Novel Synthesis and Bridgehead Functionalization of Permethylbicyclo[2.2.2]octasilane

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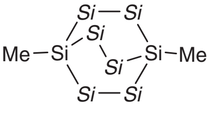
Selective bridgehead chlorination of permethylbicyclo[2.2.2]octasilane **1** giving the corresponding 1-chloro- (**2a**) and 1,4-dichlorobicyclooctanes **3a** was achieved using BCl_3 in chloroform. 1-Chlorobicyclooctane **2a** resists the reactions with various nucleophiles such as phenyllithium and lithium aluminum hydride but reacts with KC_8 affording the corresponding silylpotassium **2b** in quantitative yield.

Much attention has been focused on oligosilanes and polysilanes having the unique electronic properties due to σ-conjugation through the silicon framework.[1] Because aryl- and vinyloligosilanes have been known to show effective σ–π conjugation between the oligosilane σ-orbitals and the π orbitals,[2] oligosilanes may be good linkers between two functional π-electron systems. Whereas a few studies of the donor–acceptor systems linked by linear oligosilane chains have been reported,[3] the characteristics are often obscured by the strong conformation dependence of the σ-conjugation and σ–π conjugation. Bicyclo[2.2.2]octasilane-1,4-diyl is highly promising as a superior linker of two aromatic π-electron systems because it has a rigid σ framework[4] with three-fold symmetry around the axis through two bridgehead silicon atoms, and hence, both σ-conjugation in the oligosilane rings and the σ–π conjugation between the oligosilane and aromatic π systems do not depend on the conformation around the C (aromatic)–Si bond. Although permethylbicyclo[2.2.2]octasilane **1**[5,6] has long been known, no fuctionalization of **1** has been reported. Very recently, we are aware of the studies of Marschner and co-workers who have developed a successful method for the synthesis and functionalization of compounds with bicyclo[2.2.2]octasilane skeleton.[7] We wish herein to report our independent novel synthesis of **1** and its bridehead-selective functionalization.



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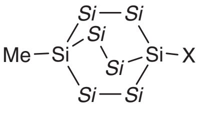
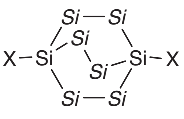


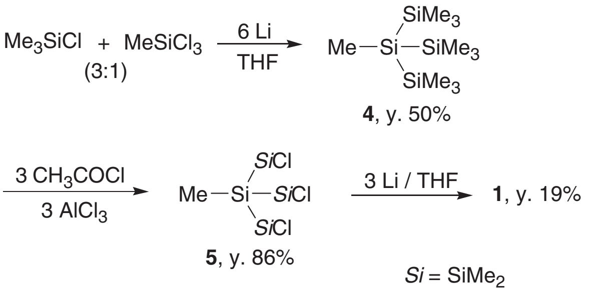
2a, X = Cl;
2b, X = K;
2c, X = H;
2d, X =$SiMe_3$.



3a, X = Cl

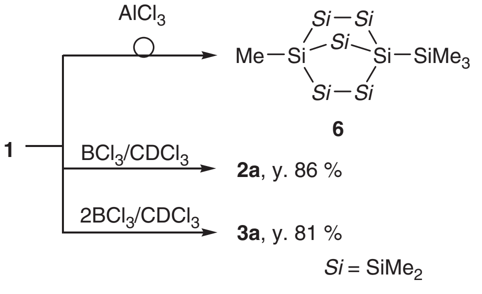
Si = $SiMe_2$

The reaction of tris(chlorodimethylsilyl)(methyl)silane **5**,[8] which was prepared via **4**[9] from a 1:3 mixture of methyltrichlorosilane and trimethylchlorosilane, with lithium metal in tetrahydrofuran at ambient temperature gave **1** in 19% yield;[10] the total yield of **1** from the chloromonosilane mixture was 8.2%. The yield of **1** obtained here is comparable with those reported by West et al.[5] and Ishikawa, Kumada, et al.,[6] who synthesized **1** using the direct coupling reactions of a 3:1 mixture of Me_2SiCl_2 and $MeSiCl_3$ with sodium-potassium alloy and lithium metal in 5.0 and 3.3% yields, respectively, together with many other byproducts. Because the molecular weights of most byproducts obtained by our method were apart from that of **1**, the isolation of **1** from a product mixture was found to be easier than the previous methods.



Scheme 1.

Bridgehead chlorination of **1** was achieved using BCl_3.[11] A mixture of **1** (116 mg, 0.267 mmol) and a 1 M BCl_3 hexane solution (0.26 mL) was dissolved in chloroform-*d* (0.4 mL) in a sealed tube. The tube was kept at 70 °C for 30 h. To the reaction mixture was added a small amount of THF to quench excess BCl_3, and then volatile materials were removed in vacuo. Sublimation at 160 °C (0.15 mmHg) from the remaining crude products gave colorless crystals of 1-chlorobicyclo[2.2.2]octasilane (**2a**) in 86% yield (102 mg, 0.224 mmol).[12] A similar reaction of **1** with two equivalents of BCl_3 at 100 °C for 10 days in a sealed tube underwent stepwise to give the corresponding 1,4-dichlorinated derivative of **1** (**3a**) in 81% yield.[13]



Scheme 2.

The use of BCl_3 is essential for the successful regioselective chlorination of **1**. The reactions of permethylcyclohexasilane and **1** with a catalytic amount of $AlCl_3$ have been shown to undergo a skeletal rearrangement to give (trimethylsilyl)nonamethylcyclopentasilane[14] and 1-silylbicyclo[2.2.1]heptasilane **6**, respectively,[6] and hence, the reaction cannot be applied for the chlorination of **1**. The reactions of **1** with $SbCl_5$[15] and $GaCl_3$[16] at room temperatures gave complex mixtures with 1,2-dichlorotetramethyldisilane as main products in 39 and 24% yields, respectively.

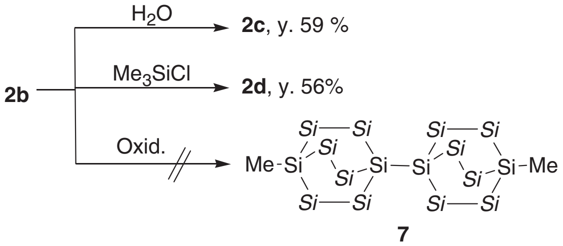
The selectivity of the chlorination would be explained by the difference of the nucleophilicity of methyl groups on the bridgesilicon and bridgehead-silicon atoms; the latter methyl groups should be more nucleophilic because they are connected with the silicon atoms substituted by three silyl substituents. A weak chlorinated Lewis acid like BCl_3 would be required to avoid the undesired skeletal rearrangement of **1** and to enhance the regioselectivity.

In contrast to the sterically prohibited nucleophilic substitution at bridgehead carbon atoms, 1-chloro-1-silabicyclo[2.2.2]octane and other bridgehead chlorosilanes are known to undergo facile nucleophilic substitution at the bridgehead positions with various reagents through the front-side attack of the nucleophiles. However, **2a** did not react with water, phenyllithium, or lithium aluminum hydride in THF. Probably, not only sterically but also electronically, the bridgehead position of **2a** is less reactive than those of 1-chloro-1-silabicycloalkanes.[17]

1-Chlorobicyclooctasilane **2a** reacts however with KC_8 in THF to afford the corresponding silylpotassium **2b**. Dry oxygen-free THF-d_8 (0.5 mL) was introduced to a mixture of **2a** (27.4 mg, 0.0602 mmol) and KC_8 (19.5 mg, 0.144 mmol) in a Schlenk tube with a magnetic stirrer at 20 °C under vacuum. The temperature of the mixture was raised to room temperature over 6 h. After insoluble materials were removed by decantation, NMR spectral analysis of the solution showed almost quantitative formation of the corresponding silylpotassium **2b** (Eq 1).[18,19] An alternative method for the preparation of bridgehead silylpotassium compounds, 1-potassio-4-trimethylsilylbicyclo[2.2.2]octasilane and the related 1,4-dipotassiobicyclooctasilane, has been developed recently by Marschner et al., in which 1,4-bis(trimethylsilyl)bicylo[2.2.2]octasilane was treated with potassium *t*-butoxide and 18-crown-6 in toluene.[7]

$$\mathbf{2a} \xrightarrow[\text{THF}]{\text{excess KC}_8} \mathbf{2b} \qquad (1)$$

When excess water and trimethylchlorosilane were added to the solution of **2b**, the corresponding 1-hydrido- (**2c**)[20] and 1-trimethylsilyl-derivatives of **1** (**2d**)[7] were isolated in 59 and 56% yields, respectively.



Scheme 3.

No formation of the coupling dimer of **2a** (**7**) was observed during the reduction of **2a** by KC_8 or the oxidation of **2b** using 1,2-dibromoethane,[21] $NOBF_4$,[22] or $GeCl_2$.[23] Further works on the derivatization of **1** are now in progress.

References and Notes

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10 Synthesis of **1**: Lithium metal (1.61 g, 232 mmol) was added to the tetrahydrofuran solution (450 mL) of tris(chlorodimethylsilyl)methylsilane[7] (**5**, 20.5 g, 63.4 mmol), and stirred for 1 day at ambient temperature. The color of solution turned to brown, then filtered and hydrolysis by dilute hydrochloric acid. The organic phase was extracted with ether, and volatile material was removed in vacuo. Kuger-Rohr distillation (200 °C, 0.01 mmHg) gave colorless crystals of **1** (2.60 mg, 5.98 mmol) in 19% yield.

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12 **2a**: colorless crystals; mp > 400 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.12 (s, 3H), 0.23 (s, 18H), 0.30 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −14.2, −4.13, −3.31; ^{29}Si NMR (59 MHz, $CDCl_3$) δ −81.8 (SiMe), −38.7 ($SiMe_2$), −35.8 ($SiMe_2$), −3.93 (SiCl); MS (EI, 70 eV) *m/z* (%) 456 ($M^+ + 2$, 40), 454 (M^+, 100). Anal. Found: C, 34.36; H, 8.45%. Calcd for $C_{13}H_{39}ClSi_8$: C, 34.27; H, 8.63%.

13 **3a**: colorless crystals; mp > 400 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.40 (s, 36H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.38; ^{29}Si NMR (59 MHz, $CDCl_3$) δ −34.4, −7.42; MS (EI, 70 eV) *m/z* (%) 476 (M^+, 8), 366 (100). HRMS Found 476.0325, Calcd for $C_{12}H_{36}Cl_2Si_8$ 476.0323.

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18 **2b**: ^{1}H NMR (400 MHz, THF-d_8) δ 0.04 (s, 3H), 0.08 (s, 18H), 0.13 (s, 18H); ^{13}C NMR (150 MHz, THF-d_8) δ −16.1, −3.53, 1.62; ^{29}Si NMR (79 MHz, THF-d_8) δ −174.1, −80.8, −42.8, −34.7.

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20 Spectral data for **2c**: colorless crystals; mp > 400 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.20 (s, 3H), 0.28 (s, 18H), 0.38 (s, 18H), 3.00 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$) δ −14.4, −5.89, −3.41; ^{29}Si NMR (79 MHz, $CDCl_3$) δ −109.1 (SiH), −80.5 (SiMe), −39.8 ($SiMe_2$) −39.5 ($SiMe_2$); MS (EI, 70 eV) *m/z* (%) 420 (M^+, 100). HRMS Found 419.1205, Calcd for $C_{13}H_{39}Si_8(M^+ - H)$ 419.1200.

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