Selective Si–Si Bond Cleavage of Decaisopropylbicyclo[2.2.0]hexasilane with Hydrobromic Acid and Hydrochloric Acid

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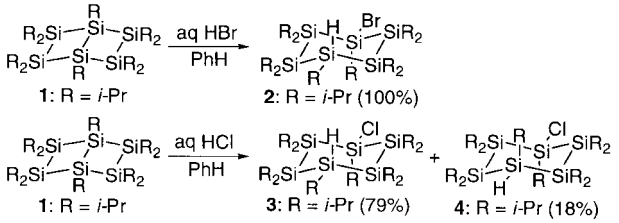
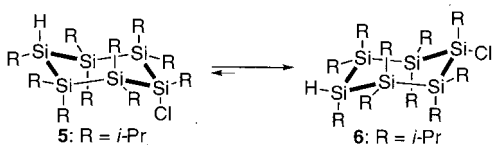
In the reactions of decaisopropylbicyclo[2.2.0]hexasilane (**1**) with hydrobromic acid and hydrochloric acid, the bridgehead Si–Si bond of **1** was selectively cleaved to give 1-halo-1,2,2,3,3,4,5,5,6,6-decaisopropylcyclohexasilanes. The X-ray crystallographic analysis of the products indicates that the cis-addition of the acids to the Si–Si bond is preferable.

Although the cleavage of the Si–Si bonds of polysilanes by electrophiles has been well documented,[1,2] only a few examples of the cleavage of the Si–Si bonds by hydrohalogenic acids and hydrogen halides have appeared. Thus, Watanabe et al.[3] and West et al.[4] reported that the strained Si–Si bonds of the cyclotetrasilanes such as $[(i\text{-Pr})_2\text{Si}]_4$ and $(\text{Et}_2\text{Si})_4$ have been cleaved by hydrogen chloride, hydrochloric acid, and hydrobromic acid. However, to the best of our knowledge, no report has dealt with the stereochemistry of the cleavage reaction. Ladder oligosilanes,[5] which have been studied by our group, seem to be the suitable system for studying the stereochemistry of the Si–Si bond cleavage with acids, while similar stereochemical information is not easily accessible in linear and monocyclic oligosilanes. We report herein the ring-opening reactions of decaisopropylbicyclo[2.2.0]hexasilane (**1**) with hydrobromic acid and hydrochloric acid.

The reaction of **1** with hydrobromic acid quantitatively gave only *trans*-1-bromo-1,2,2,3,3,4,5,5,6,6-decaisopropylcyclohexasilane (**2**, cis-adduct).[6] The reaction of **1** with hydrochloric acid gave *trans*-1-chloro-1,2,2,3,3,4,5,5,6,6-decaisopropylcyclohexasilane (**3**, cis-adduct) in 79% yield and *cis*-1-chloro-1,2,2,3,3,4,-5,5,6,6-decaisopropylcyclohexasilane (**4**, trans-adduct) in 18% yield.[7] In these reactions, no other Si–Si bond cleavage products were obtained, showing that the bridgehead Si–Si bond is exclusively cleaved. Compound **1** did not react with hydrofluoric acid. The reactions of 1,4-di-*tert*-butyl-2,2,3,3,5,5,6,6-octaisopropylbicyclo[2.2.0]hexasilane with hydrobromic acid and hydrochloric acid were attempted, but no reactions took place. This result is ascribed to the steric hindrance by the *tert*-butyl groups on the bridgehead silicon atoms.



The structures of **2**–**4** were determined by X-ray crystallography (Figures 1–3).[8–10] The cyclohexasilane rings of **2**–**4** adopt the chair conformations. A remarkable feature of the trans-adduct **4** is the fact that the hydrogen and chlorine atoms occupy equatorial positions and the geminal isopropyl groups occupy axial positions. If the isopropyl groups occupied equatorial positions, the steric repulsion among the isopropyl groups and four vicinal isopropyl groups would be large due to the quadruple gauche interaction. When the isopropyl groups occupy axial positions, the steric repulsion is reduced to double anti and double gauche interactions. The 1,3-diaxial interaction among the isopropyl groups seems less important because of the long Si–Si bond lengths (2.402(1)–2.406(1) Å). This proposal is confirmed by MM2 calculations; the steric energy of **6** is smaller by 61.5 kJ mol^{-1} than that of **5**. Similar results have also been reported in other isopropyl-substituted cyclohexasilanes[5c] and cyclohexane.[11] The cis-adducts **2** and **3** have relatively planar structures of the hydrogen-substituted Si(4) atoms. The sum of the Si(3)–Si(4)–Si(5),



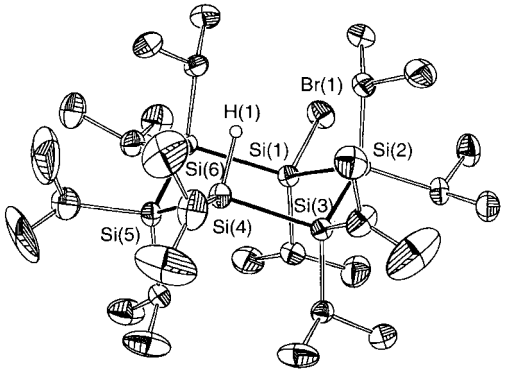


Figure 1. Molecular structure of **2**. Selected bond lengths (Å): Br(1)–Si(1) 2.293(2), Si(1)–Si(2) 2.423(2), Si(1)–Si(6) 2.415(2), Si(2)–Si(3) 2.402(2), Si(3)–Si(4) 2.390(2), Si(4)–Si(5) 2.385(3), Si(5)–Si(6) 2.406(3).

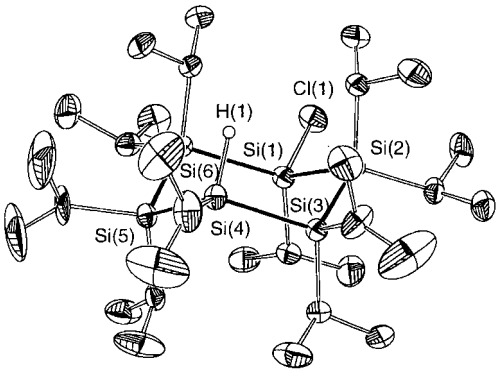


Figure 2. Molecular structure of **3**. Selected bond lengths (Å): Cl(1)–Si(1) 2.124(4), Si(1)–Si(2) 2.419(4), Si(1)–Si(6) 2.417(4), Si(2)–Si(3) 2.397(4), Si(3)–Si(4) 2.387(4), Si(4)–Si(5) 2.385(4), Si(5)–Si(6) 2.400(4).

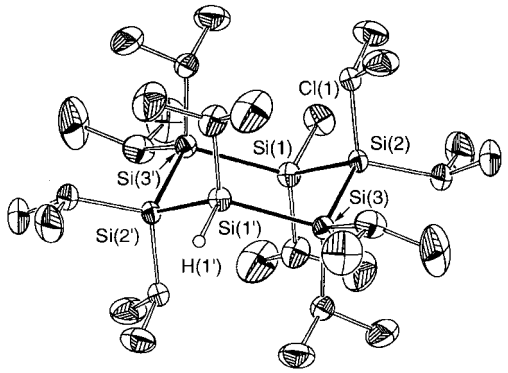
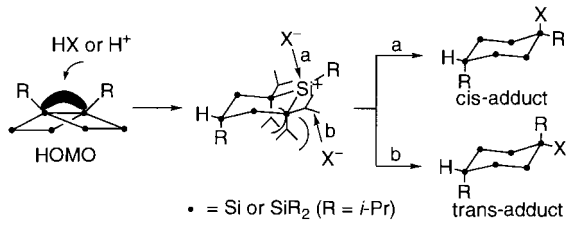


Figure 3. Molecular structure of **4**. The chlorine atom on Si(1) and the hydrogen atom on Si(1') are disordered, and the occupancy of both atoms is 0.5. Selected bond lengths (Å): Cl(1)–Si(1) 2.086(2), Si(1)–Si(2) 2.406(1), Si(1)–Si(3') 2.406(1), Si(2)–Si(3) 2.402(1).

Si(3)–Si(4)–C(*i*-Pr), and Si(5)–Si(4)–C(*i*-Pr) bond angles is 346.4° in both **2** and **3**. These values show that the geometry of the Si(4) atoms is almost intermediate between an ideal sp^2 silicon atom (360°) and an ideal sp^3 silicon atom (328.5°).[12]

The selective cleavage of the bridgehead Si–Si bond of **1** is explained by the MO calculation. The lobes of the HOMO are preferentially localized in the bridgehead Si–Si bond. During the first step of the reaction, the bridgehead Si–Si bond is attacked by the hydrogen halide or a hydrogen ion to give the silyl cation intermediate in which the geminal isopropyl group of the hydrogen atom occupies an axial position. The silyl cation is attacked by a halide ion from two directions (paths a and b). In path a, the halide ion can approach the silyl cation center without significant steric hindrance, while the halide ion suffers significant steric repulsion by two neighboring axial isopropyl groups in path b. Therefore, the cis-adduct **3** is favorably formed in the reaction with hydrochloric acid. For hydrobromic acid, the steric repulsion in path b is much greater than that of the chloride ion, and only the cis-adduct **2** is formed.



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Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

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6 A solution of **1** (50.3 mg, 0.0839 mmol) in benzene (5 mL) was vigorously stirred with hydrobromic acid (10 mL) at room temperature for 13 h. The organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. The solvent was removed by evaporation, and the residue was washed with methanol to give **2** (57.1 mg, 100%) as colorless crystals. **2**: mp 224 °C; ^{1}H NMR (C_6D_6) δ 1.32 (d, 6H, *J* = 7.5 Hz), 1.33–1.35 (m, 24H), 1.36 (d, 6H, *J* = 7.5 Hz), 1.39 (d, 6H, *J* = 7.5 Hz), 1.43 (d, 6H, *J* = 7.5 Hz), 1.49 (d, 6H, *J* = 7.5 Hz), 1.57 (d, 6H, *J* = 7.5 Hz), 1.59–1.73 (m, 3H), 1.85 (sept, 2H, *J* = 7.5 Hz), 1.87 (sept, 2H, *J* = 7.5 Hz), 3.98 (s, 1H); ^{13}C NMR (C_6D_6) δ 12.7, 15.5, 16.49, 16.51, 17.8, 19.5, 22.0, 22.5, 22.8, 23.1, 23.2, 23.5, 23.56, 23.62, 23.9, 24.2; ^{29}Si NMR (C_6D_6) δ –51.8, –17.2, –12.5, 24.4; IR (KBr, cm^{-1}) 2880, 2080, 1460, 1380, 1360, 1230, 1065, 1020, 1000, 990, 920, 880; MS *m/z* (%) 678 (M^+(^{79}Br), 25), 635 (^{79}Br, 18), 485 (52), 371 (100), 327 (^{79}Br, 56), 228 (91), 73 (49), 58 (77); HRMS. Found: 678.3358. Calcd for $C_{30}H_{71}BrSi_6$: 678.3356.
7 **3**: mp 240–248 °C; ^{1}H NMR (C_6D_6) δ 1.33 (d, 6H, *J* = 7.5 Hz), 1.335 (d, 6H, *J* = 7.5 Hz), 1.341 (d, 6H, *J* = 7.5 Hz), 1.35 (d, 12H, *J* = 7.5 Hz), 1.37 (d, 6H, *J* = 7.5 Hz), 1.38 (d, 6H, *J* = 7.5 Hz), 1.41 (d, 6H, *J* = 7.5 Hz), 1.44 (d, 6H, *J* = 7.5 Hz), 1.53 (d, 6H, *J* = 7.5 Hz), 1.62 (sept, 1H, *J* = 7.5 Hz), 1.65 (sept, 2H, *J* = 7.5 Hz), 1.83 (sept, 2H, *J* = 7.5 Hz), 1.85 (sept, 2H, *J* = 7.5 Hz), 3.97 (s, 1H); ^{13}C NMR (C_6D_6) δ 12.7, 15.4, 16.2, 16.5, 17.3, 20.5, 21.2, 22.5, 22.8, 23.1, 23.2, 23.3, 23.4, 23.5, 23.8, 24.2; ^{29}Si NMR (C_6D_6) δ –52.0, –16.0, –12.8, 29.6; IR (KBr, cm^{-1}) 2870, 2070, 1460, 1380, 1360, 1230, 1065, 1020, 1010, 990, 920, 880; MS *m/z* (%) 634 (M^+(^{35}Cl), 18), 591 (^{35}Cl, 19), 485 (27), 371 (100), 329 (66), 228 (68), 73 (45), 58 (57), 55 (66); HRMS. Found: 634.3834. Calcd for $C_{30}H_{71}ClSi_6$: 634.3860. **4**: mp 254–260 °C; ^{1}H NMR (C_6D_6) δ 1.33 (d, 6H, *J* = 7.5 Hz), 1.34 (d, 12H, *J* = 7.5 Hz), 1.35 (d, 6H, *J* = 7.5 Hz), 1.37 (d, 6H, *J* = 7.5 Hz), 1.38 (d, 12H, *J* = 7.5 Hz), 1.41 (d, 12H, *J* = 7.5 Hz), 1.43 (d, 6H, *J* = 7.5 Hz), 1.62 (sept, 2H, *J* = 7.5 Hz), 1.64 (sept, 1H, *J* = 7.5 Hz), 1.71 (sept, 1H, *J* = 7.5 Hz), 1.78 (sept, 6H, *J* = 7.5 Hz), 3.88 (s, 1H); ^{13}C NMR (C_6D_6) δ 12.7, 15.7, 16.09, 16.13, 20.7, 21.0, 22.85, 22.88, 22.91, 22.93, 23.0, 23.1, 23.6, 23.7, 24.3; ^{29}Si NMR (C_6D_6) δ –52.0, –16.0, –12.8, 29.6; IR (KBr, cm^{-1}) 2870, 2030, 1460, 1380, 1360, 1220, 1060, 1020, 990, 920, 880; MS *m/z* (%) 634 (M^+(^{35}Cl), 25), 591 (^{35}Cl, 25), 485 (32), 371 (100), 329 (76), 228 (65), 73 (34), 58 (53); HRMS. Found: 634.3843. Calcd for $C_{30}H_{71}ClSi_6$: 634.3860.
8 Crystal data for **2**: $C_{30}H_{71}BrSi_6$, F_w = 680.31, orthorhombic, space group *Pbca*, *a* = 17.877(2), *b* = 30.502(2), *c* = 14.750(2) Å, *V* = 8043(1) Å^3, *Z* = 8, D_c = 1.124 g cm^{-3}, *R* = 0.054, R_w = 0.051 (w = $1/\sigma^2(F_o)$) for 4202 observed reflections.
9 Crystal data for **3**: $C_{30}H_{71}ClSi_6$, F_w = 635.85, orthorhombic, space group *Pbca*, *a* = 17.877(1), *b* = 30.380(2), *c* = 14.704(2) Å, *V* = 7985(1) Å^3, *Z* = 8, D_c = 1.058 g cm^{-3}, *R* = 0.056, R_w = 0.051 (w = $1/\sigma^2(F_o)$) for 2206 observed reflections.
10 Crystal data for **4**: $C_{30}H_{71}ClSi_6$, F_w = 635.85, monoclinic, space group $P2_1/n$, *a* = 9.898(2), *b* = 18.031(1), *c* = 11.980(1) Å, β = 112.753(9)°, *V* = 1971.7(5) Å^3, *Z* = 2, D_c = 1.071 g cm^{-3}, *R* = 0.052, R_w = 0.040 (w = $1/\sigma^2(F_o)$) for 2605 observed reflections.
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