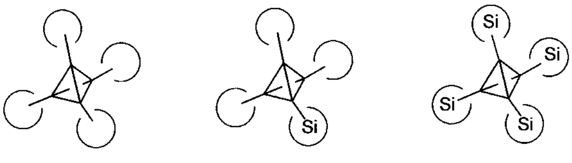
Tetrakis(trimethylsilyl)cyclobutadiene and Tetrakis(trimethylsilyl)tetrahedrane[**]

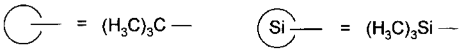
Günther Maier,* Jörg Neudert, and Oliver Wolf

Dedicated to Professor Hansgeorg Schnöckel
on the occasion of his 60th birthday

Tetrakis(trimethylsilyl)tetrahedrane (**3**) is of interest in several respects. The "corset effect", that is, the stabilization by the accumulation of four voluminous substituents,[1] should be smaller in **3** than in the tetra-*tert*-butyl derivative **1**, the first stable tetrahedrane,[1] because of the longer C–Si bonds.[2] On the other hand the four σ-donor substituents in **3** should particularly favor the tetrahedrane ring skeleton, an observation we made previously in the case of tri-*tert*-butyl(trimethylsilyl)tetrahedrane (**2**).[3] These influences will add up to a high barrier for the thermal isomerization of tetrahedrane **3** into cyclobutadiene **8**. Another aspect is even more enticing: The high s-character of the bonds pointing from the ring skeleton to the substituents[1c, 4] should enable the trimethylsilyl groups of **3** to be easily replaced. On this basis a route to tetralithiotetrahedrane[5]—and perhaps even to the unsubstituted tetrahedrane—can be envisaged.

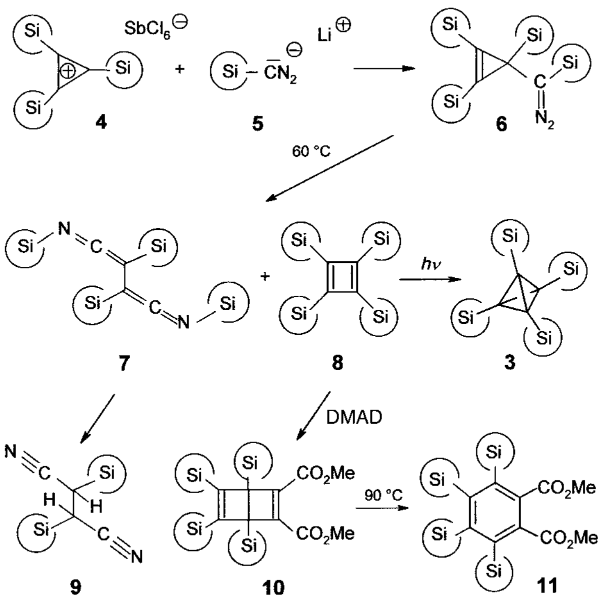


1 **2** **3**



One apparent procedure for the synthesis of tetrahedrane **3** is the photoisomerization of tetrakis(trimethylsilyl)cyclobutadiene (**8**). In analogy to tetra-*tert*-butyl-[6] and tri-*tert*-butyl(trimethylsilyl)cyclobutadiene,[3] the starting materials for tetrahedranes **1** and **2**, it is also possible to prepare **8** by using the "cyclopropenyldiazomethane route". The report of Sekiguchi et al.[7] on an alternative way to **8**, namely by the mild oxidation of the corresponding cyclobutadiene dianion, is the motive for us (in agreement with the Japanese group) to describe our own efforts directed to the generation of cyclobutadiene **8** and tetrahedrane **3** (Scheme 1).

Trimethylsilyl[1,2,3-tris(trimethylsilyl)-2-cyclopropen-1-yl]diazomethane (**6**) can be isolated as a yellow oil in 11% yield through the coupling of tris(trimethylsilyl)cyclopropenylium hexachloroantimonate[8] (**4**) with lithiated (trimethylsilyl)diazomethane (**5**). Six further products are also formed, whose structures were elucidated.



Scheme 1. Syntheses of **7**, **3**, and **8** as well as the confirmation reactions.

Many attempts were needed to find the appropriate conditions for the transformation of **6** into cyclobutadiene **8**. Neither the photochemical[6] nor the CuCl-catalyzed thermal[3] elimination of nitrogen succeeded. However, cyclobutadiene **8** is formed (according to NMR-spectroscopic analysis in 45% yield) upon warming **6** in an inert medium (benzene, cyclohexane, methylcyclohexane) to 60 °C. Surprisingly bis(ketenimine) **7** is observed as a second product, which means that on thermal excitation, diazo compound **6** partly splits off nitrogen and the thus-generated carbene undergoes a ring expansion to cyclobutadiene **8**. Parallel to this reaction an isomerization of cyclopropenyl diazomethane **6** into tetrakis(trimethylsilyl)pyridazine occurs, which immediately undergoes a ring opening accompanied by migration of two trimethylsilyl groups under the reaction conditions to give the 2,3-bis(trimethylsilyl)-1,3-butadiene-1,4-dione-bis(trimethylsilyl)imine (**7**). This reaction is reminiscent of the isomerization of hexakis(trimethylsilyl)benzene to the thermodynamically more stable 1,1,3,4,6,6-hexakis(trimethylsilyl)-1,2,4,5-hexatetraene, reported by Sakurai and Sekiguchi et al.[9]

Both thermolysis products **7** and **8** are sensitive to air and moisture. This fact complicates their separation into pure components. The presence of cyclobutadiene **8** can be proved not only by NMR spectroscopy (see Table 1) but also by the following experiment: The addition of dimethyl acetylenedicarboxylate (DMAD) to the reaction mixture after thermolysis of diazo compound **6** enables adduct **10** to be isolated, which at 90 °C gives quantitatively the dimethyl ester of tetrakis(trimethylsilyl)phthalic acid (**11**). After evaporation of the solvent from the solution of **7** and **8** in vacuo, it is possible to capture preferentially the more volatile bis(ketenimine) **7** under high vacuum conditions. The IR spectrum of **7**, obtained from this procedure and measured in an argon matrix at 10 K, showed a band at 2112 cm^{-1}, which is typical for a ketenimine.

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Table 1. NMR spectroscopic data of compounds **6**–**11**.[a]

6: yellow oil; ^1H NMR ($CDCl_3$): $\delta = 0.26$ (18H), 0.15 (9H), −0.03 (9H); ^{13}C NMR ([D_8]toluene): $\delta = 141.1$ (C=C), 38.6 ($C=N_2$), 16.4 (ring-C), −0.1 (2 $SiMe_3$), −0.35 ($SiMe_3$), −0.4 ($SiMe_3$)

7: colorless oil; ^1H NMR (C_6D_6): $\delta = 0.35$ (18H), 0.20 (18H); ^{13}C NMR (C_6D_{12}): $\delta = 177.1$ (C=*C*=N), 26.3 (*C*=C=N), 0.5 ($SiMe_3$), 0.4 ($SiMe_3$)

8: red-brown crystals; ^1H NMR (C_7D_{14}): $\delta = 0.09$ (36H); ^{13}C NMR (C_7D_{14}): $\delta = 171.59$ (ring-C), 0.08 ($SiMe_3$)

9: colorless solid (m.p. 139 °C); ^1H NMR (C_6D_6): $\delta = 1.46$ (2H), 0.06 (18H); ^{13}C NMR (C_6D_{12}): $\delta = 119.3$ ($C\equiv N$), 16.4 (C-H), −3.2 ($SiMe_3$)

10: colorless solid (m.p. 95 °C); ^1H NMR ($CDCl_3$): $\delta = 3.56$ (6H), 0.21 (18H), 0.20 (18H); ^{13}C NMR ($CDCl_3$): $\delta = 171.9$ (C=O), 163.0 (C=C), 148.0 (C=C), 65.3 (ring-C), 51.3 (OMe), 1.5 ($SiMe_3$), 1.3 ($SiMe_3$)

11: colorless solid (m.p. 165 °C); ^1H NMR ($CDCl_3$): $\delta = 3.79$ (6H), 0.32 (18H), 0.28 (18H); ^{13}C NMR ($CDCl_3$): $\delta = 171.3$ (C=O), 166.9 (C=C), 144.9 (C=C), 135.7 (C=C), 52.2 (OMe), 4.6 ($SiMe_3$), 3.4 ($SiMe_3$)

[a] ^1H NMR: 400.1 MHz, ^{13}C NMR: 100.6 MHz, chemical shifts are relative to TMS. All compounds gave correct elemental analyses or high resolution mass spectra.

Together with the NMR data and the fact that hydrolysis yields the dinitrile **9** of 2,3-bis(trimethylsilyl)succinic acid, the structure of **7** can be assumed with confidence.

The many attempts to photoisomerize **8** into tetrahedrane **3** by variation of the wavelength, temperature, and solvent demanded high persistence. Practically all variants led to a fragmentation into two molecules of bis(trimethylsilyl)acetylene. However, there was one exception: Irradiation of the mixture of **7** and **8** in deuterated methylcyclohexane at −130 °C in a photoreactor (254 nm) for a long time resulted in the appearance of signals in the NMR spectra, which, by comparison with those measured for **2**,[3] could arise from tetrakis(trimethylsilyl)tetrahedrane (**3**). The final proof of the successful photochemically induced transformation of **8** into **3** was achieved with a pure sample of cyclobutadiene **8** which was given to us by Sekiguchi.[7, 10] The NMR signals of **8** had nearly disappeared after irradiation of the sample for 70 hours under the above-mentioned conditions. The newly formed NMR signals of practically equal intensities can be attributed to bis(trimethylsilyl)acetylene [^1H: $\delta = 0.12$; ^{13}C: $\delta = 0.01$ ($SiMe_3$), 113.48 (acetylenic-C)] and tetrakis(trimethylsilyl)tetrahedrane (**3**) [^1H: $\delta = 0.10$; ^{13}C: $\delta = -0.03$ ($SiMe_3$), −20.46 (ring-C)]. The strong upfield shift of the ring-C atoms is typical for tetrahedranes.[1, 3]

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[1] a) G. Maier, S. Pfriem, U. Schäfer, R. Matusch, *Angew. Chem.* **1978**, *90*, 552–553; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 520–521; b) G. Maier, S. Pfriem, U. Schäfer, K.-D. Malsch, R. Matusch, *Chem. Ber.* **1981**, *114*, 3965–3987; c) review: G. Maier, *Angew. Chem.* **1988**, *100*, 317–341; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 309–332.

[2] G. Maier, H. W. Lage, H. P. Reisenauer, *Angew. Chem.* **1981**, *93*, 1010–1011; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 976–977, and references therein.

[3] a) G. Maier, D. Born, *Angew. Chem.* **1989**, *101*, 1085–1087; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1050–1052; b) G. Maier, D. Born, I. Bauer, R. Wolf, R. Boese, D. Cremer, *Chem. Ber.* **1994**, *127*, 173–198.

[4] T. Loerzer, R. Machinek, W. Lüttke, L. H. Franz, K.-D. Malsch, G. Maier, *Angew. Chem.* **1983**, *95*, 914; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 878–879.

[5] a) G. Rauscher, T. Clark, D. Poppinger, P. von R. Schleyer, *Angew. Chem.* **1978**, *90*, 306; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 276; b) citation [19] in ref. [1c].

[6] G. Maier, F. Fleischer, *Liebigs Ann.* **1995**, 169–172.

[7] A. Sekiguchi, M. Tanaka, T. Matsuo, H. Watanabe, *Angew. Chem.* **2001**, *113*, 1721–1723; *Angew. Chem. Int. Ed.* **2001**, *40*, 1675–1677, following communication.

[8] G. Maier, D. Volz, J. Neudert, *Synthesis* **1992**, 561–564.

[9] H. Sakurai, K. Ebata, C. Kabuto, A. Sekiguchi, *J. Am. Chem. Soc.* **1990**, *112*, 1799–1803.

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From a Cyclobutadiene Dianion to a Cyclobutadiene: Synthesis and Structural Characterization of Tetrasilyl-Substituted Cyclobutadiene[**]

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The fascinating chemistry of cyclobutadiene (CBD) and its derivatives has been studied from the point of view of their structures, properties, and reactivities.[1, 2] The parent molecule, CBD, was initially generated by the oxidative treatment of $[(\eta^4\text{-}C_4H_4)Fe(CO)_3]$ with Ce^{IV} ions.[3] After that, it was observed—through the use of photochemical reactions—at low temperature in inert matrices,[4] and at room temperature in a hemicarcerand.[5] In contrast, some CBD derivatives, stabilized by steric effects, have been isolated, and parts of their molecular structures determined by X-ray crystallography.[6] For the most part, these compounds were prepared by the photolysis of cyclopentadienone derivatives or diazo compounds. However, the methods used to prepare CBD are sometimes very tedious and have undesirable side photoreactions.[7]

Recently, we succeeded in synthesizing the dilithium salt of the tetrakis(trimethylsilyl)cyclobutadiene dianion, the first aromatic CBD^{2-} ion with a six π-electron system, by the reaction of the cobalt complex of CBD derivative **2** with lithium metal in THF.[8] An interesting aspect is that CBD^{2-} is one of the best candidate precursors for CBD. Herein we report on a new and easy synthetic route from a CBD dianion to a CBD derivative that proceeds by a two-electron oxidation reaction.

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