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A novel synthesis of tetramesityldisilene

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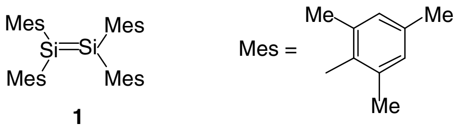
Abstract—Dimesityldiclorosilane undergoes reductive coupling with potassium–graphite to afford a mixture of cyclic polysilanes in a high yield and purity; this mixture is quantitatively converted to the title compound by photochemical irradiation.

Tetramesityldisilene (**1**) is a representative of stable disilenes, a fascinating class of compounds containing the silicon–silicon double bond, which have received considerable attention since their discovery.[1]



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At the outset of a new project aimed at elucidating the mechanism of the reaction between disilenes and electrophiles using the approach developed for analogous studies of carbon–carbon double bond reactivity,[2] we required a convenient route to our starting materials (e.g., **1**). Unfortunately, we experienced difficulties in consistently obtaining the desired compound **1** using the known low-temperature photolysis of 2,2-dimesityl-1,1,1,3,3,3-hexametyltrisilane, followed by crystallization of its THF solvate.[3] This problem prompted us to investigate alternative approaches to **1**. Stable disilenes have also been obtained by reductive Wurtz-type coupling from dichlorosilanes[4] or photolysis of cyclic trisilanes.[5] In general, the former methods employ more accessible starting materials but apply preferentially to the synthesis of silyl-substituted disilenes or di-silenes bearing very hindered substituents. The second method is the one affording disilenes most cleanly, but cyclic trisilanes are not easily prepared in good yields and purity.

We wish to report herein a two-step synthesis of **1** involving reductive Wurtz-type dehalogenation of dimesityldichlorosilane **3** to a mixture of cyclic polysilanes (**4a**–**c**) followed by the photolysis of these intermediates. The advantages of this new synthesis are the following: simple operating conditions; high yield and ease of purification of all synthetic intermediates; production of **1** as a by-product-free solution, which can be used as a stock of **1** for reactivity studies.

Dichlorosilane **3**, the key intermediate of our synthesis, was prepared in a high yield and purity by the condensation of tetrachlorosilane with the stoichiometric amount of mesityllithium, prepared in turn by lithium/bromine exchange between mesitylbromide (**2**) and *tert*-butyllithium; such a procedure turned out to be more practical than the published one involving the isolation of mesityllithium.[3]

Unsatisfactory results were obtained during our attempts to optimize reagents and conditions in order to obtain **1** by the reductive coupling of **3** with alkali metal, mainly due to difficulties encountered in the separation of **1** from inorganic and organic by-products. The analysis of reaction mixtures from alkali metal reduction of **3** demonstrated that substantial amounts of polycyclic silanes were formed as well as tetramesityldisilane, an over-reduction product, whose formation could not be suppressed (Scheme 1).

We found, however that the reaction of **3** with a stoichiometric amount of potassium graphite in THF at 0 °C afforded a clean mixture of cyclic polysilanes **4**, which could be isolated in a good yield and high purity by

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Keywords: Disilene; Polysilane; Cyclic.

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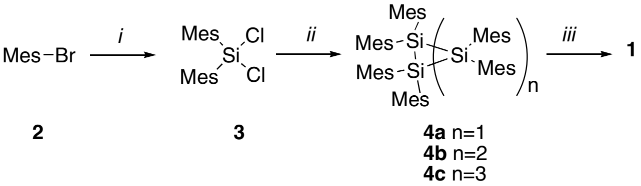

Scheme 1. Reagents and conditions: (i) *tert*-BuLi (2 mol), THF, −78 to 0 °C, then $SiCl_4$; (ii) KC_8, THF, 0 °C; (iii) hexane, UV irradiation with 70 W high pressure mercury lamp, 0 °C.

filtration through silica gel using hexane as the eluant. The composition of the mixture was determined on the basis of HPLC–MS analysis: cyclic trisilane **4a** turned out to be the main component (79%), whereas tetrasilane **4b** (7%) and pentasilane **4c** (14%) were present in lower but still significant proportions. The attempts to separate **4a** from the mixture of cyclic polysilanes **4** by recrystallization were unsuccessful. We found, however that the above mixture of cyclic silanes **4** can be used to produce disilene **1** in a photochemical reaction; this is consistent with the general tendency of polysilanes to generate silylenes, whose dimerization leads to disilenes. Thus, when an hexane solution of **4** in a quartz Schlenk flask was irradiated with a high pressure mercury lamp at 0 °C, a permanent yellow colouration developed after 30 min; UV analysis showed the absorption maximum at 422 nm typical of **1** and, from its intensity, an almost complete conversion (>97% yield) of **4a**–**c** into **1** was calculated.[6] The solution of **1** from the photolysis of **4a**–**c** under the above conditions turned out to be remarkably stable up to 7 days at 0 °C, as shown by UV monitoring. No attempt was made to isolate pure **1** from this solution. Further indirect evidence for the completeness of the photochemical conversion of **4a**–**c** into **1** was provided by quenching experiments: the reaction of **1** generated from **4a**–**c** with air or methanol gave a product distribution (NMR, HPLC) practically identical to those obtained from authentic **1**.[7,8]

In conclusion, the mixture of cyclic polysilenes **4a**–**c**, cleanly obtained by the reductive coupling of dichloride **3**, is a suitable precursor to **1** via photolysis. Preliminary data have shown that solutions of **1** produced in this way are suitable for accurate kinetic studies of Si═Si double bond reactivity; these results will appear in due course.

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References and notes

1. Reviews: (a) Okazaki, R.; West, R. *Organomet. Chem.* **1996**, *39*, 233; For recent synthetic and reactivity studies, see: (b) Ichinohe, M.; Kinjo, R.; Sekiguchi, A. *Organometallics* **2003**, *22*, 4261; (c) Samuel, M. S.; Jenkins, H. A.; Hughes, D. W.; Baines, K. M. *Organometallics* **2003**, *22*, 1603; (d) Wiberg, N.; Niedermayer, W.; Polborn, K.; Mayer, P. *Chem. Eur. J.* **2002**, *8*, 2730; (e) Hajgato, B.; Takahashi, M.; Kira, M.; Veszpremi, T. *Chem. Eur. J.* **2002**, *8*, 2126; (f) Bravo-Zhivotovskii, D.; Melamed, S.; Kapon, M.; Apeloig, Y. *Organometallics* **2002**, *21*, 2049; For recent theoretical studies, see: (g) Auer, D.; Strohmann, C.; Arbuznikov, A. V.; Kaupp, M. *Organometallics* **2003**, *22*, 2442; (h) Takahashi, M.; Sakamoto, K. *Organometallics* **2002**, *21*, 4212.
2. For a recent overview see: (a) Lenoir, D.; Chiappe, C. *Chem. Eur. J.* **2003**, *9*, 1036; (b) Chiappe, C.; Detert, H.; Lenoir, D.; Pomelli, C. S.; Ruasse, M. F. *J. Am. Chem. Soc.* **2003**, *125*, 2864; (c) Chiappe, C.; De Rubertis, A.; Detert, H.; Lenoir, D.; Schleyer, P. von R.; Wannere, C. S. *Chem., Eur. J.* **2002**, *8*, 967.
3. Tan, R.; Yokelson, H. B.; Gillette, G. R.; West, R. *Inorg. Synth.* **1992**, *29*, 19.
4. Kira, M.; Ohya, S.; Iwamoto, T.; Ichinohe, M.; Kabuto, C. *Organometallics* **2000**, *19*, 1817, See also Ref. 1b.
5. Masamune, S.; Murakami, S.; Hanzawa, Y.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150.
6. West, R. *Pure. Appl. Chem.* **1984**, *56*, 163.
7. Fink, M. J.; De Young, D. J.; West, R. *J. Am. Chem. Soc.* **1983**, *105*, 1070.
8. All reactions were carried under an argon atmosphere and the solvents were freshly distilled from sodium/benzophenone under argon. For the photochemical reaction, a 70 W Hg high-pressure immersion lamp (Hanau model TQ81) was used. HPLC–UV–ESI-MS spectra: compounds were separated on a C-18 reverse phase column (Phenomenex Luna C 18(2); 3; 150 × 2 mm.); the eluant method consisted of a 30-min linear gradient from 90:10 to 95:5 water (containing 10 mmol/l ammonium acetate) and 2-propanol; UV apparatus was set at 230 nm; mass spectra were obtained using a Thermo Finnigan TSQ 7000 triple-quadrupole mass spectrometer equipped with an electro spray ionization source and a closed collision gas chamber. UV spectra were recorded on a Cary 2200 spectrophotometer.
Dichlorodimesitylsilane (**3**). To a THF solution (200 mL) of **1** (14.93 g, 75.0 mmol), magnetically stirred while cooled in a dry ice/acetone bath, *tert*-BuLi (100 mL of a 1.5 M pentane solution, 150.0 mmol) was added dropwise and the reaction mixture was further stirred at −78 °C for 30 min. A solution of tetrachlorosilane (6.37 g, 37.5 mmol) in THF (50 mL) was then added dropwise. The cooling bath was removed and the mixture was allowed to stir for 6 h. The precipitate was removed by filtration and the filtrate evaporated to dryness; the residue was digested in hexane (50 mL); any undissolved material was removed by filtration and the filtrate was partially evaporated and cooled to 0 °C, which caused the separation of **3** (9.08 g; 95%) as a colourless crystalline solid, with a mp of 124 °C (Lit.[3] mp 121).
Mixture of cyclic silanes **4a**–**c**. Potassium graphite was prepared by heating potassium (0.87 g, 22.3 mmol) and graphite (2.15 g, 180 mmol) together in Schlenk flask. THF (20 mL) was added and to the resulting suspension magnetically stirred while cooled in a ice–water bath; dichloride **3** (3.37 g, 10 mmol) dissolved in THF (15 mL) was then added dropwise. After 1 h stirring, external cooling was discontinued and, after 1 h stirring at room temperature, the precipitate was filtered off and the filtrate evaporated to dryness. The residue was digested in hexane and the solid material was filtered off; the filtrate was evaporated to give a residue from which **4** (2.2 g, 83%) was obtained by flash chromatography (eluant: hexane) as a white powder. Calcd for $C_{18}H_{22}Si$: C 81.14, H 8.32; found: C 81.02, H 8.25. ^{29}Si NMR: (79.49 MHz): −51.3, −52.38, −52.95. HPLC–MS

peaks: 58.25 min (79%, **4a**) *m*/*z* 816.6 $[M+NH_4]^+$; 68.39 min (7%, **4c**) *m*/*z* 1085.8 $[M+NH_4]^+$; 87.73 min (14%, **4b**) *m*/*z* 1349.0 $[M+NH_4]^+$.

Photolysis of **4a**–**c***: tetramesityldisilene* (**1**). A solution of **4** (0.6 g) in hexane (10 mL) contained in a quartz Schlenk flask was exposed from the distance of 1.0 cm to a high pressure mercury lamp while immersed in a ice/water bath. A bright yellow colour rapidly developed; UV spectra of samples taken from the reaction after 30 min irradiation were practically superimposable to those reported for authentic **1** (λ_{max} 422) and showed a stationary 0.1 M concentration of **1** (97% yield, based on ε_{max} 11,000).[6] Aliquots were quenched with methanol or air; in both cases no starting material was present and the reaction products were identical to those obtained from the authentic samples of **1**.[7]