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Thermal isomerization of 1,2-diadamantoyltetrakis(trimethylsilyl)disilane via a 2,3-disilabutadiene intermediate

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Abstract

Heating a benzene solution of 1,2-diadamantoyltetrakis(trimethylsilyl)disilane (**1a**) at 120 °C gave an isomerization product, 3,4-diadamantyl-2,2-bis(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1,2-disilacyclobutene (**2**), in 24% yield. Similar treatment of **1a** in the presence of an excess of methanol at 120 °C afforded a methanol adduct in 39% yield. A mechanistic interpretation including a 2,3-disiladiene intermediate is described for the formation of **2**.

Keywords: Silene; Disiladiene; Acylpolysilane

1. Introduction

Acylpolysilanes are of important organosilicon compounds as the precursors of silenes [1]. A photochemically [2] and thermally induced [3] 1,3-silyl shift from the polysilane unit to the carbonyl oxygen gives high yields of silenes including stable ones. However, acylpolysilanes studied so far have been restricted to rather simple ones, until recently. Recently, we have synthesized 2,2-bis(acyl)trisilanes [4] and 1,2-bis(acyl)disilanes [5] as the first example of oligosilanes having two acyl groups in the molecule. We also prepared 1,2-bis[tris(trimethylsilyl)silylcarbonyl]alkanes in which two acylpolysilane units are linked by an ethylene chain and investigated their thermally induced rearrangement [6]. Interestingly, silenes produced from the 1,3-silyl shift of 1,2-bis[tris(trimethylsilyl)silylcarbonyl]alkanes undergo further isomerization, which can be explained in terms of the Cope-type rearrangement.

In the hope of generating novel reactive organosilicon species, we studied thermal reaction of 1,2-diadamantoyltetrakis(trimethylsilyl)disilane [5]. The reaction gave an isomerization product that may be best explained by assuming a 2,3-disiladiene intermediate.

2. Results and discussion

When a benzene solution of 1,2-diadamantoyltetrakis(trimethylsilyl)disilane (**1a**) was heated at 120 °C for 12 h, an isomerization product, 3,4-diadamantyl-2,2-bis(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1,2-disilacyclobutene (**2**), was obtained in 24% isolated yield (Scheme 1). In this reaction, many unidentified products were found to be formed in low yields by the ^{1}H-NMR spectrum of the reaction mixture. However, attempted isolation of the by-products by silica gel column chromatography and preparative gel permeation chromatography was unsuccessful. We also examined the thermolysis of 1,2-dimesitoyltetrakis(trimethylsilyl)disilane (**1b**). However, heating **1b** at 120 °C gave a much more complex mixture, from which no major products were separated.

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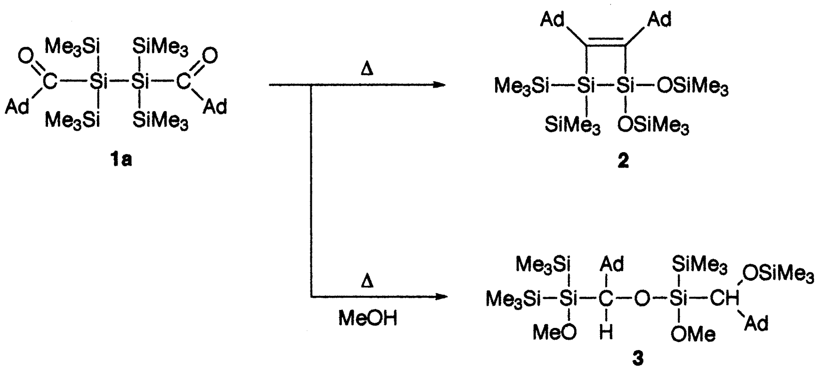


Scheme 1.

The structure of **2** was verified by spectrometric and elemental analysis (see Section 3). We also carried out the X-ray single crystal analysis of **2**. The structure was not sufficiently solved to discuss the detailed structural parameters ascribed to both the poor crystal quality and the large thermal displacement of the substituents in particular for trimethylsiloxy groups even at −173 °C, as indicated by the rather large residuals ($R = 0.134$, $R_w = 0.151$). However, the molecular structure bearing an unsymmetrically substituted disilacyclobutene ring was undoubtedly determined as shown in Fig. 1. In the structure, the inner ring bond distances are in the normal range but a little shorter than those previously reported for other disilacyclobutene derivatives [7]. The Si(1)–Si(3) and Si(1)–Si(4) bonds are elongated to an extent, relative to the standard strain-free Si–Si bond distance (e.g. Si–Si = 2.375(4)–2.386(4) Å for compound **3a**), probably due to the steric repulsion between the substituents. The silacyclobutene ring in **2** is almost planar, as evidenced by the torsion angle of Si(1)–Si(2)–C(1)–C(2) = 5.4(5)°.

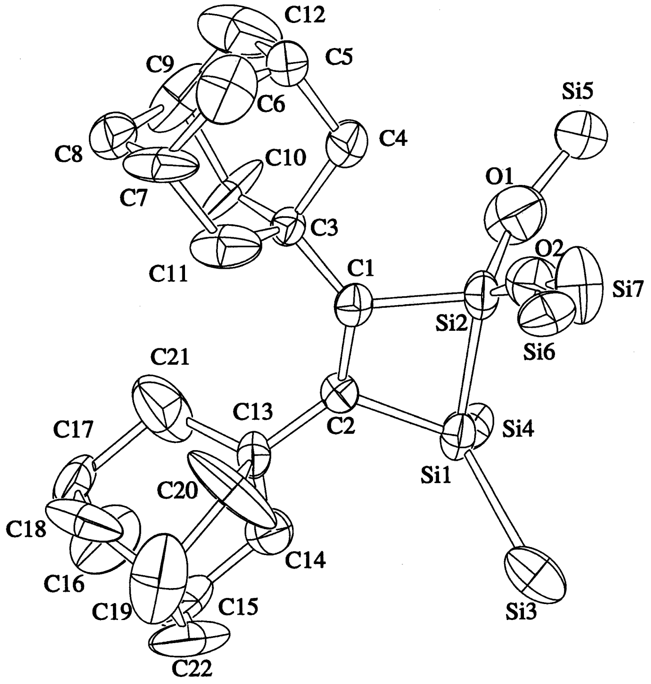


Fig. 1. ORTEP drawing of compound **2**. Trimethylsilyl group attached to O2 was refined by applying a disorder model. Thermal ellipsoids are drawn at 50% probability. Protons are omitted for clarity. Methyl groups on silicon atoms are also omitted. Selected bond distances (Å) and angles (°): Si(1)–Si(2), 2.290(5); Si(1)–Si(3), 2.465(6); Si(1)–Si(4), 2.417(4); Si(1)–C(2), 1.913(9); Si(2)–C(1), 1.86(1); C(1)–C(2), 1.39(1); Si(2)–Si(1)–C(2), 73.6(3); Si(1)–Si(2)–C(1), 78.7(3); Si(2)–C(1)–C(2), 101.6(7); C(2)–C(1)–C(3), 134.2(8); Si(2)–C(1)–C(3), 124.3(7); Si(1)–C(2)–C(1), 105.7(6); Si(1)–C(2)–C(13), 121.1(6); and C(1)–C(2)–C(13), 133.1(8).

Next we carried out a trapping experiment by using methanol. Thus, when **1a** was heated in benzene at 120 °C for 12 h in the presence of an excess of methanol, a 1:2 methanol adduct (**3**) was obtained in 39% yield. Several other unidentified methanol adducts were also found to be formed in low yields. Compound **3** consists of two diastereomers. One of the diastereomers (**3a**) crystallized from ethanol and the crystal structure was solved by an X-ray diffraction study, and the ORTEP drawing is depicted in Fig. 2.

A possible mechanistic interpretation for the formation of **2** and **3** is shown in Scheme 2, which includes the 1,3-silyl shift producing a silene (**A**) as the initial step. Silene **A** would undergo a further 1,3-silyl shift to produce a 2,3-disiladiene intermediate (**B**), which is followed by intramolecular [2+2] cycloaddition to afford a 1,2-disilacyclobutene intermediate (**C**). A series of isomerization of **C** with increasing number of thermally stable Si–O bonds would produce **2**. In the presence of methanol, initially formed silene intermediate **A** would be trapped by methanol to give an adduct (**D**). Subsequent isomerization of **D** producing a silene intermediate (**E**), followed by addition of methanol to the resulting silene, gives 1:2 adduct **3**.

An alternative route to **3** may involve a 1,3-shift of adamantoylbis(trimethylsilyl)silyl group in **1a** giving silene (**F**), followed by addition of methanol, as shown in Scheme 2. The methanol adduct (**G**) undergoes a silyl shift leading to **H**, which reacts again with methanol to give **3**. However, this route seems to be minor, if any,

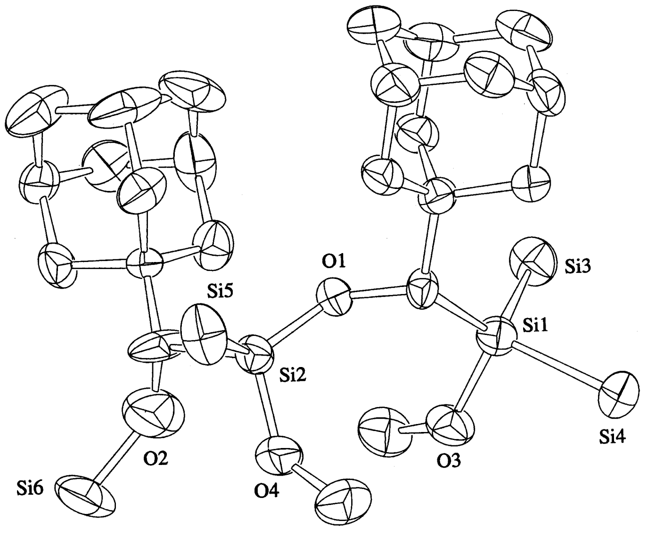
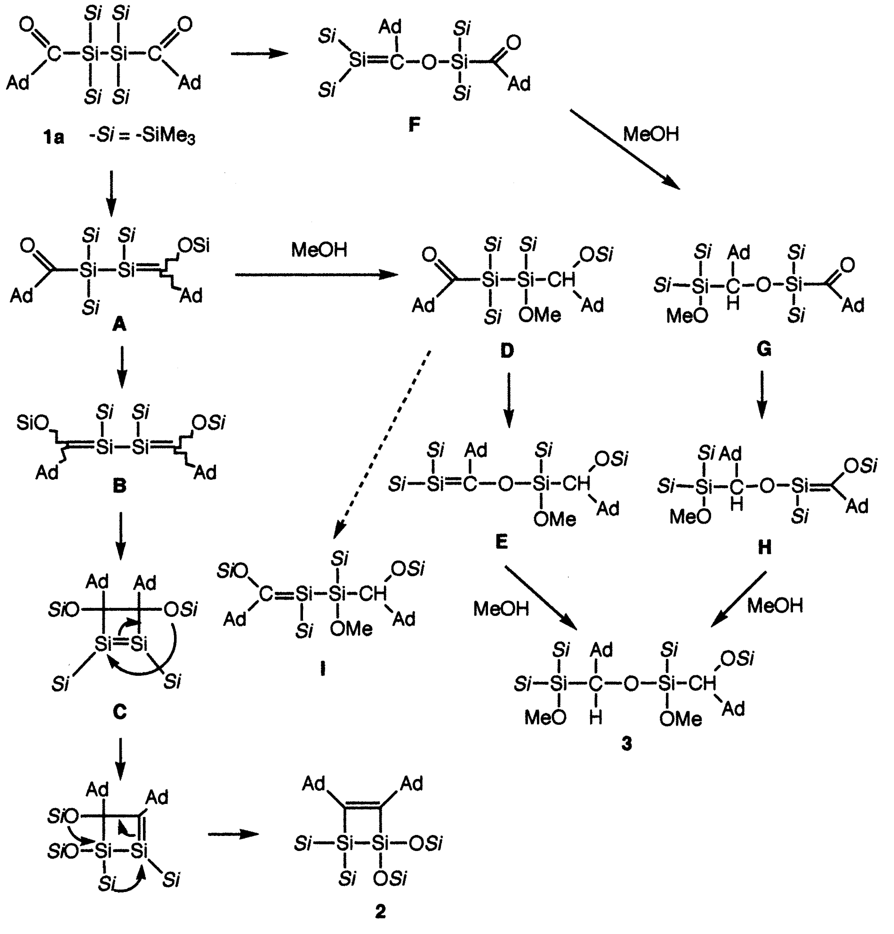


Fig. 2. ORTEP drawing of compound **3a**. Thermal ellipsoids are drawn at 50% probability. Protons are omitted for clarity. Methyl groups on silicon atoms are also omitted.

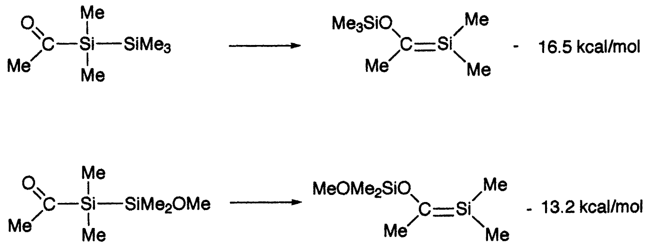
since no product originated from silene **F** could be isolated in the reaction without methanol.

It may be possible to consider the formation of silene **I** from **D** via a 1,3-trimethylsilyl shift. However, no methanol adducts of **I** were isolated from the reaction mixture as the major products. Presumably, the formation of silene **E** from **D** would be more favored than that of **I** having a bulky silyl group directly attached to the highly crowded silene unit. In **E**, the steric congestion seems to be reduced by introducing a siloxy bond between the large silyl group and the silene unit, relative to **I**. It may be also plausible to consider another reason that the initial formation of a siloxy bond on the central Si in **D** would facilitate accumulation of more siloxy bonds onto the same silicon atom. Thus, the migration of the methoxydisilanyl group in **D** would take place in preference to the trimethylsilyl shift, leading to the formation of **E**. Indeed, the results of ab initio MO calculations of model reactions at HF/6-31G** level of the theory suggest that migration of a methoxy-substituted silyl group is less endothermic by about 3.3 kcal mol^{-1} as shown in Scheme 3. We could not isolate any methanol adducts of disiladiene **B** from the trapping experiment, probably due to the rapid quenching of silene **A** with methanol.

Since compound **3** possesses three chiral centers, the fact that only two diastereomers were formed as the major products would indicate that diastereoselective



Scheme 2.



Scheme 3.

reaction(s) were involved for the formation of **3**. Kira and coworkers [8] have previously reported that methanol addition to a silene proceeds in two competing fashions, i.e. intramolecular proton transfer from a 1:1 silene–methanol complex intermediate leading to a syn adduct and intermolecular proton transfer from second molecule of methanol to the complex intermediate to produce an anti-adduct. However, it seems to be reasonable to assume that intramolecular process occurs exclusively in the reactions of sterically bulky silenes such as **A** and **H**.

In conclusion, we demonstrated that 1,2-bis(acyl)disilanes may be used as the precursors of 2,3-disiladienes. Despite the fact that many papers concerning the synthesis and properties of silenes have been published [1], it is true that a little is known for bis(silenes) [9].

3. Experimental

3.1. General

Mass spectra were measured on a Hitachi M-80B spectrometer. NMR spectra were recorded on JEOL EX-270 and Lambda-400 spectrometers using tetramethylsilane as an internal standard. IR spectra were measured on a Perkin–Elmer FT1600 spectrophotometer. MO calculations were carried out by using Gaussian 98 revision A.9 program (Gaussian, Inc., Pittsburgh, PA).

3.2. Materials

Benzene and methanol were dried over sodium–potassium alloy and magnesium methoxide, respectively, and distilled just before use. Compounds **1a** and **1b** were prepared as reported in the literature [5].

3.3. Isomerization of 1a

In a sealed glass tube was placed 93 mg (0.14 mmol) of **1a** and 1 ml of benzene, and the tube was heated at 120 °C for 12 h. After evaporation of the solvent, the residue was subjected to silica gel column chromatography, then preparative gel permeation chromatography to give 22 mg (24% yield) of **2**: MS *m/z* 674 [M$^+$]; ^{1}H-NMR ($CDCl_3$) δ 0.36 (s, 18H), 0.44 (s, 18H), 1.63–1.87 (m, 12H), 2.08 (br s, 12H), 2.22 (br s, 6H); ^{13}C-NMR ($CDCl_3$) δ 1.2, 2.7, 29.6, 29.8, 37.0, 37.2, 40.4, 42.4, 44.1, 45.2, 176.4, 177.8; ^{29}Si-NMR ($CDCl_3$) δ −18.0, −8.5, 9.3, 29.3; Exact MS Found: 674.3664; Calc. for $C_{34}H_{66}O_2Si_6$: 674.3679.

3.4. Reaction of 1a in the presence of methanol

In a sealed glass tube was placed 42 mg (0.63 mmol) of **1a**, 0.2 ml of methanol and 0.5 ml of benzene, and the tube was heated at 120 °C for 12 h. After evaporation of the solvent, the residue was subjected to silica gel column chromatography, then preparative gel permeation chromatography to give 18 mg (39% yield) of **3** as the diastereomeric mixture: MS *m/z* 665 [M$^+$ −$SiMe_3$]; ^{1}H-NMR ($CDCl_3$) δ 0.10 (s, 7.2H), 0.11 (s, 1.8H), 0.17 (s, 7.2H), 0.20 (s, 1.8H), 0.212 (s, 7.2H), 0.216 (s, 1.8H), 0.220 (s, 1.8H), 0.26 (s, 7.2H), 1.53–1.74 (m, 24H), 1.94–1.99 (m, 6H), 3.16 (s, 0.8H), 3.22 (s, 0.2H), 3.50 (s, 0.6H), 3.52 (s, 2.4H), 3.60 (s, 0.6H), 3.64 (s, 2.4H), 4.01 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ 0.3, 1.3, 1.5, 1.6, 28.5, 28.7, 37.0, 37.3, 37.7, 37.8, 40.0, 40.7, 79.2, 79.4, 81.3, 81.7; carbon signals for the minor isomer could not be observed. Anal. Found: C, 58.43; H, 10.03. Calc. for $C_{36}H_{74}O_4Si_6$: C, 58.47; H, 10.09%.

3.5. X-ray crystallographic analysis of 2 and 3a

The crystals of **2** and **3a** suitable for X-ray crystallography were obtained by recrystallization from ethanol at −30 °C. Crystal data, experimental conditions and summary of structural refinement for **2** and **3a** are presented in Table 1. The structures were solved by direct method [10] and were expanded using DIRDIF94 Fourier technique [11]. The non-hydrogen atoms were refined anisotropically. Neutral atom scattering factors were taken from Cromer and Waber [12]. Anomalous dispersion effects were included in F_{calc} [13]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [14]. The values for the mass attenuation coefficients are those of Creagh and Hubbell [15]. All calculations were performed using the teXsan [16] crystallographic software package of Molecular Structure Corporation.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 196630 for **2** and 196629 for **3a**. 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-

Table 1
Crystal data, experimental conditions and summary of structural refinement for **2** and **3a**

	2	**3a**
Molecular formula	$C_{34}H_{66}O_2Si_6$	$C_{36}H_{74}O_4Si_6$
Molecular weight	675.41	739.49
Space group	$P\bar{1}$ (#2)	$P2_1/n$ (#14)
Cell dimensions		
a (Å)	10.4000(5)	18.652(4)
b (Å)	12.0497(7)	13.033(3)
c (Å)	18.476(1)	20.400(2)
α (°)	99.972(2)	90
β (°)	103.166(3)	114.79(1)
γ (°)	108.579(1)	90
V (Å^3)	2059.8(2)	4502(1)
Z	2	4
D_{calc} (mg m^{-3})	1.089	1.091
$F(0\,0\,0)$	740.00	1624.00
Crystal size (mm^3)	$0.5 \times 0.4 \times 0.2$	$0.4 \times 0.1 \times 0.1$
Crystal color	colorless	colorless
μ(Mo–K$_\alpha$) (cm^{-1})	2.29	2.17
Diffractometer	Rigaku RAXIS	Rigaku AFC-7R
Temperature (K)	100	296
Scan type	imaging plate	$\omega - 2\theta$ (16° min^{-1})
Scan width (°)	$0 < 2\theta < 55$	$0 < 2\theta < 54.9$
Number of unique reflections	8863	8286
Number of observed reflections	4466 ($I > 5\sigma(I)$)	2802 ($I > 3\sigma(I)$)
Ref/par	10.76	6.8
R	0.134	0.065
R_w [a]	0.151	0.068

[a] Weighting scheme is $(\sigma(F_o)^2 + 0.0004|F_o|^2)^{-1}$.

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