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Synthesis of a Cyclotrigermane and Its Conversion to a Digermene

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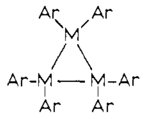
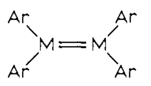
Our recent communication described the synthesis of hexakis(2,6-dimethylphenyl)cyclotrisilane (**1**), which has exhibited unusual physical and chemical properties.[1] Of particular interest is its near-quantitative photoconversion to tetrakis(2,6-dimethylphenyl)disilene (**2**), representing one of the first silicon–silicon double-bond-containing compounds ever prepared in crystalline form.[2] This remarkable outcome has naturally led to application of the same methodology to the corresponding germanium series. We describe herein the synthesis and full characterization of hexakis(2,6-dimethylphenyl)cyclotrigermane (**3**) and also present evidence to demonstrate that the cyclotrigermane **3** also undergoes photochemical cleavage to provide extremely air-sensitive tetrakis(2,6-dimethylphenyl)digermene (**4**) which has been purified to an extent of 75%. Thus, both the cyclotrigermane and digermene systems often discussed in the literature have now been characterized for the first time.[3,4]



1 : M = Si
3 : M = Ge



2 : M = Si
4 : M = Ge

Ar = 2,6-dimethylphenyl

The Cyclotrigermane 3. The synthesis of **3** follows, in essence, the method originally developed by Kipping for the synthesis of cyclopolysilanes.[5] Bis(2,4-pentanedionato)germanium dichloride (**5**)[6] is converted to bis(2,6-dimethylphenyl)germanium dichloride (**6**),[7] which is reductively cyclclized to provide **3** in a manner similar to that described earlier for **1**.[1] Thus, addition of 2,6-dimethylphenylmagnesium bromide (0.03 mol) in tetrahydrofuran (30 mL) to a suspension of **5** (0.015 mol) in benzene (150 mL) and then heating the reaction mixture at reflux for 2 h provided a crude adduct which was, upon treatment with 1 N sodium hydroxide, converted to yellow bis(2,6-dimethylphenyl)germanium dihydroxide, mp 167 °C, in 25% yield.[8] Treatment of this dihydroxide with concentrated hydrochloric acid effected its quantitative conversion to **6**, mp 96–97 °C, mass spectrum (field desorption) $M^{+\cdot}$ cluster *m/z* 350–358.[9] After the addition of **6** (11.3 g, 0.032 mol) in dimethoxyethane (DME, 50 mL) to a dark green solution of lithium naphthalenide [prepared from naphthalene (8.48 g, 0.066 mol) in DME and 30% lithium dispersion (1.51 g, 0.064 mol) at −78 °C], the resulting mixture was stirred at the same temperature for 1 h and then gradually warmed to room temperature over a period of 2 h. The usual workup including flash chromatography provided two major fractions, A and B, in addition to recovered naphthalene. Fraction A (1.63 g) was an inseparable mixture of $Ar_2HGe–GeClAr_2$ and $Ar_2ClGe–GeClAr_2$ (Ar = 2,6-dimethylphenyl) as analyzed by mass spectroscopy.[10] Recrystallization of fraction B from cyclohexane provided in 17% yield a new compound, mp 234 °C dec. Its spectral properties are fully consistent with the formulation of **3** for this compound: mass spectrum (field desorption) $M^{+\cdot}$ cluster range *m/z* 840–857 in agreement with that calculated for $C_{48}H_{54}Ge_3$;[9] ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.16, 127.44, 127.99, 143.14 146.10. Resembling its silicon analogue **1**, compound **3** exhibits an ultraviolet absorption maximum at 265 nm (log ϵ 4.67, cyclohexane;[1,11] see Figure 1) and temperature-dependent ^1H NMR spectra (270 MHz, toluene-d_8) due to the expected slow rotation of the aryl rings along the germanium and carbon bonds.[1] Thus, two (methyl) singlets (δ 1.97 and 2.37) and an ABX (aromatic) multiplet observed at −53 °C collapse to one singlet (δ 2.15) and an A_2X singlet (δ 6.74, d, *J* 7.4 Hz, 2 H; δ 6.93, t, *J* = 7.4 Hz, 1 H) at 82 °C. The structure of **3** in crystalline form follows.

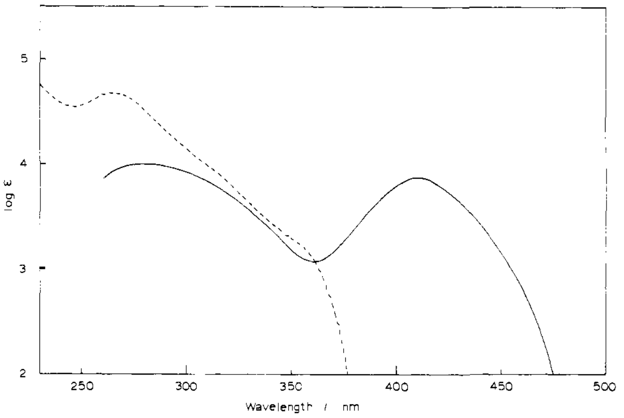


Figure 1. Ultraviolet spectra of **3** (dotted line) and **4** (solid line) in cyclohexane.

Crystallographic Analysis of 3. Crystals of **3** solvated with cyclohexane, $C_{48}H_{54}Ge_3\cdot1.5C_6H_{12}$, are triclinic with a = 11.634 (2) Å, b = 15.053 (3) Å, c = 17.568 (3) Å, α = 81.64 (1)°, β = 86.35 (1)°, γ = 88.27 (1)°, U = 3037 Å^3, space-group $P\bar{1}$, Z = 2.

As the crystals rapidly desolvate on removal from solution, a small single crystal (approximate dimensions 0.15 × 0.20 × 0.32 mm) was transferred *under solution* into a Lindemann glass capillary tube. Excess solution was carefully drawn off and the tube sealed leaving a small drop at one end of the tube to maintain a vapor pressure of the solvent. Data were measured by using monochromatized CuKα radiation (graphite monochromator) on a Nicolet R3m diffractometer. A total of 6253 independent reflections were measured (θ < 50°) with the ω-scan measuring

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(1) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150.

(2) West et al. also succeeded in preparing another derivative, tetramesityldisilene via a different route. West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1980**, *214*, 1343 (also see *Chem. Eng. News* **1981**, *Dec 21*, 8).

(3) For short reviews of cyclopolygermanes, see: (a) Satgé, J.; Massol, M.;Revière, P. *J. Organomet. Chem.* **1973**, *56*, 11. (b) Lesbre, M.; Mazerolles, P.; Satgé, J. "The Organic Compounds of Germanium"; Interscience Publishers: New York, 1971; Chapter 9. (c) Ishikawa, M.; Kumada, M. *Rev. Silicon, Germanium, Tin, Lead Compd.* **1979**, *4*, 46. (d) Armitage, D. A. "Inorganic Rings and Cages"; Edward Arnold: New York, 1972; Chapter 4, p 160.

(4) For trapping digermene species, see: (a) Mazerolles, P.; Joanny, M.; Tourrou, G. *J. Organomet. Chem.* **1973**, *60*, C3. (b) Rivière, P.; Castel, A.; Satgé, J. *Ibid.* **1981**, *212*, 351.

(5) Kipping, F. S. *Proc. Chem. Soc.* **1911**, *27*, 143.

(6) Morgan, G. T.; Drew, H. D. K. *J. Chem. Soc.* **1924**, *105*, 1261.

(7) Following the procedure for the synthesis of diorganotin dichlorides: Chandrasekaran, R. K.; Venkataraman, S.; Koola, J. D. *J. Organomet. Chem.* **1981**, *215*, C43.

(8) IR ($CHCl_3$) 3640, 3400 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.1 (s, 2 H), 2.5 (s, 12 H), 6.8–7.3 (m, 6 H).

(9) More information is supplied in the supplementary material.

(10) This mixture was reduced with lithium aluminum hydride at room temperature to provide quantitatively $Ar_2HGe–GeHAr_2$: IR ($CHCl_3$) ν for Ge–H, 2030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.19 (s, 24 H), 5.64 (s, 2 H), 6.87 (d, *J* = 7. 6 Hz, 8 H), 7.07 (t, *J* = 7.6 Hz, 4 H); mass spectrum (field description) $M^{+\cdot}$ cluster range *m/z* 562–576, matchable to that calculated for $C_{32}H_{38}Ge_2$.[9]

(11) For ultraviolet spectra of cyclopolygermane [$(Ph_2Ge)n$ with n = 4–6], see: Neumann, W. P.; Kühlein, K. *Tetrahedron Lett.* **1963**, 1541.

0002-7863/82/1504-6136$01.25/0

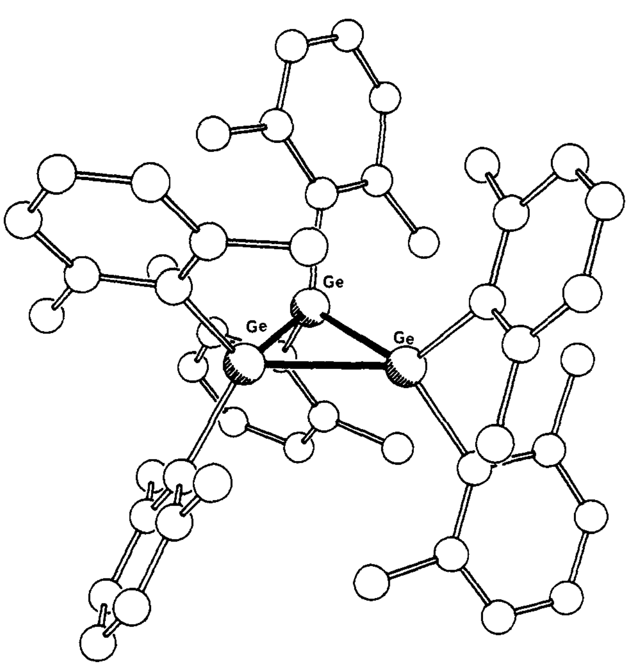

Figure 2. Crystal structure of **3**. Ge–Ge bond lengths (Å): 2.543, 2.543, 2.537. Ge–Ge bond angles (deg): 59.9, 60.1. C–Ge bond lengths (Å): 1.977–2.015.

routine, and of these 5084 had $|F_o| > 3\sigma(|F_o|)$ and were considered to be observed. The structure was solved by the heavy-atom method, and the nonhydrogen atoms were refined anisotropically. The hydrogen atoms, with the exception of the methyl groups, which were refined as rigid bodies, were placed at calculated positions and allowed to ride on their parent carbons. Refinement was by full-matrix least-squares analysis to $R = 0.074$. The cyclohexane molecules are disordered and partially occupy three independent positions in the asymmetric unit. In one site two principal orientations were found.

As shown in Figure 2, the three germanium atoms form an essentially equilateral triangle with Ge–Ge bond lengths of 2.543 (1), 2.543 (1), and 2.537 (1) Å, respectively,[12] and bond angles of between 59.9 (1) and 60.1 (1)°. The planes formed by each of the pairs of Ge–Ar bonds are all rotated in the same sense by between 7.2 and 8.6° from the normal to the plane of the germaniums. The Ge–Ar bonds are in the range 1.977 (8)–2.015 (12) Å. Thus, the molecule has approximate D_3 symmetry, in contrast to the symmetry exhibited by the silicon analogue **1**, where the three silicon atoms form an isosceles triangle. The Ge–Ge bond length of **3** are apparently the longest every found for the bond of this type,[12] and the slow rotation of the phenyl rings along the C–Ge bonds shown above by ^{1}H NMR spectra is expected from the steric congestion created between several pairs of the methyl groups.

Photoconversion of 3 to 4. Irradiation of **3** in cyclohexane-d_{12} with a low-pressure mercury lamp at room temperature provides a new (yellow) product (**4**) as evidenced by the appearance of a set of ^{1}H NMR signals: δ 2.18 (s), 6.83 (d, $J = 7.2$ Hz), 6.96 (t, $J = 7.2$ Hz), with a relative intensity of 6:2:1. Since **4** is also labile under this condition and undergoes slow photoinduced polymerization, the concentration of **4** reaches a maximum (approximately 65% yield)[13] when **3** is 75%[13] consumed.[14] Ultraviolet spectroscopy also serves the purpose of following this photochemical reaction (see Figure 3), and indeed the electronic spectrum of pure **4** can be calculated with resonable accuracy (error in $\epsilon \simeq 10\%$) as the concentration of **4** and **3** is estimated by ^{1}H NMR spectroscopy (see Figure 1).[15] The addition of degassed methanol to a photolysate (60% conversion of **3**) immediately causes decoloration of the solution and provides Ar_2HGe–$Ge(OMe)Ar_2$ (**7**)[16] in 65% yield in addition to recovered **3**.[17] From this spectral and chemical evidence, we conclude that **4** is indeed tetrakis(2,6-dimethylphenyl)digermene. 2,6-Dimethylphenylgermylene, assumed to be the other photofragment, has not been trapped, and it is yet to be determined if this species dimerizes to form **4**. Pyrolysis of **3** at 160 to 165 °C provides Ar_3GeH (**8**)[18] as well as a small quantity of **4**.

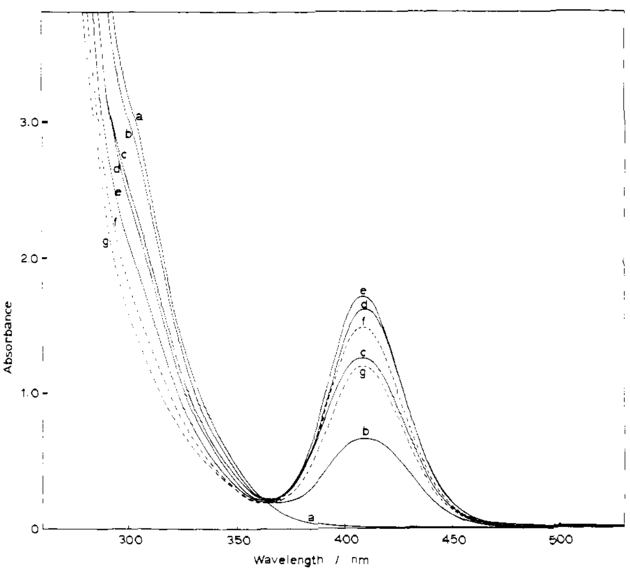

Figure 3. Photolysis of **3** (2.6×10^{-1} mM in cyclohexane-d_6) followed by ultraviolet spectroscopy: (a) before irradiation; (b) after 7 s of irradiation; (c) 20 s; (d) 30 s; (e) 40 s; (f) 50 s; (g) 66 s.

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Supplementary Material Available: Listings of atom coordinates and temperature factors, bond lengths, bond angles, and anisotropic temperature factors of hexakis(2,6-dimethylphenyl)cyclogermane as well as detailed information concerning the high-resolution mass spectra of new compounds (9 pages). Ordering information is given on any current masthead page.

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(12) The Ge–Ge bond lengths are 2.465 Å in $(Ph_2Ge)_4$ (a) (Ross, L.; Dräger, M. *J. Organomet. Chem.* **1980**, *199*, 195), 2.463 and 2.457 Å in $(Ph_2Ge)_6$ (b) (Dräger, M.; Ross, L. *Z. Anorg. Allg. Chem.* **1981**, 476, 95), and 2.374 Å in $(Me_2Ge)_6$ (c) (Jensen W.; Jacobson, R *Cryst. Struct. Commun.* **1975**, *4*, 299). The Ge–C bond lengths are 1.951–1.976 Å in a, 1.959–1.981 Å in b, and 1.92–1.97 Å in c.

(13) Hexamethylethane was used as internal standard in order to estimate the concentration of **3** and 4.

(14) A mass spectrum (electron impact, 70 eV) of this photolysis shows the parent peaks corresponding to $(Ar_2Ge)_2$ with the proper relative intensities,[9] whereas that of **3** measured under the identical conditions indicates the presence of the overlapping $[(Ar_2Ge)_2 - 1]$ and $(Ar_2Ge)_2$ peaks in this region. It is clearly noticeable that a peak at m/z 559 corresponding to $[(Ar_2Ge)_2 - 1]$ is missing in the spectrum of the photolysate.[9]

(15) Due to the extreme sensitivity of compound **4** to O_2 and moisture, we have not been able to isolate pure 4. All handling was done in a drybox with O_2 concentration less than 5 ppm. Attempted purification of 4 taking advantage of the solubility difference between 4 and **3** in several hydrocarbon solvents raised the purity of 4 to 75%.

(16) 7: IR ($CHCl_3$) ν for Ge–H 2020 cm^{-1}; mass spectrum (field desorption) $M^{+\cdot}$ cluster m/z 592–606 matchable to that calculated for $C_{33}H_{40}Ge_2O$;[9] ^{1}H NMR (250 MHz, benzene-d_6) δ 2.27 (s, 12 H), 2.35 (s, 12 H), 3.48 (s, 3 H), 5.79 (s, 1 H), 6.80 (d, $J = 7.5$ Hz, 4 H), 6.87 (d, $J = 7.5$ Hz, 4 H), 7.01 (t, $J = 7.5$ Hz, 2 H), 7.03 (t, $J = 7.5$ Hz, 2 H).

(17) Compound **3** is infinitely stable in its methanolic solution.

(18) **8**: IR ($CHCl_3$) ν for Ge–H 2030 cm^{-1}; mass spectrum (field desorption) $M^{+\cdot}$ cluster m/z 386–394, in agreement with that calculated for $C_{24}H_{28}Ge$;[9] ^{1}H NMR (250 MHz, cyclohexane-d_{12}) δ 2.15 (s, 18 H), 5.92 (s, 1 H), 6.87 (d, 6 H), 7.03 (t, 3 H).