One-Pot Synthesis of a Tetragermabutadiene and Its Reactions with Oxygen and Sulfur[1]

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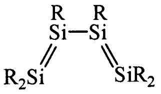
Hexakis(2,4,6-triisopropylphenyl)tetragermabuta-1,3-diene (**2**) is easily accessible by the reaction of the Grignard compound RMgBr, R = 2,4,6-$i\mathrm{Pr}_3\mathrm{C}_6\mathrm{H}_2$, with GeCl_2·dioxane and magnesium. Treatment of **2** with sulfur furnishes a thiatetragermacyclopentene derivative with an endocyclic Ge═Ge double bond. The reaction of **2** with dry air yields a compound with a 2,4,7,8-tetraoxa-1,3,5,6-tetragermabicyclo[4.1.1]octane skeleton.

Introduction

We recently prepared the compounds **1**[2] and **2**[3] as the first and as yet only examples of molecules containing conjugated Si═Si and Ge═Ge double bonds, respectively. Starting from a tetraaryldisilene, compound **1** was constructed by a sequence of metalation, halogenation, and intermolecular coupling reactions[2] and has since been characterized by a series of 1,2- and 1,4-addition as well as cycloaddition reactions.[4]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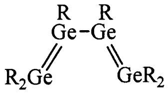
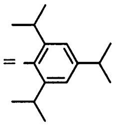

2

R =


Compound **2** is accessible from a tetraaryldigermene by an analogous sequence of reactions. Although compound **1** is formed in yields of up to 60%, the synthesis of **2** requires tedious separation steps and furnishes a maximum yield of 11%, which has up to now hindered the further characterization of this compound. We now describe a simple, one-pot synthesis of **2** and report on the first reactions of this tetragermabutadiene.

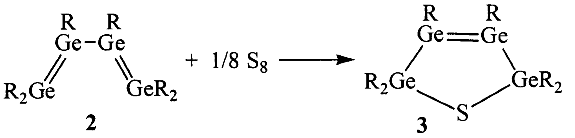
Results and Discussion

Slow, dropwise addition of a solution of GeCl_2·dioxane in THF at −50 °C to a mixture of 2,4,6-triisopropylphenylmagnesium bromide and magnesium in the same solvent leads at first to a red solution, which upon warming to room temperature takes on a black-blue color. Replacement of THF by *n*-pentane and repeated crystallizations from this solvent afford black crystals with analytical and spectroscopic data identical to those of an authentic sample of **2**[3] (eq 1).

$$4\,\mathrm{GeCl_2\cdot D} + 6\,\mathrm{RMgBr} + \mathrm{Mg} \xrightarrow[-\mathrm{D}]{} \mathbf{2} + 4\,\mathrm{MgCl_2} + 3\,\mathrm{MgBr_2} \quad (1)$$

D = 1,4-dioxane

Although the yield of this synthetic route still only amounts to about 30%, the one-pot procedure does allow the isolation of **2** on a gram scale from readily accessible or commercially available starting materials and thus makes first investigations of the reactions of the tetragermabutadiene possible.



(2)

Reactions of **1** with sulfur or, in the presence of triethylphosphane, with selenium and tellurium proceeded through formal [4+1] cycloadditions to afford the corresponding chalcogenatetrasilacyclopentenes with endocyclic Si═Si double bonds in yields of 80% each.[5] Compound **2** also reacts with sulfur to smoothly give the thiatetragermacyclopentene **3** as yellow needles isolated in 75% yield (eq 2).

An X-ray crystallographic analysis of **3** (Figure 1) reveals the presence of an almost planar five-membered ring (sum of the endocyclic angles: 539.5°). With an average value of 2.45 Å the Ge(1)−Ge(2) and Ge(3)−Ge(4) bonds are of the typical size for Ge−Ge single bonds. The Ge═Ge double bond length of 2.2841(5) Å is somewhat longer than the corresponding bonds in the as yet only other known molecules with endocyclic Ge═Ge bonds, namely, $(t\mathrm{Bu_3Si})_4\mathrm{Ge_3}$[6] with 2.239 Å and $(t\mathrm{Bu_3Si})_3\mathrm{Ge_3Br}$[7] with 2.2743 Å. Like most other digermenes, compound **3** shows a *trans*-bending of the substituents referred to the Ge(2)−Ge(3) vector, which, in this case,

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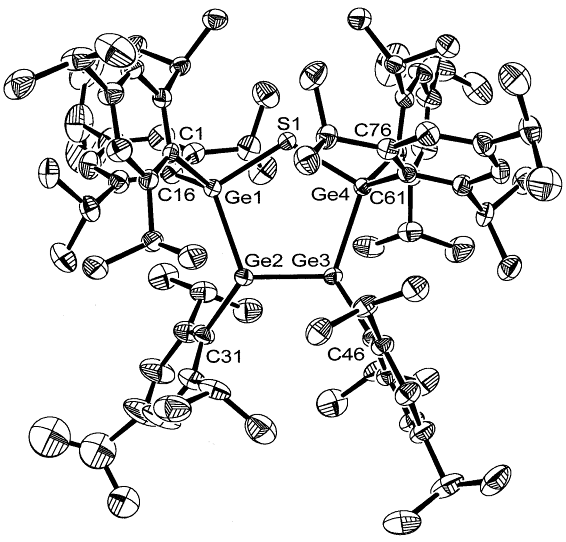


Figure 1. Molecule of **3** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (deg): Ge(1)−Ge(2) = 2.4526(4), Ge(2)−Ge(3) = 2.2841(5), Ge(3)−Ge(4) = 2.4482(4), Ge(1)−S = 2.2669(8), Ge(4)−S = 2.2666(8), Ge(1)−Ge(2)−Ge(3) = 108.620(15), Ge(2)−Ge(3)−Ge(4) = 107.898(16), Ge(3)−Ge(4)−S = 102.93(2), Ge(4)−S−Ge(1) = 116.46(3), S−Ge(1)−Ge(2) = 102.54(2).

is very pronounced with values of 29.9° at Ge(2) and 35.7° at Ge(3).

Selenium and tellurium also react with **2** in the presence of triethylphosphane as chalcogen transfer reagent; however the yields of products that can be isolated are so low that their unambiguous characterization has not yet been possible.

Oxygen reacts with simple digermenes through 1,2-addition at the Ge=Ge double bond to afford 3,4-digermadioxetanes that rearrange to 2,4-digermadioxetanes only at higher temperatures or under irradiation.[8] Disilenes also react with oxygen initially through 1,2-addition to 3,4-disiladioxetanes; however, only cyclodisiloxanes can be isolated.[9] Analogously, the action of dry air on **1** leads to a product in which two cyclodisiloxane rings are linked by a disiloxane bridge.[10] If the two double bonds of **2** were to react like simple digermenes, the compound **4** or a rearrangement product of this molecule would be formed. The reaction of **2** with dry air gave a product isolated in 77% yield for which the analytical data were indicative of a 1:2 adduct of diene **2** and O_2. However, the X-ray crystallographic data of the pale yellow crystals gave an unexpected result. Neither the compound **4** nor a possible rearrangement product thereof had been formed. Instead the product proved to be compound **5**, with a tetraoxatetragermabicyclo[4.1.1]octane skeleton (Scheme 1). In contrast to our expectations, the folded cyclodigermoxane ring (fold angle = 14.5°) in the bicyclic system was not formed by addition of O_2 to one of the two double bonds but rather must be the result of a [2+4] cycloaddition of O_2 to the terminal germanium atoms of **2** to afford compound **6**, followed by a 1,2-addition of a second oxygen molecule to the newly formed double bond to give the intermediate **7**. Rearrangement reactions of the two O−O bonds of **7** should then furnish the isolated product **5** (Scheme 2).

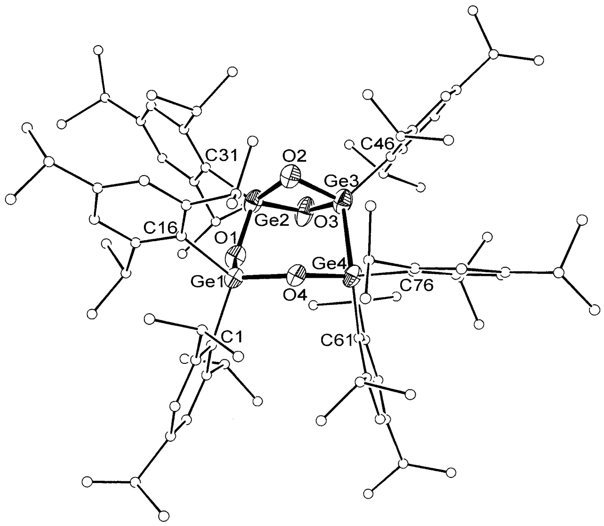
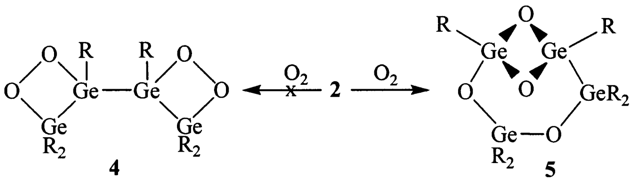
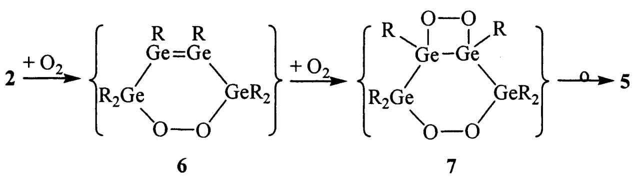


Figure 2. Molecule of **5** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (deg): Ge(1)−O(1) = 1.789(3), O(1)−Ge(2) = 1.754.(3), Ge(2)−O(2) = 1.806(4), Ge(2)−O(3) = 1.774(3), O(2)−Ge(3) = 1.820(3), O(3)−Ge(3) = 1.831(4), Ge(3)−Ge(4) = 2.4997(8), Ge(4)−O(4) = 1.814(3), O(4)−Ge(1) = 1.792(3), Ge(1)−O(4)−Ge(4) = 132.17(18), Ge(1)−O(1)−Ge(2) = 124.71(18), Ge(2)−O(2)−Ge(3) = 90.66(15), Ge(2)−O(3)−Ge(3) = 91.31(16), O(3)−Ge(2)−O(2) = 88.24(17), O(3)−Ge(3)−O(2) = 86.14(15).

Scheme 1



Scheme 2



Although the formation of the bicyclic compound **5** cannot yet be interpreted unequivocally, it seems clear that the conjugated double bonds in **2** can exhibit different reaction modes from those that are possible for digermenes with isolated double bonds.

Experimental Section

General Procedures. All manipulations were carried out in oven-dried glassware under an atmosphere of dry argon. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker ARX 500 spectrometer using C_6D_6 as solvent. The UV/vis spectra were recorded with a Comspec spectrometer with fiber optics. Elemental analyses were performed by Analytische Laboratorien, D-51779 Lindlar, Germany.

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1,1,2,3,4,4-Hexakis(2,4,6-triisopropylphenyl)tetragermabuta-1,3-diene (2). At −50 °C a solution of $GeCl_2$·dioxane (5.15 g, 22.2 mmol) in THF (40 mL) was added dropwise to a mixture of 2,4,6-triisopropylphenylmagnesium bromide, prepared from 1-bromo-2,4,6-triisopropylphenylbenzene (9.79 g, 34.6 mmol) and excess magnesium (1.3 g, 53 mmol) in THF (30 mL). The color of the mixture changed from yellow to red. The mixture was allowed to come to room temperature. THF was removed from the black mixture, the black residue was extracted with *n*-pentane (250 mL), and all insoluble products were filtered off. After cooling for 24 h at −30 °C all insoluble compounds were again filtered off. The filtrate was concentrated to a volume of 100 mL and stored for 5 days at −30 °C. After this time the crude product was filtered off and recrystallized from *n*-pentane to furnish 2.6 g (31% yield) of black crystals of **2**. The analytical and spectroscopic data were identical to those of an authentic sample of **2**.[3]

2,2,3,4,5,5-Hexakis(2,4,6-triisopropylphenyl)-1-thia-2,3,4,5-tetragermacyclopent-3-ene (3). Sulfur (1.0 g, 31.2 mmol, large excess) was added to a solution of **2** (0.80 g, 0.43 mmol) in toluene (30 mL), and the mixture heated under reflux for 3 h. During this time the color changed from blue-black to yellow. Toluene was replaced by *n*-pentane (40 mL), excess sulfur was filtered off, and the solvent was evaporated. Crystallization from toluene provided yellow needles of **3** (0.61 g, 77%): mp 199−201 °C; ^1H NMR δ 0.19 (d, 6 H, $^3J = 6.6$ Hz), 0.48 (d, 6 H, $^3J = 6.6$ Hz), 0.49 (d, 6 H, $^3J = 6.1$ Hz), 0.52 (d, 6 H, $^3J = 6.6$ Hz), 0.63 (d, 6 H, $^3J = 6.6$ Hz), 0.71 (d, 6 H, $^3J = 7.1$ Hz), 0.91 (d, 6 H, $^3J = 6.6$ Hz), 1.11 (d, 6 H, $^3J = 7.1$ Hz), 1.15 (d, 6 H, $^3J = 7.1$ Hz), 1.18 (d, 6 H, $^3J = 6.6$ Hz), 1.21 (d, 6 H, $^3J = 6.1$ Hz), 1.27 (d, 6 H, $^3J = 6.6$ Hz), 1.28 (d, 6 H, $^3J = 7.1$ Hz), 1.32 (d, 6 H, $^3J = 6.6$ Hz), 1.40 (d, 6 H, $^3J = 6.6$ Hz), 1.43 (d, 6 H, $^3J = 6.6$ Hz), 1.64 (d, 6 H, $^3J = 6.6$ Hz), 1.75 (d, 6 H, $^3J = 6.6$ Hz), 2.69 (sept, 2 H), 2.82 (sept, 2 H) 3.18 (sept, 2 H), 3.63 (sept, 2 H), 3.89 (sept, 4 H), 3.94 (sept, 2 H), 4.64 (sept, 2 H), 7.15 (m, 12 H); ^{13}C NMR δ 21.49, 24.02, 24.07, 24.10, 24.14, 24.18, 24.36, 24.61, 24.67, 24.86, 25.34, 26.15, 26.28, 26.83, 27.76, 29.24, 35.98, 37.87, 121.66, 121.78, 122.75, 122.80, 123.58, 123.82, 127.80, 127.99, 128.19, 128.29, 128.50, 129.03, 129.27, 138.95, 140.74, 146.70, 149.00, 140.54, 149.66, 150.67, 153.04, 154.20, 154.51, 155.78; UV/vis (*n*-hexane) λ_{max} (ϵ) 400 (1750 nm). Anal. Calcd for $C_{90}H_{138}Ge_4S$: C, 70.08; H, 9.02; S, 2.08. Found: C, 69.88; H, 9.05; S. 2.19. Single crystals of **3** were grown from methylcyclopentane at +4 °C.

1,3,3,5,5,6-Hexakis(2,4,6-triisopropylphenyl)-2,4,8-tetraoxa-1,3,5,6-tetragermabicyclo[4.1.1]octane (5). At 0 °C dry air was passed over a solution of **2** (0.60 g, 0.40 mmol) in toluene (30 mL). After 10 min the color of the solution had changed from blue-black to yellow. Toluene was distilled off, the residue was redissolved in *n*-pentane (40 mL), and the insoluble products were filtered off. Crystallization from toluene furnished pale yellow crystals of **5** (0.48 g, 77%): mp 241−244 °C; ^1H NMR δ 0.15 (d, 6 H, $^3J = 6.6$ Hz), 0.18 (d, 6 H, $^3J = 6.6$ Hz), 0.26 (d, 6 H, $^3J = 6.6$ Hz), 0.33 (d, 6 H, $^3J = 6.6$ Hz), 0.38 (d, 6 H, $^3J = 6.6$ Hz), 0.46 (d, 6 H, $^3J = 6.6$ Hz), 0.51 (d, 6 H, $^3J = 6.6$ Hz), 0.52 (d, 6 H, $^3J = 6.6$ Hz), 0.62 (d, 6 H, $^3J = 6.6$ Hz), 1.45 (m, 6H), 1.48 (d, 6 H, $^3J = 6.6$ Hz), 1.53 (d, 6 H, $^3J = 6.6$ Hz), 1.58 (d, 6 H, $^3J = 6.0$ Hz), 1.61 (d, 6 H, $^3J = 6.6$ Hz), 1.69 (d, 6 H, $^3J = 6.6$ Hz), 1.73 (d, 6 H, $^3J = 6.6$ Hz), 1.78 (d, 6 H, $^3J = 6.6$ Hz), 1.85 (d, 6 H, $^3J = 6.6$ Hz), 2.65 (sept, 4 H), 2.75 (sept, 2 H) 2.96 (sept, 2 H), 3.26 (sept, 2 H), 3.55 (sept, 2 H), 4.23 (sept, 2 H), 4.46 (sept, 2 H), 4.57 (sept, 2 H), 6.73 (s, 2 H), 6.76 (s, 2 H), 6.80 (s, 2 H), 6.85 (s, 2 H), 6.92 (s, 2 H), 7.03 (s, 2 H); ^{13}C NMR δ 21.36, 22.93, 23.40, 23.70, 23.81, 23.95, 24.02, 24.11, 24.36, 24.44, 24.56, 24.74, 24.97, 25.15, 26.70, 28.57, 34.30, 34.38, 34.58, 35.85, 38.25, 121.49, 121.88, 122.19, 122.40, 122.74, 123.16, 123.29, 123.58, 123.91, 124.01, 125.63, 127.80, 127.99, 128.18, 128.50, 129.27, 129.98, 137.77, 141.29, 149.74, 149.94, 152.16, 152.54, 154.36, 155.73. Anal. Calcd for $C_{90}H_{138}Ge_4O_4$: C, 68.65; H, 8.83. Found: C, 68.63; H, 8.59. Single crystals of **5** were grown from toluene at −30 °C.

Table 1. Crystallographic Data for 3 and 5

	3	**5**
empirical formula	$C_{90}H_{138}Ge_4S\cdot 2C_6H_{12}$	$C_{90}H_{138}Ge_4O_4\cdot 1.5C_7H_8$
fw	1710.74	1712.56
a (Å)	14.4535(5)	16.8134(3)
b (Å)	17.0514(9)	21.0889(6)
c (Å)	22.7739(13)	27.1986(6)
α (deg)	110.735(6)	90
β (deg)	101.723(5)	98.253(2)
γ (deg)	97.573(5)	90
V (Å^3)	5010.8(4)	9544.1(4)
Z	2	4
d(calcd) (g cm^{-3})	1.134	1.192
cryst size (mm)	0.38 × 0.17 × 0.10	0.20 × 0.15 × 0.06
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
$2\theta_{max}$ (deg)	52	52
no. of reflns measd	61 022	79 739
no. of unique reflns	17 981	17 646
lin abs coeff (mm^{-1})	1.250	1.295
no. of params	929	828
R ($I > 2\sigma(I)$)	0.0363	0.0515
wR_2 (all data)	0.0872	0.1098
GOF (F^2)	0.904	0.796

Crystallographic Analyses. Crystal and numerical data of structure determinations are given in Table 1. In each case the crystal was mounted in an inert oil. Data collection was performed with a Stoe IPDS area detector at 193(2) K using graphite-monochromated Mo Kα radiation (0.71073 Å). The structures were solved by direct phase determination and refined by full-matrix least-squares techniques against F^2 with the SHELXL-97 program system.[11] Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically. The data have been deposited with the Cambridge Crystallographic Data Centre: CCDC 195 983 (**3**) and CCDC 195 984 (**5**).

Acknowledgment. Financial support of our work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Listing of atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020956D

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