; H, 12.61.

Preparation of 1,2-Dichlorotetramethyldisilane (3a). Freshly distilled benzoyl chloride (0.32 mL; 2.76 mmol) was added dropwise to **2a** (388 mg; 1.38 mmol) at 0 °C over 2 min. After being stirred at 0 °C for 1 h, the mixture was distilled bulb-to-bulb to give 205 mg (80% yield) of **3a**:[3] bp 120–130 °C/90 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 0.37 (s, 12H).

Preparation of 1,2-Dichlorotetraisopropyldisilane (3b). By Acetyl Chloride. To a solution of **2b** (385 mg; 1.03 mmol) in dichloromethane (1 mL) was added freshly distilled acetyl chloride (1.50 mL; 20.7 mmol) at 0 °C, and the mixture was stirred at room temperature for 3 h. After evaporation of the solvent *N*,*N*-dimethylacetamide was removed under reduced pressure up to 130 °C/28 mmHg by bulb-to-bulb distillation. The residue was further distilled bulb-to-bulb to give 294 mg (purity 90%, 85% yield) of **3b**:[17] bp 115–135 °C/0.60 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 1.16 (d, J = 5.8 Hz, 24 H), 1.20–1.35 (m, 4H). Anal. Calcd for $C_{12}H_{28}Si_2Cl_2$: C, 48.14; H, 9.43. Found: C, 47.91; H, 9.63.

By Dry HCl. Through a solution of **2b** (395 mg; 1.06 mmol) in dry THF (10 mL) was bubbled dry hydrogen chloride, generated from ammonium chloride (6.9 g; 127 mmol) and concentrated sulfuric acid (4.8 mL; 85 mmol), at 0 °C for 40 min with stirring. White salts precipitated almost immediately. GLC analysis showed the disappearance of **2b**. The mixture was diluted with dry hexane (10 mL) and filtered with suction. The filtrate was concentrated, and the residue was purified by bulb-to-bulb distillation at 110–120 °C/1.0 mmHg (bath temperature) to give 270 mg (purity 95%, 80% yield) of **3b**.

Preparation of 1,2-Dichloro-1,2-di-*n*-hexyl-1,2-dimethyldisilane (3c). By Dry HCl. Dry hydrogen chloride was passed through a solution of **2c** (1.09 g; 2.45 mmol) in dry ether (15 mL) at 0 °C for 1 h. Workup similar to that above followed by bulb-to-bulb distillation (125–145 °C/0.90 mmHg, bath temperature) gave rather impure **3c**[18] as a nearly 1:1 *meso*/*dl* mixture in moderate yield (674 mg; purity 65%, 55% yield estimated). ^{1}H NMR (C_6D_6): δ 0.49 (s, 6H), 0.51 (s, 6H), 0.89–0.99 (m, 10H), 1.25–1.55 (m, 16H). Use of THF as solvent resulted in lowering of the yield due to the formation of a more complex mixture.

Preparation of 1,2-Diethoxy-1,2-di-*n*-hexyl-1,2-dimethyldisilane (4c). To a suspension of ammonium chloride (51 mg; 0.94 mmol) in dry ethanol (5.0 mL) was added **2c** (710 mg; 95% pure; 1.68 mmol) at room temperature, and the mixture was stirred for 2 h. Excess ethanol and the resulting diethylamine were removed under reduced pressure, and the residue was diluted with dry hexane and filtered. The filtrate was concentrated and then distilled bulb-to-bulb to give 560 mg (purity 90%; 87% yield) of **4c**: bp 128–148 °C/0.8 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 0.40 (s, 6H), 0.85–1.00 (m, 10H), 1.23 (t, J = 6.9 Hz, 6H), 1.30–1.70 (m, 16H), 3.71 (q, J = 6.9 Hz, 4H). Anal. Calcd for $C_{18}H_{42}O_2Si_2$: C, 62.36; H, 12.21. Found: C, 62.11; H, 12.34.

Preparation of 1,1,2,2-Tetraethoxydimethyldisilane (7). In a manner similar to the above, **6** (348 mg; 0.93 mmol) gave 200 mg (87% yield) of **7**:[3] bp 50–60 °C/0.7 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 0.40 (s, 6H), 1.24 (t, J = 7.0 Hz, 12H), 3.86 and 3.87 (dq, J = 7.0 Hz, 8H).

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(17) (a) Weidenbruch, M.; Peter, W. *J. Organomet. Chem.* **1975**, *84*, 151. (b) Watanabe, H.; Inose, J.; Fukushima, K.; Kougo, Y.; Nagai, Y. *Chem. Lett.* **1983**, 1711.

(18) Ishikawa, M.; Hatano, T.; Hasegawa, Y.; Horio, T.; Kunai, A.; Miyai, A.; Ishida, T.; Tsukahara, T.; Yamanaka, T.; Koike, T.; Shioya, *J. Organometallics* **1992**, *11*, 1604.