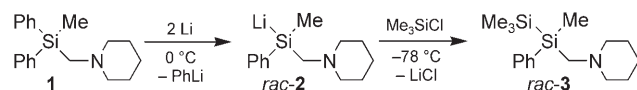


A Highly Enantiomerically Enriched Lithiosilane by Selective Cleavage of a Silicon–Phenyl Bond with Lithium**

Carsten Strohmann,* Christian Däschlein, Marco Kellert, and Dominik Auer

Preparative access to enantiomerically enriched lithiosilanes^[1,2] is very restricted and usually requires an aromatic substituent on the silicon atom.^[3] We reported recently on the selective cleavage of the silicon–phenyl bond in a diphenyl(aminomethyl)silane with lithium metal (Scheme 1).^[4] Building on this result, we won-

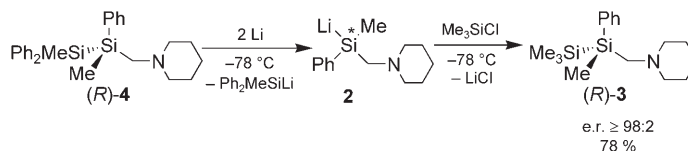


Scheme 1. Selective cleavage of a silicon–phenyl bond in the diphenylsilane **1** with lithium and formation of the disilane *rac*-**3**.

dered whether this reaction could also be used for the synthesis of highly enantiomerically enriched lithiosilanes. This new selective type of reaction appeared particularly attractive for the synthesis of an enantiomerically enriched lithiosilane that is not substituted with aryl groups. However, it was not conclusive whether a Si–Ph bond can be cleaved with lithium under preservation of the stereoinformation at the Si center. Herein we describe the synthesis of the highly enantiomerically enriched lithiosilane **2** (see Scheme 3) by cleavage of a Si–Ph bond and conversion of **2** into highly enantiomerically enriched oligosilanes.

Alkyl-substituted oligosilanes with four or more connected Si centers with *trans* conformation are sought-after model systems for an understanding of the electronic properties of corresponding polysilanes. Such oligosilanes are hitherto not sufficiently characterized structurally, and highly enantiomerically enriched systems with stereogenic Si centers have until now not been structurally investigated.^[5,6]

The enantiomerically pure disilane (*R*)-**4**, described by us in earlier work, can be converted into the enantiomerically pure lithiosilane **2** by cleavage of the Si–Si bond with lithium (Scheme 2).^[2c] After subsequent trapping with Me₃SiCl the



Scheme 2. Synthesis of (*R*)-**3** by cleavage of the Si–Si bond in (*R*)-**4** with lithium.

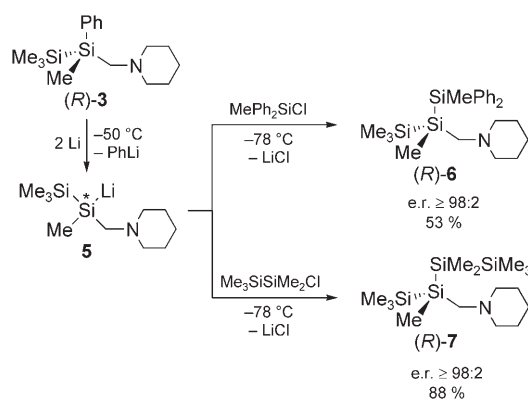
enantiomerically pure disilane (*R*)-**3** is obtained with retention of the configuration over both reaction steps.^[2c] Compound (*R*)-**3** comprises both a Si–Si bond and a Si–Ph bond as potential reaction sites for conversions with lithium metal. In initial conversions of *rac*-**3** with lithium at 0 °C in THF the Si–Ph bond was cleaved selectively with the formation of *rac*-**5**, and by subsequent reaction with Ph₂MeSiCl the racemic trisilane *rac*-**6** was obtained. To be able to prepare the corresponding highly enantiomerically enriched lithiosilane **5** and transform it under preservation of the stereoinformation, it must have sufficiently high configurational stability in solution. It was known from earlier experimental work that the highly enantiomerically enriched lithiosilane **2** racemizes within a few hours at temperatures above 0 °C, and thus its synthesis was carried out at –78 °C.^[2c,7] Then, to be able to estimate the configurational stability of **5** in comparison to **2**—in accompaniment to the experimental work—the inversion barriers for an inversion process through a formally free silyl anion in the gas phase were determined on the basis of two model systems by means of quantum chemical calculations [MP2/6-31 + G(d)].^[8] The model compound Me₂PhSi[–] (model system for **2**) with an inversion barrier of 135 kJ mol^{–1} is configurationally slightly more stable than the model compound Me₂(H₃Si)Si[–] (model system for **5**) with 125 kJ mol^{–1}.^[9] Thus, no stable configuration can be assumed in the experiment for **5** also at temperatures above 0 °C. Therefore, the cleavage of the Si–C bond of (*R*)-**3** was first carried out at –78 °C, but no reaction was observed. Only at a temperature of –50 °C was the Si–C bond in (*R*)-**3** completely cleaved. After five hours reaction time **5** was treated separately with Ph₂MeSiCl and Me₃SiSiMe₂Cl at –78 °C, and the silanes (*R*)-**6** and (*R*)-**7** were obtained after workup in yields of 53 % and 88 % and with enantiomeric ratios of ≥ 98:2 (Scheme 3).

The absolute configuration of (*R*)-**3** was determined by single-crystal X-ray structural analysis of the hydrochloride (*R*)-**3**·HCl (Figure 1).^[10] The absolute configuration of (*R*)-**7** was elucidated by single-crystal X-ray structural analysis of (*R*)-**7**·H₂SO₄ (Figure 2).^[10] The conversion of (*R*)-**3** into (*R*)-**7** (cleavage and trapping reaction) thus runs with overall retention of the configuration at the Si center. We suggest

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Supporting information for this article is available on the WWW under <http://www.angewandte.com> or from the author.



Scheme 3. Selective cleavage of the silicon–phenyl bond in the phenylsilane (R)-3 with lithium and synthesis of the trisilane (R)-6 and tetrasilane (R)-7.

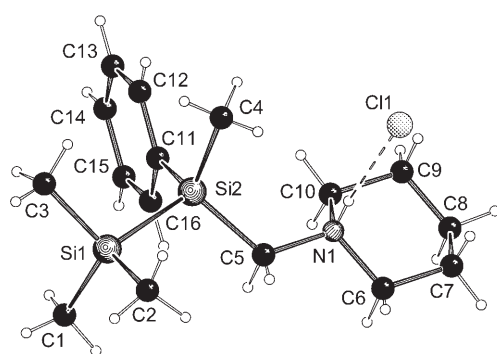


Figure 1. Molecular structure and numbering scheme of (R)-3·HCl in the crystal (Schakal plot; molecule 1 of two molecules). Selected bond lengths [Å]: Si1–Si2 2.346(4), Si2–C4 1.884(7), Si2–C5 1.896(7).

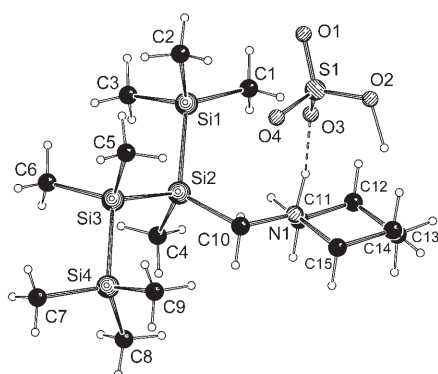


Figure 2. Molecular structure and numbering scheme of (R)-7·H₂SO₄ in the crystal (Schakal plot; molecule 1 of two molecules). Selected bond lengths [Å] and angles [°]: Si1–Si2 2.3683(19), Si2–C4 1.890(5), Si2–C10 1.915(5), Si2–Si3 2.3508(18), Si3–Si4 2.350(2); C4–Si2–C10 107.6(2), C4–Si2–Si3 107.80(17), C10–Si2–Si3 103.88(15), Si3–Si2–Si1 110.80(7), Si4–Si3–Si2 111.94(7), N1–C10–Si2 119.6(3), Si1–Si2–Si3–Si4 –176.62(7).

the identical reaction path for the reaction of the enantiomerically pure lithiosilane 5 with MePh₂SiCl to the enantiomerically pure compound 6 so that the *R* configuration likewise arises for the corresponding reaction product.

Both (R)-3·HCl and (R)-7·H₂SO₄ crystallize from Et₂O in the monoclinic crystal system in space group *P*2₁, whereby in each case two molecules are contained in the asymmetric unit. The Si–Si bond lengths are in the usual range with values between 2.342(2) and 2.371(2) Å. The tetrasilane (R)-7·H₂SO₄ shows an all-*trans* conformation of the Si centers for both molecules [torsion angles: Si1–Si2–Si3–Si4 –176.62(7)°, Si5–Si6–Si7–Si8 174.65(7)°]. A helical conformation, induced by the defined stereogenic center, as discussed for chiral polysilanes, cannot thus be observed for the tetrasilane (R)-7·H₂SO₄ in the crystal structure.^[5]

It is known that poly- and oligosilanes show intense absorption bands in the near-UV range which are generated by their special electronic properties (delocalization of the bonding σ electrons along the silicon framework).^[5,6,11] More recent studies on linear oligosilanes show that this delocalization is most effective for the *anti* conformation.^[12] Such an *anti* conformation was observed in the solid state for the salt of the tetrasilane (R)-7·H₂SO₄. Even if it is not possible to assume with certainty that the *anti* conformation also predominates in solution, the UV absorption spectrum of (R)-7 (293 K, cyclohexane) exhibits a maximum at 232 nm. Thus, (R)-7 shows a UV absorption spectrum in the same absorption region as that of the $\sigma \rightarrow \sigma^*$ transition of the tetrasilane Si₄Me₁₀ at 293 K (233 nm).^[13,14] In current investigations we are attempting to elucidate the effect of chain extension and protonation at the nitrogen center on the conformation and the resulting electronic behavior.

An enantiomerically enriched lithiosilane has been synthesized by cleavage of a Si–C bond for the first time. With this new preparative approach the first highly enantiomerically enriched, non-aryl-substituted lithiosilane 5 has been obtained. Bond cleavage and reactions with chlorosilanes run with overall retention of configuration. The first molecular structure of an enantiomerically enriched tetrasilane in the solid state could also be determined. This new synthetic strategy allows the construction of (aminomethyl)-functionalized, highly enantiomerically enriched oligosilanes and provides a route to corresponding polysilanes.

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- [1] Fundamental work on enantiomerically enriched lithiosilanes: a) L. H. Sommer, R. Mason, *J. Am. Chem. Soc.* **1965**, *87*, 1619–1620; b) L. H. Sommer, J. E. Lyons, H. Fujimoto, *J. Am. Chem. Soc.* **1969**, *91*, 7051–7061; c) E. Colomer, R. J. P. Corriu, *J. Organomet. Chem.* **1977**, *133*, 159–168.
- [2] Selected work on lithiosilanes: a) M. Omote, T. Tokita, Y. Shimizu, I. Imae, E. Sharikawa, Y. Kawakami, *J. Organomet. Chem.* **2000**, *611*, 20–25; b) C. Strohmann, O. Ulbrich, D. Auer, *Eur. J. Inorg. Chem.* **2001**, 1013–1018; c) C. Strohmann, J. Hörnig, D. Auer, *Chem. Commun.* **2002**, 766–767; d) C. Strohmann, M. Bindl, V. C. Vraaß, J. Hörnig, *Angew. Chem.* **2004**, *116*, 1029–1032; *Angew. Chem. Int. Ed.* **2004**, *43*, 1011–1014; e) D. Scheschke, *Angew. Chem.* **2004**, *116*, 3014–3016; *Angew. Chem. Int. Ed.* **2004**, *43*, 2965–2967; f) D. Auer, M.

- Kaupp, C. Strohmman, *Organometallics* **2004**, *23*, 3647–3655; g) M. Oestreich, G. Auer, M. Keller, *Eur. J. Org. Chem.* **2005**, 184–195; h) M. Nanjo, M. Masayuki, Y. Ushida, Y. Awamura, K. Mochida, *Tetrahedron Lett.* **2005**, *46*, 8945–8947; i) H.-W. Lerner, *Coord. Chem. Rev.* **2005**, *249*, 781–798; j) D. Bravo-Zhivotovskii, I. Ruderfer, S. Melamed, M. Botoshansky, B. Tumanskii, Y. Apeloig, *Angew. Chem.* **2005**, *117*, 749–753; *Angew. Chem. Int. Ed.* **2005**, *44*, 739–743; k) C. Strohmman, C. Däschlein, D. Auer, *J. Am. Chem. Soc.* **2006**, *128*, 704–705.
- [3] a) K. Tamao, A. Kawachi, *Adv. Organomet. Chem.* **1995**, *38*, 1–58; b) P. D. Lickiss, C. M. Smith, *Coord. Chem. Rev.* **1995**, *145*, 75–124; c) A. Sekiguchi, V. Y. Lee, M. Nanjo, *Coord. Chem. Rev.* **2000**, *210*, 11–45.
- [4] C. Strohmman, D. Schildbach, D. Auer, *J. Am. Chem. Soc.* **2005**, *127*, 7968–7969.
- [5] Selected work on chiral oligosilanes: a) H.-S. Oh, I. Imae, Y. Kawakami, S. S. S. Raj, T. Yamane, *J. Organomet. Chem.* **2003**, *685*, 35–45; b) T. Sanji, N. Kato, M. Tanaka, *Macromolecules* **2006**, *39*, 7508–7512; c) M. Fujiki, *J. Organomet. Chem.* **2003**, *685*, 15–34; d) A. Ohira, S.-Y. Kim, M. Fujiki, Y. Kawakami, M. Naito, G. Kwak, A. Saxena, *Chem. Commun.* **2006**, 2705–2707; e) K. Terao, N. Kikuchi, T. Sato, A. Teramoto, M. Fujiki, T. Dobashi, *Langmuir* **2006**, *22*, 7975–7980.
- [6] Selected work on oligosilanes: a) H. Teramae, J. Michl, *Chem. Phys. Lett.* **1997**, *276*, 127–132; b) M. C. Piqueras, R. Crespo, J. Michl, *J. Phys. Chem. A* **2003**, *107*, 4661–4668; c) H. Reinke, C. Krempner, *J. Organomet. Chem.* **2003**, *685*, 134–137; d) T. Sanji, A. Yoshiwara, H. Sakurai, M. Tanaka, *Chem. Commun.* **2003**, 1506–1507; e) H. Mallesha, H. Tsuji, K. Tamao, *Organometallics* **2004**, *23*, 1639–1642; f) C. Krempner, M. Köckerling, C. Mamat, *Chem. Commun.* **2006**, 720–722; g) U. Jäger-Fiedler, M. Köckerling, R. Ludwig, A. Wulf, C. Krempner, *Angew. Chem.* **2006**, *118*, 6907–6911; *Angew. Chem. Int. Ed.* **2006**, *45*, 6755–6759.
- [7] D. Auer, J. Hörnig, C. Strohmman in *Organosilicon Chemistry V: From Molecules to Materials* (Eds.: N. Auner, J. Weis), Wiley-VCH, Weinheim, **2003**, p. 167–170.
- [8] Gaussian 03 (Revision B.04): M. J. Frisch et al.; see the Supporting Information.
- [9] Further inversion barriers for silyl anions are found in: M. Flock, C. Marschner, *Chem. Eur. J.* **2005**, *11*, 4635–4642, and references therein.
- [10] Complete crystallographic data are found in the Supporting Information. CCDC-626823 [(*R*)-**7**-H₂SO₄] and CCDC-626824 [(*R*)-**3**-HCl] contain the detailed crystallographic data for this publication. The data may be obtained free of charge from the Cambridge Crystallographic Data Centre through www.ccdc.cam.ac.uk/data_request/cif.
- [11] a) H. Tsuji, A. Fukazawa, S. Yamaguchi, A. Toshimitsu, K. Tamao, *Organometallics* **2004**, *23*, 3375–3377; b) H. Y. Jung, Y.-A. W. Park, B. R. Yoo, K. Tamao, I. N. Jung, *Organometallics* **2004**, *23*, 4910–4914.
- [12] a) K. Tamao, H. Tsuji, M. Terada, M. Asahara, S. Yamaguchi, A. Toshimitsu, *Angew. Chem.* **2000**, *112*, 3425–3428; *Angew. Chem. Int. Ed.* **2000**, *39*, 3287–3290; b) H. Tsuji, M. Terada, A. Toshimitsu, K. Tamao, *J. Am. Chem. Soc.* **2003**, *125*, 7486–7487.
- [13] K. Obata, M. Kira, *Organometallics* **1999**, *18*, 2216–2222.
- [14] (*R*)-**7**-H₂SO₄ in CH₂Cl₂ (*c* = 3.92 × 10^{−2} mol L^{−1}) also exhibits an absorption maximum at 230 nm.