Table I. Some Physical Properties of New Compounds

3b: mp 239-241 °C; mass spectrum (rel intensity) M^+ 552 (100); NMR δ (CCl_4) 0.20 (3 H, s, CH_3), 6.4-7.7 (29 H, m, Ph)

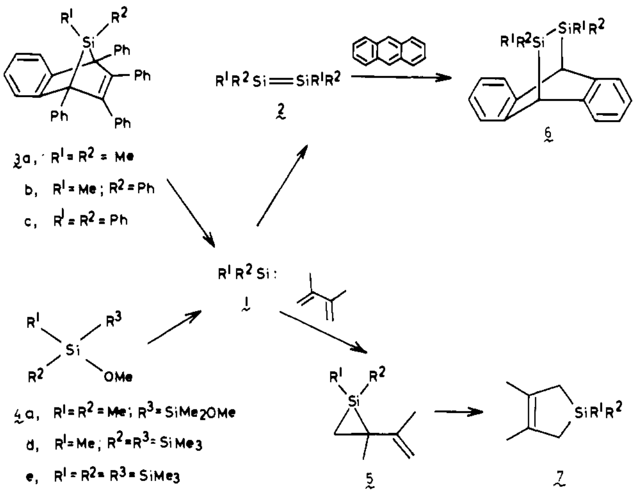
4d: bp 77 °C (20 mmHg); mass spectrum (rel intensity) M^+ 220 (4.9), *m/e* 73 (100); NMR δ (CCl_4) 0.12 (18 H, s), 0.34 (3 H, s), 3.34 (3 H, s)

4e: bp 63 °C (0.5 mmHg); mass spectrum (rel intensity) M^+ 278 (1.5), *m/e* 73 (100); NMR δ (CCl_4) 0.14 (27 H, s), 3.35 (3 H, s)

6d: bp 160-180 °C (0.2 mmHg); mass spectrum (rel intensity) M^+ 410 (24.9), *m/e* 232 (100); NMR δ (CCl_4), trans, −0.07 (6 H, s), −0.12 (18 H, s), 4.08 (2 H, s), 7.0-7.2 (8 H, m, arom), and cis, −0.26 (6 H, s), 0.00 (18 H, s), 4.10 (2 H, s), 7.0-7.2 (8 H, m, arom)

6e: mp 275 °C; mass spectrum (rel intensity) M^+ 526 (4.3), *m/e* 348 (100); NMR δ (CCl_4) 0.06 (36 H, s) 4.27 (2 H, s), 6.8-7.2 (8 H, m, arom)

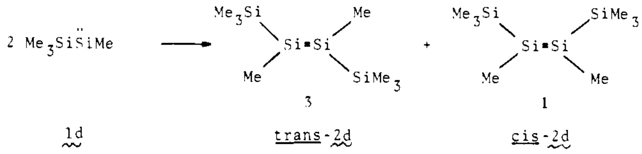
Scheme I



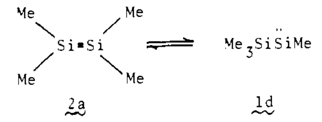
is also not reactive enough to be susceptible to silylene insertion. Therefore, we favor the mechanism shown in Scheme I.

Methoxypolysilanes are also well-defined silylene generators[9] and, indeed, the dimethylsilylene generated from **4a** afforded **6a** by reaction with anthracene. The yield of **6a** from **4a** was highly temperature dependent. Thus, at 300 °C, no adduct was found in the thermolyzed mixture of **4a** and anthracene, but **6a** was obtained as a trace at 350 °C and in 6.2% yield at 390 °C. Methyl(trimethylsilyl)silylene (**2d**) and the bis(trimethylsilyl)silylene (**2e**), more bulky silylenes, generated from **4d** and **4e**, gave the corresponding adducts **6d** (72% yield, 350 °C, 4 h) and **6e** (48% yield, 250 °C, 3 h), respectively, in higher yields. These results indicate that dimerization of silylenes competes with insertion into the Si-OMe bond of the precursor.[10] Some physical properties of new compounds are summarized in Table I.[11]

Interestingly, an ~1:1 mixture of trans and cis isomers of **6b** was obtained from **4b** (350 °C). Since *cis*- and *trans*-1,2-diphenyl-1,2-dimethyldisilene are configurationally stable under these conditions,[12] the result implies no stereochemical preference in the dimerization of the phenylmethylsilylene. However, **4d** gave two isomers of **6d** in the ratio 3:1 at 250 °C. Therefore, the methyl(trimethylsilyl)silylene dimerized stereoselectively to the disilenes in favor of one isomer which was tentatively assigned to be trans.



Very recently, Wulff, Goure, and Barton[13] reported that tetramethyldisilene (**2a**) isomerizes to **1d** and that **1d** also isomerizes to **2a** to some extent in vapor phase.



However, in our experimental conditions, there is no indication of such a rearrangement. In fact, we generated **1d** in the hope of obtaining **2a** which has been known to be trapped by anthracene,[4] but no **6a** was detected. The discrepancy between these experiments may arise from the different experimental conditions, but we reserve the explanation until new experimental results are available.

Acknowledgment. We thank Toshiba Silicone Co., Ltd., for gifts of chlorosilanes.

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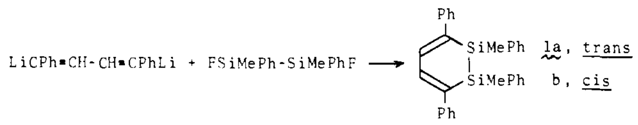
trans- and *cis*-1,2-Dimethyl-1,2-diphenyldisilene. Is Si=Si a True Double Bond?[1]

Sir:

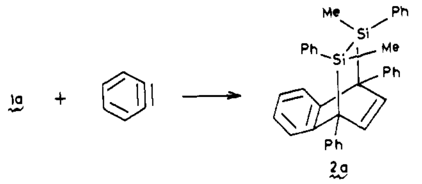
Although disilenes, the silicon-silicon double-bonded species, have been recognized as intermediates in certain reactions,[2] no experimental knowledge has been obtained on the double-bond properties such as geometrical isomerism of the Si=Si bond.[3] We report in this communication the first evidence of the geometrical isomerism of the silicon-silicon double bond.

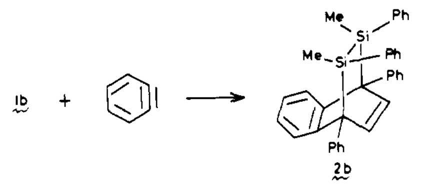
The reaction of 1,4-dilithio-1,4-diphenylbutadiene[4] with 1,2-difluoro-1,2-dimethyl-1,2-diphenyldisilane in THF gave a mixture of *trans*- and *cis*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexadiene which was separated into each isomer by silica gel chromatography.[5]

The stereochemical assignment of trans (**1a**) and cis isomers (**1b**) is not easy from the NMR results only, but can be accomplished unequivocally by examination of the NMR signals due to Si-Me groups of products of the next step (**2a** and **2b**).



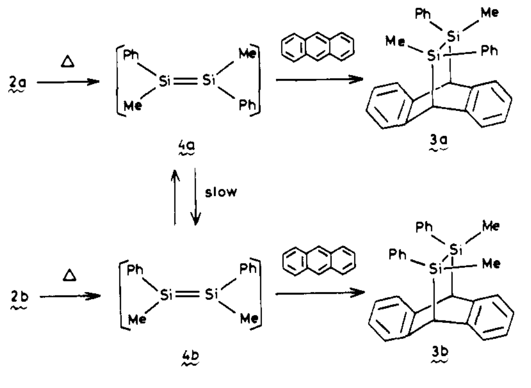
The trans isomer **1a** gave *trans*-2,3-benzo-1,4,7,8-tetraphenyl-7,8-dimethyl-7,8-disilabicyclo[2.2.2]octadiene (**2a**)[6] quantitatively by the reaction with benzyne generated from benzenediazonium 2-carboxylate in THF at 70 °C. Similarly **1b** afforded the corresponding cis isomer **2b**.[7] Two Si-Me signals appeared in the spectrum of **2a,** whereas only one appeared in that of **2b;** therefore the stereochemical assignment is obvious. Only a single product was obtained in the reaction of **1b** with benzyne and, for steric reasons, the structure of **2b** was tentatively assigned to that product. However, the conclusion obtained in the following text is not affected by the stereochemical assignment of **2b**.





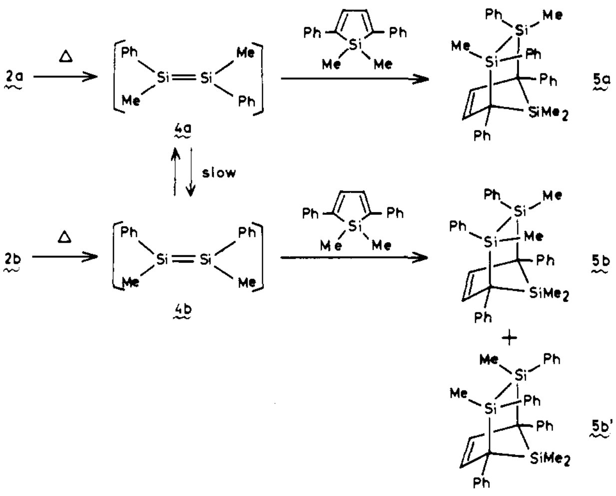
Pyrolysis of a 1:1 mixture of **2a** and anthracene in benzene in a sealed tube at 300 °C for 17 h afforded a mixture of **3a** (96%) and **3b** (4%) in 81% yield.[8] Similar pyrolysis of **2b** gave a mixture of **3a** (6%) and **3b** (94%) in 88% yield. Since 1,2-dimethyl-1,2-diphenyldisilene (**4**) produced by dimerization of PhMeSi: gives rise to a 1:1 mixture of **3a** and **3b** in the reaction with anthracene,[9] the stereospecificity observed in the reaction of **2** is quite remarkable.[10,11]

Thermolysis of **2a** and **2b** at 350 °C gave slightly less stereospecific results. Thus, **2a** afforded **3a** (94%) and **3b** (6%) in 84% yield, and **2b** gave **3a** (10%) and **3b** (90%) in 85% yield, respectively.



With a seemingly less efficient enephile, 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene, **2a** and **2b** gave somewhat less stereospecific Diels-Alder adducts. Thus, at 300 °C for 18 h, three possible adducts, **5a** (88%), **5b** (8%), and **5b′** (4%), were obtained in 82% yield.[12] Since both **5b** and **5b′** are derived from **4b,** 88% retention of configuration is observed in this case. Similar temperature dependency of **2** was also observed in this case. Thus, at 350 °C for 2.5 h, **2a** gave **5a** (73%), **5b** (18%), and **5b′** (9%). Thermolysis of **2b** in the presence of the silacyclopentadiene at 300 and 350 °C gave **5a** (18 and 29%), **5b** (56 and 50%), and **5b′** (26 and 21%) in 91 and 87% yield, respectively.

These results demonstrate clearly that the π overlap between two 3p orbitals of silicon is effective to retain the configuration; namely, the Si=Si bond is a true double bond like C=C, with slow cis-trans isomerization in the temperature range studied. Related works are in progress.



Acknowledgment. We thank Toshiba Silicone Co., Ltd., for gifts of chlorosilanes.

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(5) **1a:** mp 112–113 °C; mass spectrum (rel intensity) (M^+) *m/e* 444 (36), 197 (100); NMR δ (CCl_4) 0.20 (6 H, s, SiMe) 7.0–7.7 (22 H, m, olefinic and aromatic protons); UV λ (*n*-hexane) 235.5 nm (ε 39 700), 305.0 (9850), 354.5 (13 300). **Ib:** mp 114 °C; mass spectrum (rel intensity) (M^+) *m/e* 444 (41), 197 (100); NMR δ (CCl_4) 0.84 (6 H, s, SiMe), 7.0–7.5 (22 H, m, olefinic and aromatic protons); UV λ (*n*-hexane) 228.0 nm (ε 29 000), 299.5 (9070), 356.0 (12 100).

(6) **2a:** mp 199–200 °C; mass spectrum (rel intensity) (M^+) *m/e* 520 (12), 240 (100); NMR δ (CCl_4) 0.24 (3 H, s, SiMe), 0.36 (3 H, s, SiMe), 6.2–7.7 (26 H, m, olefinic and aromatic protons).

(7) **2b:** mp 192–193 °C; mass spectrum (rel intensity) (M^+) *m/e* 520 (9), 240 (100); NMR δ (CCl_4) 0.45 (6 H, s, SiMe), 6.48 (2 H, s, -CH=CH), 6.5–7.7 (24 H, m, aromatic protons).

(8) **3a:** mp 165 °C; mass spectrum (rel intensity) (M^+) *m/e* 418 (74), 240 (100); NMR δ (CCl_4) 0.37 (6 H, s, SiMe), 4.20 (2 H, s, -CH-Ar), 6.9–7.4 (8 H, m, aromatic protons). **3b:** mp 136–137 °C; mass spectrum (rel intensity) (M^+) *m/e* 418 (60), 240 (100); NMR δ (CCl_4) 0.31 (6 H, s, SiMe), 4.26 (2 H, s, -CH-Ar), 6.9–7.4 (8 H, m, aromatic protons).

(9) Y. Nakadaira, T. Kobayashi, T. Otsuka, and H. Sakurai, *J. Am. Chem. Soc.*, preceding paper in this issue.

(10) All of the adducts are thermally stable. For example, no change was observed for **3a** after heating at 350 °C for 3 h.

(11) The stereochemistry of **3** is not always unequivocal, the dominant isomer obtained from the trans precursor (**2a**) being assigned to the trans product (**3a**). This conclusion is supported by the use of an unsymmetric enephile, 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (see text).

(12) The mixture of these isomers could not be separated, but inspection of the NMR spectra indicated that it contained only three compounds, **5a, 5b,** and **5b′.** In the mass spectrum, the molecular ion corresponding to **5** (502.1945; calcd for $C_{32}H_{34}Si_3$, 502.1970) was obtained. It is easy to distinguish **5a** from **5b** and **5b′** by NMR. **5b** was tentatively assigned to the abundant isomer. NMR δ(CCl_4): **5a,** −0.19, 0.43, 0.61, 0.79 (3 H, s, SiMe), 6.35 (1 H, d, J = 7.0 Hz, HC=C-), 6.39 (1 H, d, J = 7.0 Hz, HC=C-), 7.0–7.5 (20 H, m, aromatic protons); **5b,** − 0.28, 0.50 (3 H, s, SiMe), 0.79 (6 H, s, SiMe), 6.35 (2 H, s, -CH=CH-), 7.0–7.5 (30 H, m, aromatic protons); **5b′,** − 0.02, 0.58 (3 H, s, SiMe), 0.80 (6 H, s, SiMe), 6.39 (2 H, s, CH=CH), 7.0–7.5 (20 H, m, aromatic protons).

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