Generation of 1,6-Disilahexapentaene in the Reduction of an Overcrowded Bis(bromodiaryl)butadiyne Leading to the Unexpected Formation of 2-Allenyl-1-benzosilole

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When the reductive debromination of an overcrowded bis(bromodiarylsilyl)butadiyne (**2**) bearing Tbt and Mes groups was performed with potassium graphite, the corresponding 2-allenyl-1-benzosilole (**3**) was isolated as a main product. The formation of **3** was most likely interpreted in terms of the initial generation of 1,6-disilahexapentaene (**1**) followed by the intramolecular double cyclization.

Allenes and cumulenes are well-known compounds in organic chemistry, and their syntheses, physical properties, reactivities, and synthetic applications have been widely studied.[1] By contrast, the chemistry of their silicon analogs (silacumulenes) has been much less explored owing to their instability under ambient conditions. Up to date, only a few kinds of kinetically stabilized silacumulenes, e.g., 1-silaallenes,[2] a 1-phospha-3-silaallene,[3] and a trisilaallene[4] have been synthesized as stable compounds. As for silacumulenes having more than two cumulative double bonds no stable examples have been reported so far, although the generation of 1-silabutatrienes has been suggested by trapping experiments.[5]

On the other hand, during the course of our studies on the kinetic stabilization of highly reactive molecules, we have already demonstrated that Tbt (2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) group can protect its 1-position remotely and effectively by the bulky bis(trimethylsilyl)methyl groups at the *o*-positions.[6] The successful results in the kinetic stabilization afforded by the Tbt group prompted us to apply this steric protection group to the stabilization of Si-containing cumulative compounds hitherto unknown, such as 1,6-disilahexapentaene, in which no substituent can be introduced onto the inner sp carbon atoms of the reactive Si=C double bond moieties. In this paper, we present our attempted synthesis of a kinetically stabilized 1,6-disilahexapentaene (**1**) (Figure 1). To the best of our knowledge, 1,6-disilahexapentaene is completely unprecedented, elusive silacumulene even as a transient species.

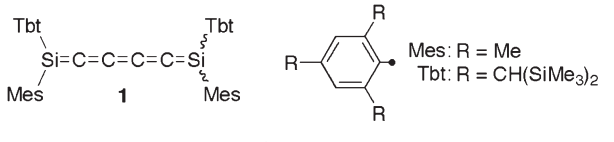
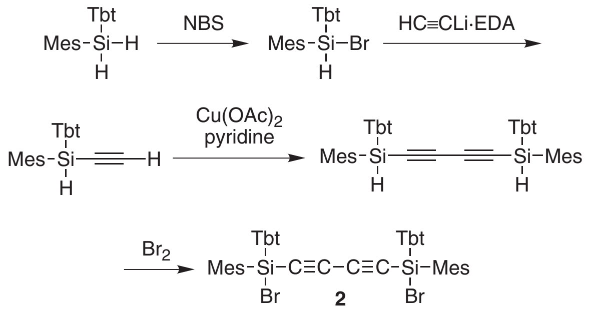


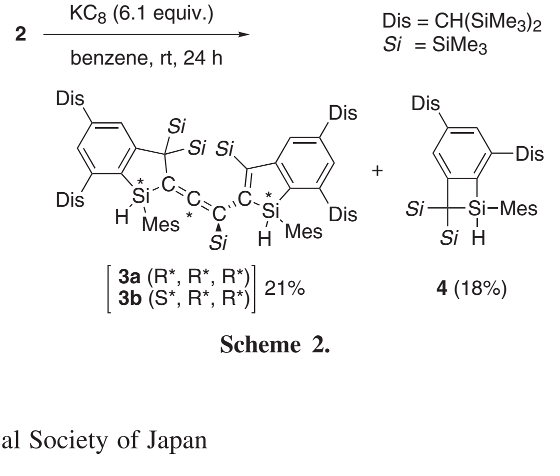
Figure 1.

It is desirable that the precursor for such a reactive silacumulene should be a stable compound without Si=C double bonds. From this point of view, we have designed and prepared an overcrowded bis(bromodiarylsilyl)butadiyne (**2**) bearing Tbt and Mes groups as the precursor for **1** (Scheme 1).



Scheme 1. Synthesis of **2**.

With the suitable precursor **2** in hand, synthesis of **1** was first attempted by the debromination of **2** with various kinds of alkyllithiums (methyllithium and *t*-butyllithium), metals (potassium, Na/K alloy, and zinc), and alkali metal arenides (lithium naphthalenide and potassium graphite). Although no evidence for the generation of **1** was obtained in most cases, the reaction of **2** with 6.1 equivalents of potassium graphite resulted in the formation of the corresponding 2-allenyl-1-benzosilole (**3**) as a mixture of isomers along with silacyclobutabenzene (**4**, 18%)[7] (Scheme 2). Compound **3** has principally four diastereomers due to its two chiral ring silicon atoms and axially chiral allene moiety, however, the ^{1}H NMR spectra of the chromatographically purified sample of **3** showed the existence of only two isomers. These two isomers were inseparable by chromatography and recrystallization, but single crystals of each isomer (**3a** and **3b**) were obtained by recrystallization of the mixture of isomers, **3a** and **3b**, from different solvents (hexane or hexane/acetone, respectively). The molecular structure of **3a** was unambiguously determined by X-ray crystallographic analysis (Figure 2).[8] Although the molecular structure of **3b** was also confined by X-ray crystallographic analysis, the refinement was not sufficient to provide accurate bond lengths and bond angles experimentally because of the disorders of the two solvated acetone molecules. The structure of **3** was also supported by ^{1}H, ^{13}C, and ^{29}Si NMR, IR, and high-resolution MS spectral data together with elemental analysis.[9] In the ^{13}C NMR spectrum of **3**,



Scheme 2.

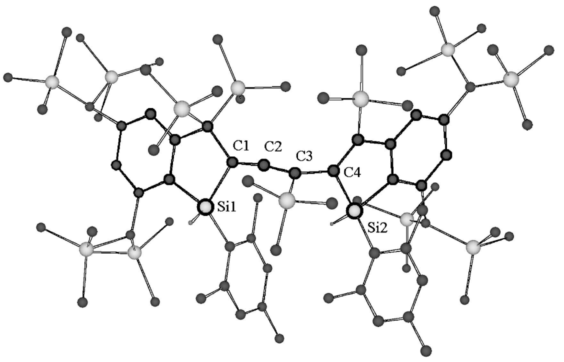
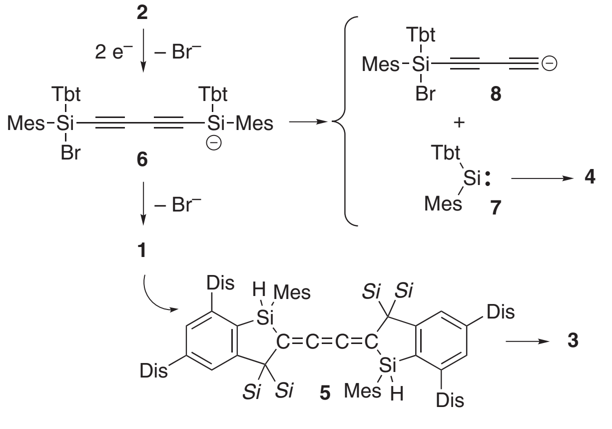


Figure 2. Ball and stick model of **3a**.

the signal of the central carbon of its allene moiety was observed at 202.5 ppm. In the IR spectrum were observed two unique absorptions at 1840 and 2182 cm^{-1}, which correspond to the stretching frequencies of allene and Si–H moieties of **3**, respectively. Although the measured sample contains two isomers, the ^{13}C NMR and IR spectra of **3** showed the signals of the allene and Si–H moieties as one peak, respectively, suggesting the severe and coincidental signal overlap of the isomers. The clear structural difference has appeared only for the peripheral moieties.[9]

As can be seen from the molecular structure of **3a** shown in Figure 2, compound **3** has closely resembled partial structures, i.e., dihydrobenzosilole and benzosilole units. The formation of such silole ring systems during the reduction of **2** is reasonably interpreted in terms of the double cyclization of the highly reactive Si=C units of the initially formed 1,6-disilahexapentaene **1** toward the *o*-benzyl positions of Tbt groups giving an intermediary 1,2,3-butatriene **5**, followed by the migration of one of the trimethylsilyl groups of **5**. Although the mechanism for the migration of a trimethylsilyl group during the final step is not clear at present, it is most likely that the intramolecular repulsion between the trimethylsilyl and mesityl groups of 1,2,3-butatriene intermediate (**5**) might be one of the driving force for this migration. If so, it is very interesting that only one of the trimethylsilyl groups of **5** migrated to give the final product **3** having a 2-allenyl-1-benzosilole skeleton. Silacyclobutabenzene **4** was probably formed by the intramolecular cyclization of silylene **7** which was generated by the elimination of anion **8** from silyl anion **6** (Scheme 3).



Scheme 3. Plausible mechanism for the generation of **3** and **4**.

In summary, we have examined the synthesis of 1,6-disilahexapentaene **1** by the reduction of butadiyne (**2**) and obtained the 2-allenyl-1-benzosilole (**3**) as the final product probably via **1**. With the hope of isolating **1** as a stable compound, further investigation on the reductive debromination of **2** under various conditions are currently in progress.

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8 Crystal data for **3a**: $C_{76}H_{140}Si_{14}$; MW = 1447.12; *monoclinic*; space group $P2_1/n$; $a = 12.651(7)$ Å, $b = 35.298(19)$ Å, $c = 20.752(11)$ Å; $\beta = 95.211(6)°$; $V = 9229(8)$ Å^3; $Z = 4$; $D_{\mathrm{calcd}} = 1.042$ g/cm^3; $\mu = 0.230$ mm^{-1}; $2\theta_{\max} = 50°$; $T = 103$ K; $R_1(I > 2\sigma(I)) = 0.0954$; wR_2 (all data) = 0.2158; GOF = 1.055 for 16149 reflections and 968 parameters, (CCDC 227229)

9 Allene **3**: a mixture of isomers; colorless crystals; ^{1}H NMR (300 MHz, 60 °C, $CDCl_3$) δ −0.34 (s, 18H), −0.22 (s, 9H), −0.10 (s, 18H), 0.040 (s, 18H), 0.042 (s, 9H), 0.06 (s, 9H), 0.07 (s, 9H), 0.35 (s, 9H), 0.37 (s, 9H), 1.23 (s, 0.5H, Tbt *p*-bzl, isomer*), 1.35 (s, 0.5H, Tbt *p*-bzl, isomer*), 1.37 (s, 0.5H, Tbt *p*-bzl, isomer*), 1.41 (s, 0.5H, Tbt *p*-bzl, isomer*), 1.93 (s, 3H, Mes *p*-Me), 2.10 (s, 3H, Mes *p*-Me), 2.18 (s, 3H, Mes *o*-Me), 2.21 (s, 3H, Mes *o*-Me), 2.39 (br s, 1H, Tbt *o*-bzl), 2.45 (br s, 1H, Tbt *o*-bzl), 2.63 (s, 3H, Mes *o*-Me), 2.66 (s, 3H, Mes *o*-Me), 5.46 (s, 1H, Si–H), 6.04 (s, 1H, Si–H), 6.30 (br s, 3H, Tbt arom), 6.54 (br s, 1H, Tbt arom), 6.60 (s, 2H, Mes arom), 6.82 (s, 2H, Mes arom) ($*$: *dl*- or *meso*- isomers, the ratio of these isomers was ≈1:1); ^{13}C NMR (75 MHz, rt, $CDCl_3$) δ 0.4 (q), 0.5 (q), 0.7 (q), 0.9 (q), 1.0 (q), 2.3 (q), 3.8 (q), 21.1 (q), 21.2 (q), 21.8 (q), 24,.2 (q), 25.1 (q), 26.6 (d), 26.8 (q), 30.4 (d), 30.7 (q), 30.8 (q), 31.1 (d), 31.8 (d), 41.5 (s), 86.5 (s, >C=), 98.6 (s, >C=), 119.2 (d), 121.0 (d), 121.8 (d), 122.7 (s), 123.9 (d), 126.7 (d), 127.8 (s), 128.1 (s), 128.4 (d), 128.7 (s), 129.0 (d), 129.2 (d), 139.5 (s), 139.7 (s), 144.7 (s), 144.9 (s), 145.1 (s), 145.5 (s), 146.4 (s), 146.6 (s), 148.0 (s), 148.9 (s), 151.9 (s), 156.0 (s), 156.4 (s), 159.7 (s), 202.5 (s, =C=); ^{29}Si NMR (59 MHz, rt, $CDCl_3$) δ −28.7, −20.4, −8.3, −3.1, 1.5, 1.6, 1.7, 2.0, 2.1, 2.8, 3.8, 7.1; IR (KBr) 2182 (Si–H stretch), 1840 (C=C=C stretch) cm^{-1}; HRMS-FAB *m/z* calcd for $C_{76}H_{140}Si_{14}$ (M^+): 1444.7725, found: 1444.7732. Anal. Calcd for $C_{76}H_{140}Si_{14}$: C, 63.08; H, 9.75. Found: C, 63.00; H, 9.82%.

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