

Radical isomerization of 9,10-dihydro-9,10-disilaanthracene derivatives: stabilization factor of silyl radicals

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Abstract

In order to examine the nature of the silyl radical in the disilaanthracene framework, separation and radical isomerization of the *cis* and *trans* isomers of the disilaanthracene derivatives were investigated. When a pentane solution of the disilaanthracene derivative was irradiated with a 400 W mercury lamp in the presence of DTBP for 4 h, both isomers readily isomerized to give a mixture of *cis* and *trans* isomers in a ratio of ca. 50:50. However, no such isomerization reaction of 9,10-dihydro-9-silaanthracene derivatives occurred under similar conditions. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Although many reductive reactions of organic halides and alcohols involving free radicals as intermediates have employed tributyltin hydride as a reducing agent, the replacement of such toxic and relatively expensive organotin compounds has been performed with other hydrogen donors. However, trialkyl- or triarylsilicon compounds are not appropriate for the purpose under mild conditions. Formation of silyl radicals from these compounds requires relatively drastic conditions because such silyl radicals are relatively unstable. On the other hand, the nature of these silyl radicals is well established [1], and they are generally believed to have a pyramidal configuration, in contrast to the usual carbon radicals. For example, the silyl radicals derived from an optically active hydrosilane undergo chlorine-abstraction reaction mostly with retention of configuration. Recently, some organosilicon compounds with reduced Si–H bond strength were discovered [2]. In particular, tris(trimethylsilyl)silane has proved to be an

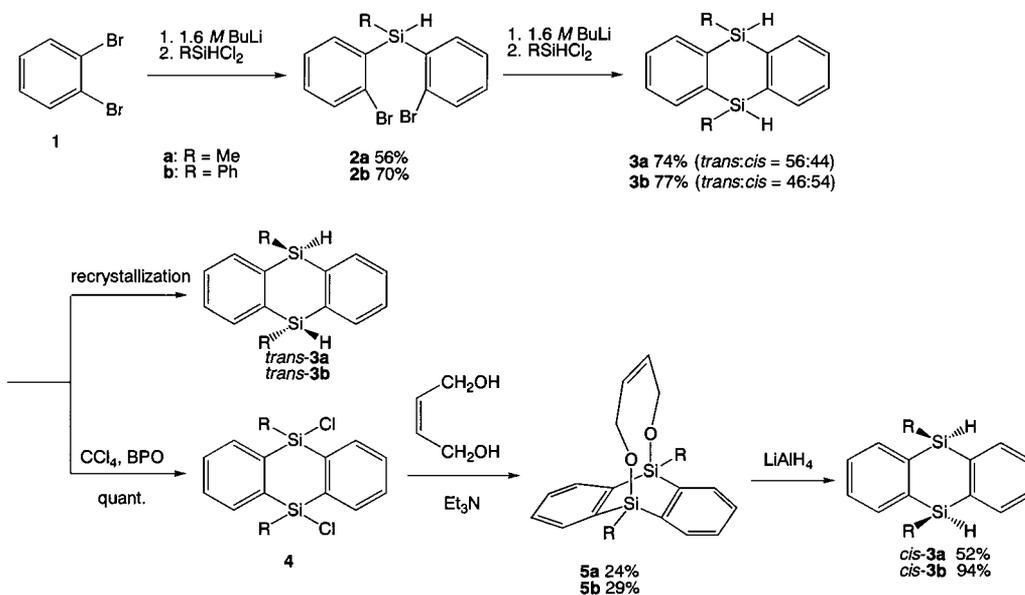
effective and versatile reducing agent, of which the Si radical is believed to be dramatically stabilized by hyperconjugation with adjacent trimethylsilyl groups and has a longer lifetime than the usual silyl radicals. We previously reported the utilization of 9,10-dihydro-9,10-disilaanthracene derivatives as reducing agents in radical-based dehalogenation and deoxygenation reactions, in which the two silicon atoms at the 9- and 10-positions were essential to generate the silyl radical efficiently [3]. In this paper, we would like to report the separation and radical isomerization reaction of *cis*- and *trans*-9,10-dimethyl-(**3a**), 9,10-diphenyl-9,10-dihydro-9,10-disilaanthracene (**3b**), and 9,10-diphenyl-9,10-dihydro-9-silaanthracene (**7**) in order to confirm the stabilization factor, and a calculation by density functional calculations (B3LYP/cc-pVDZ) for the silyl radicals.

2. Results and discussion

The synthesis and separation of *cis*- and *trans*-9,10-dimethyl-9,10-dihydro-9,10-disilaanthracene (*cis*-**3a** and *trans*-**3a**) were reported by Corey et al. [4]. By applying

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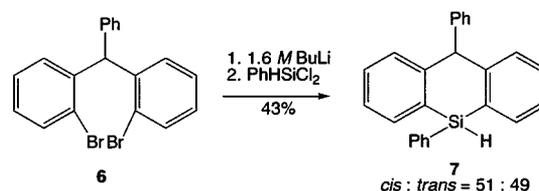


Scheme 1.

the procedure, we prepared the corresponding diphenyl derivatives, *cis*-**3b** and *trans*-**3b**, novel 9,10-dihydro-9,10-disilaanthracenes, as shown in Scheme 1. 9,10-Diphenyl-9,10-dihydro-9-silaanthracenes (*cis*-**7** and *trans*-**7**), the monosila analogues of *cis*-**3b** and *trans*-**3b**, were prepared by a modified procedure of Winkel et al. [5] (Scheme 2). The 2,2'-dibromotriphenylmethane (**6**) was condensed with phenyldichlorosilane via the corresponding dilithio derivatives to afford 9-silaanthracene **7** in 43% yield as a 51:49 mixture of *cis* and *trans* isomers. The separation of the isomers was performed by repeated column chromatography on silica gel and the structure of the *trans*-**7** was unambiguously confirmed by X-ray crystallographic analysis (vide infra).

Recently, Matsumoto et al. reported that a radical isomerization reaction of *cis*- and *trans*-9,10-di-*tert*-butyl-9,10-dihydro-9,10-disilaanthracene gave a mixture of *trans* and *cis* isomers [6]. From kinetic studies, they concluded the *cis*-isomer was slightly more stable by 0.8 kcal/mol than the *trans* isomer at 20°C and the isomerization reaction could be explained by the stabilization of the silyl radicals, due to bulky *tert*-butyl substituents. As a part of our interest in the reactivity of the disilaanthracenes, we tried a similar reaction of compounds **3a**, **3b**, and **7**. When a pentane solution of *trans*-9,10-dimethyl-9,10-dihydro-9,10-disilaanthracene (**3a**) and DTBP was irradiated with a 400-W medium-pressure mercury lamp for 1 h, a mixture of *trans*- and *cis*-**3a** (91:9) was obtained and the recovery of the total amounts of **3a** was 92%. After an additional 3 h, the reaction gave a mixture of 52:48 of *trans*- and *cis*-**3a**, and the recovery was 79%. On the other hand, *cis*-**3a** gave a mixture of *trans*- and *cis*-**3a** (35:65) after 1 h under similar conditions and the recovery was 82%.

The ratio of *trans*- and *cis*-**3a** became 52:48 after 2 h and the recovery was 73%. These results show that *trans*- and *cis*-**3a** isomerize to each other to reach an equilibrium after 2–4 h. The results are compiled in Table 1. Phenyl derivatives **3b** also gave similar results. Both isomers gave a 53:47 mixture of *trans*- and *cis*-**3b** after 4 h. For the methyl and phenyl substituted dihydrodisilaanthracene framework, *trans*- and *cis*-isomers are energetically almost equal, in contrast to the *tert*-butyl substituted compound [6]. Under similar conditions, *trans*- and *cis*-9,10-diphenyl-9,10-dihydro-9-silaanthracene (**7**) did not give the isomerized product at all. The stereochemistry of these compounds was confirmed by X-ray crystallographic analysis. These findings show the isomerization reaction is attributed to the stability of the silyl radicals generated and is not due to the bulkness of the substituent, indicating the importance of the presence of two silicon atoms at both the 9- and 10-positions. In the previous paper, we also reported that 9,10-dihydro-9-methyl-9-sila-10-thiaanthracene had a reductive ability similar to that of the disilaanthracene analogue under radical conditions [3]. From these facts, it is deduced that neither hyperconjugation nor steric hindrance contributes to stabilize the



Scheme 2.

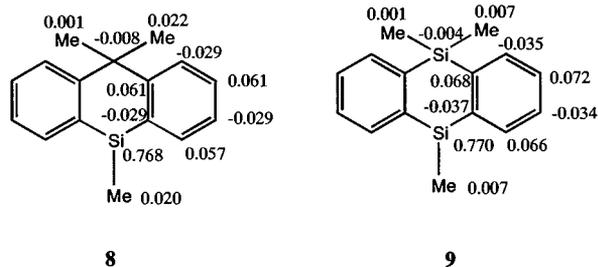
Table 1
Isomerization of silaanthracene derivatives^a

Silaanthracene	Time (h)	trans/cis	Recovery (%)
<i>trans</i> - 3a	0	100:0	–
	1	91:9	92
	2	56:44	88
	4	52:48	79
<i>cis</i> - 3a	0	0:100	–
	1	35:65	82
	2	52:48	73
	4	53:47	65
<i>trans</i> - 3b	0	96:4	–
	1	73:27	85
	2	65:35	78
	4	53:47	69
<i>cis</i> - 3b	0	2:98	–
	1	8:92	53
	2	51:49	37
	4	53:47	15
<i>trans</i> - 7	0	100:0	–
	4	100:0	91
<i>cis</i> - 7	0	0:100	–
	4	0:100	82

^a In the absence of DTBP, the isomerization reaction did not occur.

silyl radicals in these reactions, although they would have a pyramidal or a planar configuration.

Next, we calculated spin density of the silyl radicals (**8** and **9**) by Density Functional Calculations method (B3LYP/cc-pVDZ). The spin densities of the benzene rings of **9** are slightly larger than that of **8**. It shows that radical spin of the silyl radical **9**, having a convenient ring conformation for conjugation, generated from disilaanthracene derivatives is conjugated to the benzene rings, but such a contribution would be relatively small in the monosilaanthracene framework.



While the stabilization factor of the silyl radicals could not be precisely confirmed, it is proposed such stabilization arises from conjugation with benzene rings (delocalization of an electron on the silicon atom), due to suitable ring conformation of the disilaanthracene framework. Thus, stabilization by hyperconjugation and steric hindrance can be ruled out as a less important factor in our reaction systems.

3. Experimental

3.1. General

GC measurements were performed on a Shimadzu GC-18A and a GL Sciences GC-380 gas chromatograph using a 50 m × 0.25 mm methyl silicone capillary column (Quadrex). TLC was carried out on Merck silica gel 60 F₂₅₄. Flash column chromatography was performed on Merck silica gel 60 (230–400 mesh). Infrared spectra were recorded on a Perkin–Elmer 1600 infrared spectrometer. ¹H-, ¹³C-, and ²⁹Si-NMR spectra were measured in CDCl₃ solution on a Varian UNITY-400 spectrometer. All chemical shifts are reported as δ-values (ppm) relative to residual chloroform (δ_H 7.26), the central peak of deuteriochloroform (δ_C 77.0) or tetramethylsilane (δ_{Si} 0.0). *J*-Values are given in Hz. GC-MS (EI) was measured with the direct combination of GC (Hewlett–Packard GC 5890 Series II with a 25 m × 0.25 mm methyl silicone capillary column) and a JEOL JMS-AX-500 spectrometer with DA7000 data system.

3.2. 9,10-Diphenyl-9,10-dihydro-9,10-disilaanthracene (**3b**)

To a solution of 1,2-dibromobenzene (**1**, 11.8 g, 50.0 mmol) in THF (50 ml) and diethyl ether (50 ml) was added 1.6 M butyllithium in hexane (35 ml, 55 mmol) at –110°C under argon atmosphere. After being stirred for an additional 20 minutes, a solution of phenyldichlorosilane in THF (25 ml) and diethyl ether (25 ml) was added dropwise to the mixture and stirred for 2 h. Then the reaction mixture was allowed to warm up to room temperature (r.t.) and quenched with a mixture of conc. HCl (5 ml) and ethanol (12.5 ml). The mixture was diluted with diethyl ether and the organic layer was washed with brine, dried over MgSO₄, and evaporated. The residue was purified by column chromatography on silica gel (hexane) to give the silane **2b** (7.32 g, 70%) as a colorless solid, m.p. 89–90°C. ¹H-NMR (CDCl₃) δ 5.74 (s, 1 H), 7.26 (m, 4 H), 7.30 (m, 2 H), 7.40 (m, 2 H), 7.47 (m, 1 H), 7.55 (m, 2 H), 7.59 (m, 2 H). ¹³C-NMR (CDCl₃) δ 126.7, 128.2, 130.0, 131.4, 131.8, 132.6, 135.3, 135.9, 138.7. ²⁹Si-NMR (CDCl₃) δ –19.9. IR (KBr) ν_{Si–H} 2166 cm^{–1}. HRMS *m/z* 417.9199 (M⁺, calcd for C₁₈H₁₄Br⁷⁹Br⁸¹Si 417.9211).

To a solution of **2b** (2.99 g, 7.15 mmol) in THF (70 ml) was added 1.6 M butyllithium in hexane (10 ml, 16.0 mmol) at –78°C. After being stirred for 1 h, phenyldichlorosilane (2.50 g, 14.1 mmol) was added to the solution and the resultant reaction mixture was allowed to warm to r.t. and refluxed overnight. Then, the mixture was poured into water and extracted with ether. The organic layer was washed with water, dried over MgSO₄, and evaporated. The crude product was

purified by column chromatography on silica gel (hexane) to give 9,10-disilaanthracene derivative **3b** as a 54:46 mixture of *cis* and *trans* isomers (2.02 g, 78%).

The *trans*-**3b** was obtained as a colorless powder by crystallization of the mixture from EtOH, m.p. 112–114°C. ¹H-NMR (CDCl₃) δ 5.46 (s, 2 H), 7.39 (m, 10 H), 7.60 (m, 4 H), 7.66 (m, 4 H). ¹³C-NMR (CDCl₃) δ 128.2, 129.0, 129.9, 133.9, 135.7, 135.9, 140.6. ²⁹Si-NMR (CDCl₃) δ –30.3. IR (KBr) ν_{Si-H} 2121 cm⁻¹. HRMS *m/z* 364.1126 (M⁺, calcd for C₂₄H₂₀Si₂ 364.1104).

Isolation of the *cis* isomer was performed according to the procedure of Corey [4]. Thus, a solution of **3b** (289 mg, 0.794 mmol) in CCl₄ (30 ml) in the presence of benzoyl peroxide (19 mg, 0.079 mmol) was refluxed for 4.5 h. A direct analysis of the reaction mixture by GC analysis showed completion of the chlorination. To the cooled solution was added a mixture of *cis*-2-butene-1,4-diol (1.05 g, 11.9 mmol) and triethylamine (400 mg, 3.97 mmol) and the reaction mixture was stirred at r.t. overnight. The mixture was washed by water, dried over MgSO₄, and evaporated. The residue was chromatographed on silica gel (hexane:AcOEt = 95:5) to give the alkoxide **5b** (105 mg) in 28% yield. ¹H-NMR (CDCl₃) δ 4.31 (m, 4 H), 5.33 (m, 2 H), 7.36 (m, 4 H), 7.47 (m, 10 H), 7.79 (m, 4 H).

The dialkoxo 9,10-dihydro-9,10-disilaanthracene derivative **5b** (891 mg, 1.98 mmol) was reduced by LiAlH₄ (300 mg, 7.92 mmol) in refluxing ether (70 ml) for 3 h. The cooled reaction mixture was quenched with water and the insoluble materials were filtered off. The filtrate was dried over MgSO₄ and evaporated. The residue was chromatographed on silica gel (hexane) to afford *cis*-9,10-diphenyl-9,10-dihydro-9,10-disilaanthracene (*cis*-**3b**, 681 mg, 94%) as a colorless solid, m.p. 100–104°C. ¹H-NMR (CDCl₃) δ 5.50 (s, 2 H), 7.28 (m, 4 H), 7.36 (m, 2 H), 7.42 (m, 4 H), 7.49 (m, 4 H), 7.70 (m, 4 H). ¹³C-NMR (CDCl₃) δ 128.0, 129.0, 129.7, 134.0, 135.6, 135.8, 140.5. ²⁹Si-NMR (CDCl₃) δ –30.7. IR (KBr) ν_{Si-H} 2115 cm⁻¹. HRMS *m/z* 364.1139 (M⁺, calcd for C₂₄H₂₀Si₂ 364.1104).

3.3. 9,10-Diphenyl-9,10-dihydro-9-silaanthracene (7)

To a solution of 2,2'-dibromotriphenylmethane (6, 894 mg, 2.22 mmol) in ether (40 ml) was added 1.6 M butyllithium in hexane (3.5 ml, 5.6 mmol) at r.t.. Then, phenyldichlorosilane (2.6 g, 14.7 mmol) was added and the mixture was stirred overnight. Direct analysis of the reaction mixture by ¹H-NMR spectroscopy showed the ratio of the *cis* and *trans* isomers was 51:49. The residue was separated by column chromatography on silica gel (hexane). The fast fraction contained the *cis* isomer (50.0 mg, 6%) and further elution gave a mixture of *cis* and *trans* isomers (271 mg, 35%). Finally, the *trans* isomer (17.0 mg, 2%) was obtained from the last fraction. The total yield of the compound **7** was 43%.

cis-**7**, m.p. 110–111°C. ¹H-NMR (CDCl₃) δ 5.40 (s, 1 H), 5.49 (s, 1 H), 6.80 (m, 2 H), 6.92 (m, 3 H), 7.15 (m, 2 H), 7.25 (m, 3 H), 7.34 (m, 2 H), 7.43 (m, 2 H), 7.48 (m, 2 H), 7.83 (m, 2 H). ¹³C-NMR (CDCl₃) δ 56.8, 125.8, 126.1, 127.7, 128.0, 128.4, 129.4, 130.06, 130.14, 133.5, 135.1, 136.2, 145.7, 149.6, 1 C was overlapped elsewhere. ²⁹Si-NMR (CDCl₃) δ –33.6. IR (KBr) ν_{Si-H} 2127 cm⁻¹. HRMS *m/z* 348.1371 (M⁺, Calc. for C₂₅H₂₀Si 348.1334).

trans-**7**, m.p. 130–131°C. ¹H-NMR (CDCl₃) δ 5.12 (s, 1 H), 5.53 (s, 1 H), 7.04 (m, 2 H), 7.11 (m, 1 H), 7.20 (m, 4 H), 7.41 (m, 6 H), 7.50 (m, 1 H), 7.54 (m, 2 H), 7.63 (m, 2 H). ¹³C-NMR (CDCl₃) δ 57.5, 125.9, 126.0, 128.0, 128.19, 128.23, 129.5, 129.9, 130.3, 131.5, 132.1, 135.7, 136.7, 145.1, 149.7. ²⁹Si-NMR (CDCl₃) δ –34.3. IR (KBr) ν_{Si-H} 2140 cm⁻¹. HRMS *m/z* 348.1340 (M⁺, Calc. for C₂₅H₂₀Si 348.1334).

3.4. Isomerization of silaanthracene derivatives

A pentane solution of silaanthracene derivative (ca. 0.02–0.05 M, 3–5 ml) in the presence of DTBP (1.4–4.9 equivalents) in a Pyrex tube was irradiated with a 400-W medium-pressure mercury lamp. After an appropriate reaction time as shown in Table 1, the ratio of the *trans* and *cis* isomers was determined by a direct analysis of the reaction mixture using ¹H-NMR spectroscopy. The recovered yields were obtained by purification of the crude products by column chromatography on silica gel (hexane).

3.5. X-ray structure determination of *trans*-**7**

A colorless prismatic crystal of C₂₅H₂₀Si, *M* = 348.52, having approximate dimensions of 0.30 × 0.20 × 0.50 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated Mo-K_α (λ = 0.71069 Å) radiation. Monoclinic, *a* = 10.509(3), *b* = 8.463(2), *c* = 21.860(6) Å, β = 100.40(2)°, *V* = 1912.2(9) Å³ (by least-squares refinement using the setting angles of 24 carefully centered reflections in the range 22.48 < 2θ < 24.54°), space group *P*2₁/*n* (# 14), *Z* = 4, *D*_{calc} = 1.211 g cm⁻³. The data were collected at 23°C using the ω–2θ scan technique to a maximum 2θ value of 40.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.36° with a take-off angle of 6.0°. Scans of (1.00 + 0.30 tan θ)° were made at a speed of 2.0° min⁻¹ (in ω). Of the 2079 reflections measured, 1942 were unique (*R*_{int} = 0.009). The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards increased by 0.1%. The linear absorption coefficient, μ, for Mo-K_α radiation is 1.3 cm⁻¹. An empirical absorption correction based on azimuthal

scans of several reflections was applied which resulted in transmission factors ranging from 0.97 to 1.00. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier technique. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1419 observed reflections ($I > 3.00\sigma(I)$) and 236 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.041$ and $R_w = 0.031$. The standard deviation of an observation of unit weight was 3.23. The weighting schemes were based on counting statistics and included a factor ($p = 0.004$) to downweight the intense reflections. Plots of $\Sigma\omega(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.13 and $-0.23 \text{ e}^- \text{ \AA}^{-3}$, respectively. Neutral atom scattering factors were taken from Cromer and Waber [7]. Anomalous dispersion effects were included in F_{calc} [8]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [9]. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 139320. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2

1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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