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Photoswitching of the reactivity involving hydrosilylation of a 1,1,3,3-tetrahydrodisiloxane bearing two azo groups

Masaki Yamamura, Naokazu Kano and Takayuki Kawashima*

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, Japan

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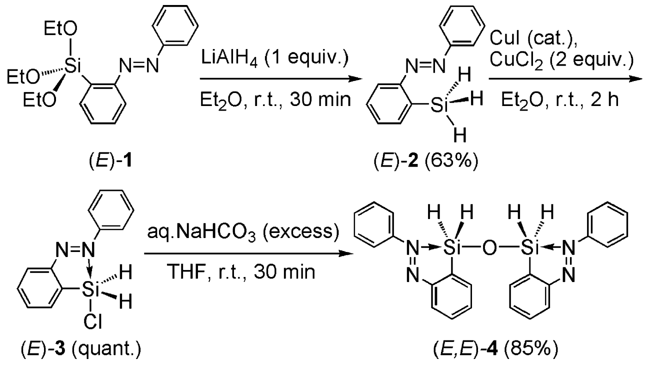
Abstract—A pentacoordinate (*E*,*E*)-1,1,3,3-tetrahydrodisiloxane bearing two azo groups gave hydrazobenzene in the fluoride ion-induced hydrolysis involving hydrosilylation of the azo groups followed by cleavage of the Si–C bonds, while a tetracoordinate (*E*,*E*)-forms formed by its photoirradiation gave an octaarylsilsesquioxane without cleavage of the Si–C bonds.

Highly coordinate hydrosilanes have been known to reduce carbonyl compounds without the intervention of a transition metal catalyst because the nucleophilicity of the hydride is increased from that of tetracoordinate hydrosilanes.[1] Such a hydrosilane is expected to be effective for reduction of various doubly bonded compounds, but hydrosilylation of azo compounds to produce the corresponding *N*-silylhydrazines has not been reported to date. Azobenzene, a most popular example of the azo compounds, has been utilized for optical molecular switches.[2] We have reported the synthesis and photoswitching of the properties and reactivity of azobenzenes bearing a heteroatom such as boron,[3] silicon,[4] and phosphorus[5] at the 2 position. Reactivity of a hydrosilane bearing a 2-(phenylazo)phenyl group is also expected to be changed by photoirradiation. We report here the synthesis of a pentacoordinate 1,1,3,3-tetrahydrodisiloxane bearing azobenzene moieties and the reduction of the azo groups by intramolecular hydrosilylation.

Reaction of triethoxysilane (*E*)-**1**[4e] with $LiAlH_4$ in ether at room temperature gave trihydrosilane (*E*)-**2** (Scheme 1).[6] Chlorination of (*E*)-**2** with $CuCl_2$ (2 equiv) and CuI (cat.)[7] at room temperature for 2 h gave chlorodihydrosilane (*E*)-**3** quantitatively and hydrolysis of (*E*)-**3** with aq $NaHCO_3$ gave 1,1,3,3-tetrahydrodisiloxane (*E*,*E*)-**4** (85%).[8]

In the ^{29}Si NMR spectra, the signal of (*E*,*E*)-**4** (δ_{Si} −58.9) was observed at a higher field than that of 1,1,3,3-tetrahydro-1,3-diphenyldisiloxane[9] (**5**) (δ_{Si} −25.4), indicating a pentacoordinate state of silicon atoms in the solution state. The coupling constant of (*E*,*E*)-**4** ($^1J_{SiH} = 248$ Hz) is larger than that of **5** ($^1J_{SiH} = 221$ Hz), revealing the change of the s-character of an orbital on the silicon atoms used for the equatorial Si–H bonds. In the UV/vis spectra, (*E*,*E*)-**4** showed a red shift of the absorption maximum ($\lambda = 335$ nm) assigned to a π–π^* transition compared with that of unsubstituted azobenzene ($\lambda = 320$ nm), similarly to all other azobenzenes coordinating to silicon atoms, suggesting the perturbation of the electronic structure of the azo moiety.[4]

Tetrahydrodisiloxane (*E*,*E*)-**4** was successfully isomerized by photoirradiation with high-pressure mercury



Scheme 1. Synthesis of pentacoordinate tetrahydrodisiloxane (*E*,*E*)-**4**.

Keywords: Hydrosilylation; Pentacoordinate silicon compound; Azobenzene.

* Corresponding author. Tel./fax: +81 3 5800 6899; e-mail: takayuki@chem.s.u-tokyo.ac.jp

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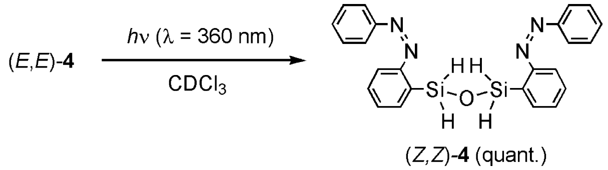
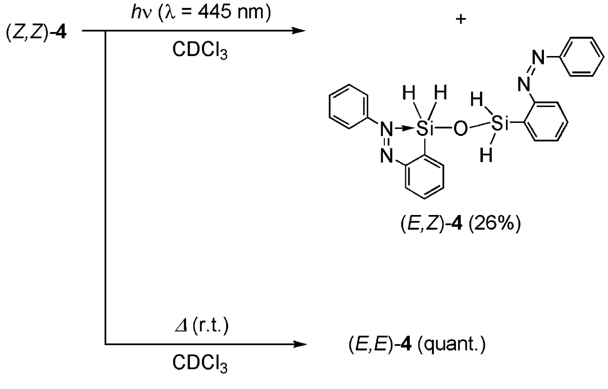


Scheme 2. Photoisomerization of (*E*,*E*)-**4** to (*Z*,*Z*)-**4** in $CDCl_3$.

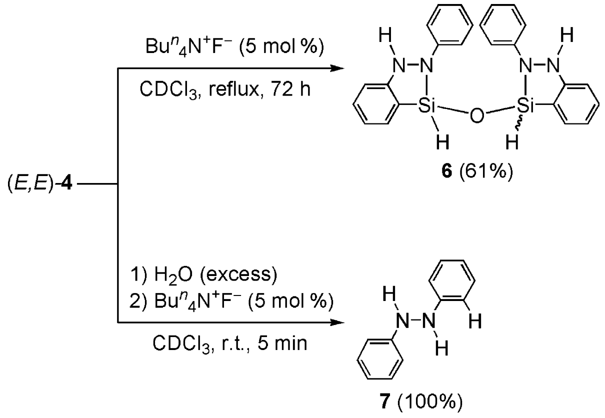
lamp through a colored-glass filter ($\lambda = 360$ nm) to give (*Z*,*Z*)-**4** quantitatively as demonstrated by the ^{1}H NMR spectra of the reaction solution (Scheme 2).[10] The quantitative photoisomerization of the azobenzene moieties is remarkable. In the ^{29}Si NMR spectrum, (*Z*,*Z*)-**4** showed one triplet (δ_{Si} −28.3 ($^1J_{SiH} = 230$ Hz)) whose chemical shift and coupling constant are similar to those of **5**, respectively, suggesting a tetracoordinate state of the silicon atoms of (*Z*,*Z*)-**4**.

Photoirradiation ($\lambda = 445$ nm) of (*Z*,*Z*)-**4** for 2 h gave a 4:26:70 mixture of (*Z*,*Z*)-**4**, (*E*,*Z*)-**4**,[11] and (*E*,*E*)-**4** (Scheme 3). The $CDCl_3$ solution of (*Z*,*Z*)-**4** was thermally isomerized to (*E*,*E*)-**4** quantitatively upon standing at room temperature for 36 h. Therefore, (*Z*,*Z*)-**4** was not isolated. These results indicate that coordination number change of the silicon atoms based on the isomerization between (*E*,*E*)-**4** and (*Z*,*Z*)-**4** is reversible and quantitative.

In the reaction of (*E*,*E*)-**4** with tetrabutylammonium fluoride (TBAF) under anhydrous conditions, the yellow solution slowly became colorless, which suggested the conversion of the azo groups to hydrazo groups (Scheme 4). In the ^{29}Si NMR spectra, two doublet signals were observed. The chemical shifts and coupling constants of the two signals (δ_{Si} −34.3 ($^1J_{Si–H} = 281$ Hz), −34.0 ($^1J_{Si–H} = 279$ Hz)) are almost the same. The products are identified as two diastereomers of cyclic aminosilane **6**, which should be colorless. In the ^{1}H NMR spectra, two peaks (δ_H 4.78, 5.05) due to H–Si protons of diastereomers of **6** are clearly distinguished and the ratio of diastereomers is estimated to be 1:1 by integration. Compounds **6** seem to be formed by intramolecular hydrosilylation of the azo groups induced by a fluoride ion. The reaction at room temperature for 5 min in the presence of water or ethanol did not give **6**, but hydrazobenzene (**7**).



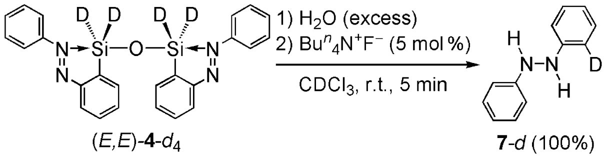
Scheme 3. Photoisomerization and thermal isomerization of (*Z*,*Z*)-**4** to (*E*,*E*)-**4** in $CDCl_3$.



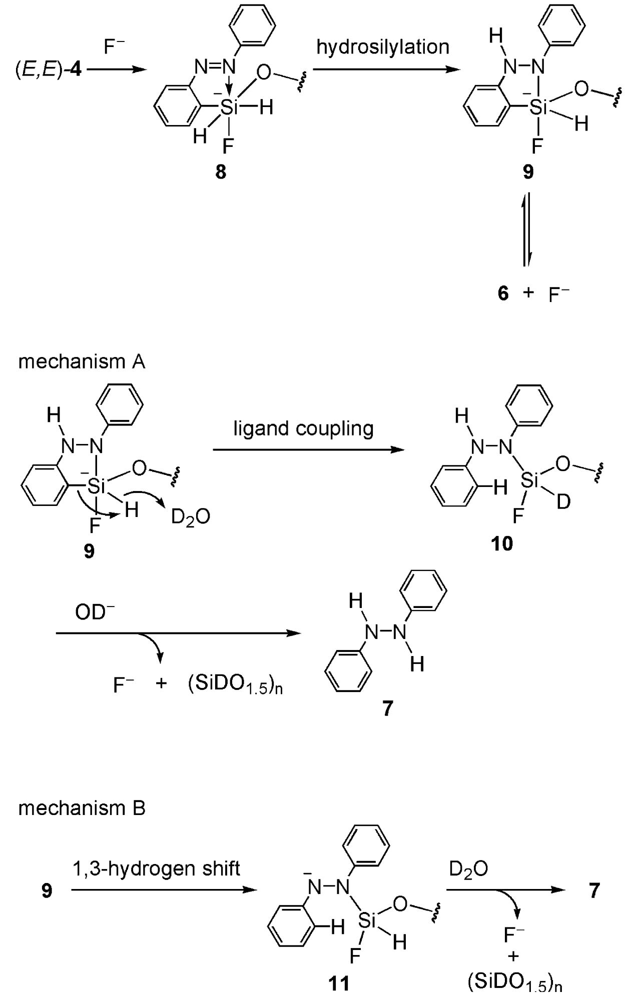
Scheme 4. Reaction of (*E*,*E*)-**4** with fluoride ion.

Even in the presence of D_2O, product **7** contained no deuterium at the benzene ring. Conversely, when 1,1,3,3-tetradeuteriodisiloxane (*E*,*E*)-**4**-d_4 was used, the D-content of **7**-*d* was 100% (Scheme 5). These results indicate that the desilylation of (*E*,*E*)-**4** was not caused by protonation of an intermediary fluorosilicate with water or ethanol as is observed in deprotective reactions of silyl groups.[12]

The formation of **6** suggests that the hydrosilylation intramolecularly proceeds via fluorosilicate **8** to give aminosilicate **9** in equilibrium with **6**. Considering the deuterium experiment, there are two plausible mechanisms for the cleavage of the Si–C bond as follows (Scheme 6): one is water-assisted ligand coupling reaction between hydrogen and aryl group in fluorosilicate **9** derived from **6** (mechanism A), and the other is 1,3-hydrogen shift in fluorosilicate **9** from nitrogen to the ipso carbon attached to the silicon atom followed by bond cleavage of the Si–C bond (mechanism B). The latter mechanism must involve the fast 1,3-shift from the NH(D) group formed by hydrosilylation of the azo group without proton exchange of NH(D) with water or ethanol, which seems very difficult under the reaction condition. The former mechanism is suggested to be more operative in this reaction, though reports on ligand coupling reactions in highly coordinate silicon compounds are so limited.[13] In the absence of water, the cleavage of the Si–C bond did not occur, indicating that water took part in the bond cleavage to result in the protonation of the silicon atom. Protonation,



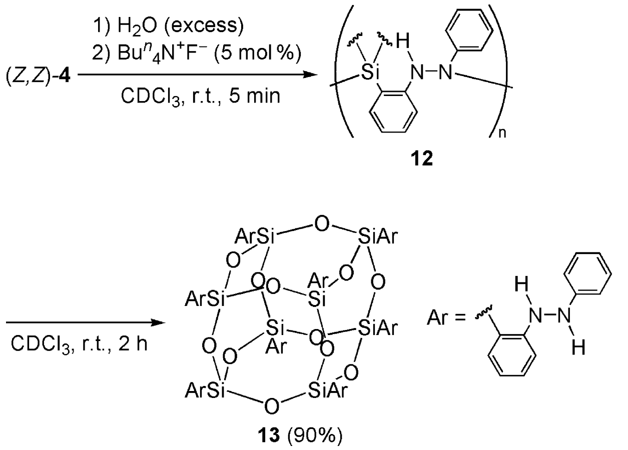
Scheme 5. Reaction of (*E*,*E*)-**4**-d_4 with fluoride ion.



Scheme 6. Plausible mechanisms for formation of hydrazobenzene (**7**) from (*E*,*E*)-**4**.

which is an exothermic reaction, seems to be the driving force of the reaction. After the cleavage of the Si–C bond, **7** was formed by hydrolysis of the Si–N bonds.

The reaction of tetracoordinate hydrosilane (*Z*,*Z*)-**4** with TBAF in the presence of water for 5 min did not give **7**, but a colorless unidentified compound that showed broad peaks in the ^{1}H NMR spectra, indicating the formation of polymeric compound **12**. Intermediate **12** disappeared after standing at room temperature for 2 h and one main product that showed sharp peaks in the ^{1}H NMR spectra was formed finally (Scheme 7). This compound showed one singlet (δ_{Si} −71.3) in the ^{29}Si NMR spectra, whose chemical shift was similar to those (δ_{Si} −73.3, −77.4) of octa(2- or 4-aminophenyl)silsesquioxane.[14] In MALDI-TOF MS of the product, a molecular ion peak was detected at *m*/*z* 1880. Thus, the product was identified as octa[2-(1-phenylhydrazino)phenyl]silsesquioxane **13**. Compound **12** seems to be formed via intermolecular hydrosilylation of the azo groups, contrary to (*E*,*E*)-**4** which underwent intramolecular hydrosilylation. Compound **13** is considered to be obtained by hydrolysis of the polymer and successive dehydrative condensation. Considering that octaphenylsilsesquioxane was a main product in hydrolysis of phenyltrichlorosilane, the formation of **13** is reasonable.[15] Thus, it is concluded that the reaction of (*Z*,*Z*)-**4** with fluoride ion resulted in intermolecular hydrosilylation of the azo groups without cleavage of Si–C bonds. The difference in reactivity between (*E*,*E*)-**4** and (*Z*,*Z*)-**4** is explained as follows: the reaction of (*E*,*E*)-**4** proceeded via cyclic aminosilane **6** that was electrophilic enough to react with fluoride ion for desilylation, whereas intermediate **6** was not formed in the reaction of (*Z*,*Z*)-**4** because the azo groups of (*Z*,*Z*)-**4** could not coordinate intramolecularly to the silicon atoms.



Scheme 7. Reaction of tetracoordinate hydrosilane (*Z*,*Z*)-**4** with fluoride ion in the presence of water.

In conclusion, the reaction of pentacoordinate tetrahydrodisiloxane (*E*,*E*)-**4** with TBAF in the presence of water resulted in desilylation to give **7**. Conversely, the reaction of tetracoordinate tetrahydrodisiloxane (*Z*,*Z*)-**4**, prepared by photoirradiation of (*E*,*E*)-**4**, caused intermolecular hydrosilylation and the final product maintained the Si–C bonds. Although the reaction intermediates were not clear, both reactions of (*E*,*E*)-**4** and (*Z*,*Z*)-**4** gave apparently different final products. The reactivity of the tetrahydrodisiloxane has been successfully changed by photoswitching of the coordination number of silicon atoms.

Acknowledgments

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8. *Compound data for* (*E*,*E*)-**4**: Yellow crystals; mp 106–107 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.27 (s, $^1J_{\mathrm{SiH}} = 247.5$ Hz, 4H), 7.49–7.52 (m, 6H), 7.56 (td, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 2H), 7.67 (td, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz, 2H), 8.04 (dd, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 4H), 8.07 (dd, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 2H), 8.20 (d, $^3J = 7.0$ Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 122.63 (*C*H), 126.69 (*C*Si), 129.22 (*C*H), 130.40 (*C*H), 130.97 (*C*H), 131.34 (*C*H), 131.52 (*C*H), 137.09 (*C*H), 149.98 (*C*N), 157.28 (*C*N); ^{29}Si NMR (99 MHz, $CDCl_3$) δ −58.9 (td, $^1J_{\mathrm{SiH}} = 247.5$ Hz, $^3J_{\mathrm{SiH}} = 5.7$ Hz); UV/vis ($CHCl_3$) $\lambda_{\max}$ (ε) 335 nm (3.3×10^4). Anal. Calcd for $C_{24}H_{22}N_4OSi_2$: C, 65.72; H, 5.06; N, 12.77. Found: C, 65.49; H, 5.17; N, 12.53.
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10. *Compound data for* (*Z*,*Z*)-**4**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.32 (s, $^1J_{\mathrm{SiH}} = 230.1$ Hz, 4H), 6.15 (d, $^3J = 8.0$ Hz, 2H), 6.84 (d, $^3J = 8.0$ Hz, 4H), 7.09 (t, $^3J = 8.0$ Hz, 2H), 7.12–7.25 (m, 8H), 7.75 (d, $^3J = 7.0$ Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 115.68 (*C*H), 120.11 (*C*H), 127.25 (*C*H), 127.45 (*C*H), 128.68 (*C*H), 130.33 (*C*H), 130.60 (*C*Si), 135.65 (*C*H), 152.99 (*C*N), 157.61 (*C*N); ^{29}Si NMR (99 MHz, $CDCl_3$) δ −28.3 (td, $^1J_{\mathrm{SiH}} = 230.1$ Hz, $^3J_{\mathrm{SiH}} = 7.7$ Hz); UV/vis ($CHCl_3$) $\lambda_{\max}$ (ε) 285 nm (1.3×10^4), 442 nm (3.2×10^3).
11. A new compound bearing both *E*- and *Z*-azobenzene units in a 1:1 ratio was identified to (*E*,*Z*)-**4**, but (*E*,*Z*)-**4** was not isolated, unfortunately. Compound data for (*E*,*Z*)-**4**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.17 (s, 2H), 5.41 (s, 2H), 6.22 (d, $^3J = 8.0$ Hz, 1H), 6.90 (d, $^3J = 8.0$ Hz, 2H), 8.18 (d, $^3J = 7.0$ Hz, 1H), other signals were not assigned because of the overlap with the signals of (*E*,*E*)-**4** and (*Z*,*Z*)-**4**.
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