

mesitylgermylene. These data are consistent with 515- and 380-nm bands of dimesitylgermylene-chlorine and -sulfur complexes and contrast markedly with the behavior of silylene or carbene with allylic compounds.⁷

Acknowledgment. Financial support for this research was provided by a Grant-in Aid for Special Project Research (No. 63106003) from the Ministry of Education, Science, and Culture of Japan.

(6) In thermal reaction of dimethylgermylene with crotyl chloride two products, direct insertion and rearranged, were obtained in the ratio 1:3.

(7) Ando, W. *Acc. Chem. Res.* 1977, 10, 179.

Digermirane and Azadigermiridine: Synthesis and Reactions

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Summary: 1,1,2-Tetrakis(2,6-diethylphenyl)digermirane (**3**) was prepared by the reaction of tetrakis(2,6-diethylphenyl)digermene (**2**) with diazomethane. The photolysis of **3** with a high-pressure mercury lamp yields germene **4** and germylene **5**. The digermirane **3** reacts with pyridine *N*-oxide, sulfur, and selenium to yield the insertion products of O, S, and Se into the germanium-germanium bond. 2,2,3,3-Tetrakis(2,6-diethylphenyl)azadigermiridine (**12**) was prepared by the reaction of **2** with phenyl azide.

Synthesis of small-ring systems involving a germanium-germanium bond have received considerable attention because of interest in the reactivity of the reactive germanium-germanium bonds in the ring.¹⁻⁶ However, digermiranes and azadigermiridines have not been isolated or very well characterized, although recently synthesis of a disilirane⁷ and an azadisiliridine⁸ was reported by Ma-

(1) (a) Ando, W.; Tsumuraya, T.; Sekiguchi, A. *Tetrahedron Lett.* 1985, 26, 4523. (b) Ando, W.; Tsumuraya, T. *Tetrahedron Lett.* 1986, 27, 5105.

(2) (a) Ando, W.; Tsumuraya, T. *Tetrahedron Lett.* 1986, 27, 3251. (b) Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics*, in press.

(3) (a) Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* 1982, 104, 6136. (b) Snow, J. T.; Murakami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* 1984, 25, 4191. (c) Collins, S.; Murakami, S.; Snow, J. T.; Masamune, S. *Tetrahedron Lett.* 1985, 26, 1281.

(4) Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* 1987, 1514.

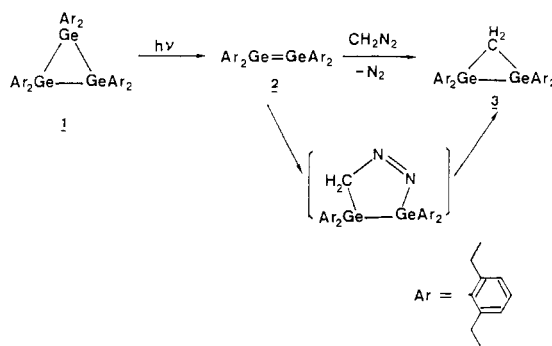
(5) (a) Espenbetov, A. A.; Struchkov, Yu. Y.; Kolesnikov, S. P.; Nefedov, O. M. *J. Organomet. Chem.* 1984, 275, 33. (b) Nefedov, O. M.; Egorov, M. P.; Gal'minas, A. M.; Kolesnikov, S. P.; Krebs, A.; Berndt, J. *J. Organomet. Chem.* 1986, 301, C21.

(6) Barrau, J.; Hamida, N. B.; Agrebi, A.; Satge, J. *Organometallics* 1987, 6, 659.

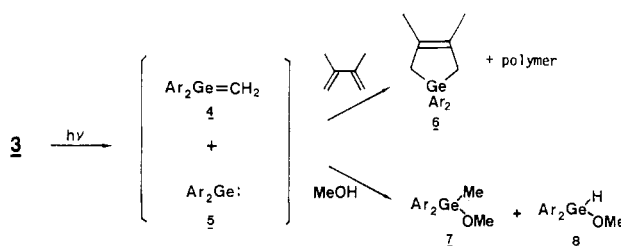
(7) Masamune, S.; Murakami, S.; Tobita, H. *J. Am. Chem. Soc.* 1983, 105, 7776.

(8) Gillette, G. R.; West, R., presented at the 19th Organosilicon Symposium, Baton Rouge, LA, April 26-27, 1985.

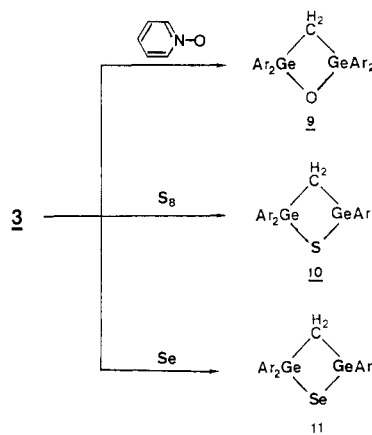
Scheme I



Scheme II



Scheme III

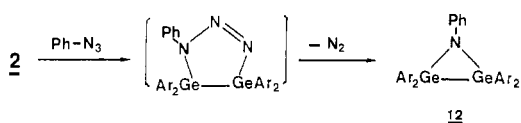


samune and West. Here, we report the first synthesis and reactions of a novel digermirane and an azadigermiridine.

Irradiation of a cyclohexane solution of hexakis(2,6-diethylphenyl)cyclotrigrermane (**1**)^{3b,4} at room temperature with a low-pressure mercury lamp afforded tetrakis(2,6-diethylphenyl)digermene (**2**) in good yield.^{3b} A cyclohexane solution of **2** (prepared from 0.5 mmol of **1**) was transferred to an ethereal solution of diazomethane (ca. 5 mmol, dried by KOH and degassed) under argon at -78 °C. After the addition was completed, the resulting mixture was warmed to room temperature. During the reaction, dinitrogen was evolved and the solution became pale yellow. Crystallization of the residue from hexane afforded 1,1,2-tetrakis(2,6-diethylphenyl)digermirane (**3**) as colorless crystals in 72% yield (based on the cyclotrigrermane **1** used) (Scheme I).

The structure of **3** was confirmed by spectroscopic analysis [¹H NMR (CDCl₃) δ 0.87 (t, *J* = 7 Hz, 24 H, CH₃), 1.30 (s, 2 H, GeCH₂Ge), 2.76 (q, *J* = 7 Hz, 8 H, CH₂), 2.91 (q, *J* = 7 Hz, 8 H, CH₂), 6.8-7.4 (m, 12 H, Ar)]; ¹³C NMR (CDCl₃) δ 6.99 (t, GeCH₂Ge), 15.32 (q, CH₃), 30.12 (t, CH₂), 125.41 (d, Ar), 128.75 (d, Ar), 138.85 (s, Ar), 149.77 (s, Ar);

Scheme IV

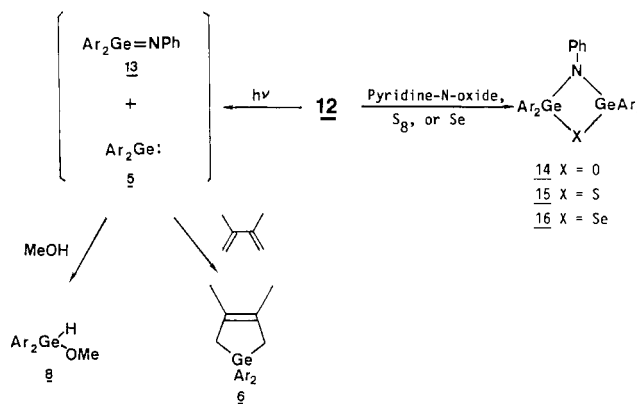


mass spectrum, m/e (relative intensity) 692 (3, M^+), 559 (8, $M^+ - Ar$), 354 (13, $Ar_2Ge=CH_2$), 340 (100, Ar_2Ge), 207 (48, $ArGe$); UV (hexane) λ_{max} 300 nm ($\log \epsilon$ 4.24)] as well as elemental analysis.⁹ In the ^{13}C NMR spectrum of **3** the characteristic three-membered ring carbon was observed at 6.99 ppm. Digermirane **3** is fairly stable toward air and moisture. The formation of **3** can be rationalized in terms of a dipolar addition of diazomethane to **2** followed by loss of N_2 .

Irradiation of a benzene solution of **3** (0.072 mmol) in the presence of an excess of 2,3-dimethyl-1,3-butadiene (5 mmol) with a high-pressure mercury lamp through a Pyrex filter for 2.5 h provided 1-germacyclopent-3-ene **6** in 50% yield^{3c} as well as polymeric material. Using a large excess of methanol as a trapping reagent led to the formation of two products, quantitative yields of methoxymethylgermane **7**¹⁰ and methoxygermane **8**.^{3c} These results clearly indicate that digermirane **3** is fragmented into the corresponding germene **4** and germylene **5** as shown in Scheme II. While germylene **5** reacted efficiently with the butadiene and methanol, germene **4** did not react with the butadiene and underwent polymerization.

Digermirane **3** is inert toward atmospheric oxygen but is readily oxidized by pyridine *N*-oxide in refluxing benzene to give 1,2,4-oxadigermetane **9**¹¹ in quantitative yield. In contrast, oxadigermetane **9** was not isolated from the reaction of **3** by *m*-chloroperbenzoic acid, probably due to the instability of **9** under acidic conditions. Elemental sulfur and selenium also reacted with **3** to give the ring expansion products **10**¹² and **11**¹³ in 87% and 94% yields, respectively (Scheme III).

Scheme V



Having the analogous digermirane-containing nitrogen, digermene **2** reacted with phenyl azide to yield colorless crystals of 2,2,3,3-tetrakis(2,6-diethylphenyl)azadigermiridine (**12**)¹⁴ in 68% yield (Scheme IV).

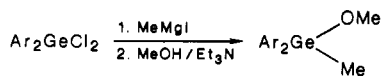
Azadigermiridine **12** is remarkably stable toward atmospheric oxygen or moisture and does not decompose even when heated to its melting point (mp 217–219 °C). Photolysis of **12** with 2,3-dimethyl-1,3-butadiene or methanol produced only products from germylene **5** in good yield. Although germanimine **13** was not trapped by butadiene or methanol, it is quite reasonable to assume that germanimine **13** and germylene **5** are generated in the photodecomposition of **12** as in the case of digermirane, thiadigermirane, and selenadigermirane.^{2b} Azadigermiridine **12** also reacted with pyridine *N*-oxide, sulfur, and selenium to yield the four-membered ring products **14**,¹⁵ **15**,¹⁶ and **16**¹⁷ in 58%, 12%, and 81% yields, respectively (Scheme V).

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Registry No. 1, 94833-02-0; 2, 94833-01-9; 3, 115385-08-5; 4, 115385-09-6; 5, 98583-18-7; 6, 98583-14-3; 7, 115385-10-9; 8, 98583-16-5; 9, 115385-11-0; 10, 115385-12-1; 11, 115406-97-8; 12, 115385-13-2; 13, 115385-14-3; 14, 115385-15-4; 15, 115385-16-5; 16, 115385-17-6; Ar_2GeCl_2 ($Ar = 2,6$ -diethylphenyl), 94833-03-1; 2,3-dimethyl-1,3-butadiene, 513-81-5.

(9) Compound **3**: mp 196–197 °C dec. Anal. Calcd for $C_{41}H_{54}Ge_2$: C, 71.15; H, 7.86. Found: C, 71.06; H, 7.90.

(10) Compound **7** was prepared independently by the reaction of dichlorobis(2,6-diethylphenyl)germane with methylmagnesium iodide followed by treatment with MeOH/ Et_3N as shown.



Compound **7**: 1H NMR ($CDCl_3$) δ 1.00 (t, $J = 7$ Hz, 12 H, CH_3), 1.02 (s, 3 H, $GeCH_3$), 2.75 (q, $J = 7$ Hz, 8 H, CH_2), 3.40 (s, 3 H, OCH_3), 6.9–7.4 (m, 6 H, Ar); high-resolution mass calcd for $C_{21}H_{26}OGe$ ($M^+ - Me$) 371.1428, found 371.1441.

(11) Compound **9**: mp 194–195 °C; 1H NMR ($CDCl_3$) δ 0.89 (t, $J = 7$ Hz, 24 H, CH_3), 2.69 (s, 2 H, $GeCH_2Ge$), 2.85 (q, $J = 7$ Hz, 16 H, CH_2), 6.9–7.3 (m, 12 H, Ar); ^{13}C NMR ($CDCl_3$) δ 15.71 (q, CH_3), 28.39 (t, CH_2), 32.88 (t, $GeCH_2Ge$), 126.06 (d, Ar), 129.37 (d, Ar), 139.55 (s, Ar), 149.03 (s, Ar); mass spectrum, m/e (relative intensity) 708 (13, M^+), 678 (11, $M^+ - O - CH_2$), 575 (13, $M^+ - Ar$), 442 (15, $M^+ - 2Ar$), 356 (27, $Ar_2Ge=O$), 354 (5, $Ar_2Ge=CH_2$), 340 (100, Ar_2Ge). Anal. Calcd for $C_{41}H_{54}OGe_2$: C, 69.55; H, 7.69. Found: C, 69.49; H, 7.70.

(12) Compound **10**: mp 121–123 °C; 1H NMR ($CDCl_3$) δ 0.91 (t, $J = 7$ Hz, 24 H, CH_3), 2.82 (q, $J = 7$ Hz, 8 H, CH_2), 2.84 (q, $J = 7$ Hz, 8 H, CH_2), 2.93 (s, 2 H, $GeCH_2Ge$), 6.9–7.3 (m, 12 H, Ar); ^{13}C NMR ($CDCl_3$) δ 15.49 (q, CH_3), 28.82 (t, CH_2), 37.66 (t, $GeCH_2Ge$), 126.23 (d, Ar), 129.21 (d, Ar), 140.85 (s, Ar), 148.38 (s, Ar); mass spectrum, m/e (relative intensity) 724 (1, M^+), 591 (100, $M^+ - Ar$), 372 (13, $Ar_2Ge=Se$), 354 (26, $Ar_2Ge=CH_2$), 340 (52, Ar_2Ge). Anal. Calcd for $C_{41}H_{54}SGe_2$: C, 68.01; H, 7.52. Found: C, 67.56; H, 7.65.

(13) Compound **11**: mp 128–129 °C; 1H NMR ($CDCl_3$) δ 0.92 (t, $J = 7$ Hz, 24 H, CH_3), 2.63 (q, $J = 7$ Hz, 8 H, CH_2), 2.84 (q, $J = 7$ Hz, 8 H, CH_2), 3.27 (s, 2 H, $GeCH_2Ge$), 6.9–7.3 (m, 12 H, Ar); ^{13}C NMR ($CDCl_3$) δ 15.49 (q, CH_3), 28.93 (t, CH_2), 40.79 (t, $GeCH_2Ge$), 126.17 (d, Ar), 129.15 (d, Ar), 140.37 (s, Ar), 148.17 (s, Ar); mass spectrum, m/e (relative intensity) 770 (15, M^+), 637 (100, $M^+ - Ar$), 418 (15, $Ar_2Ge=Se$), 354 (41, $Ar_2Ge=CH_2$), 340 (73, Ar_2Ge). Anal. Calcd for $C_{41}H_{54}SeGe_2$: C, 63.86; H, 7.05. Found: C, 63.68; H, 7.16.

(14) Compound **12**: 1H NMR ($CDCl_3$) δ 0.71 (t, $J = 7$ Hz, 24 H, CH_3), 2.62 (q, $J = 7$ Hz, 8 H, CH_2), 2.68 (q, $J = 7$ Hz, 8 H, CH_2), 6.5–7.4 (m, 17 H, Ar, Ph); ^{13}C NMR ($CDCl_3$) δ 14.97 (q, CH_3), 30.35 (t, CH_2), 119.30 (d), 123.82 (d), 125.64 (d), 128.11 (d), 129.16 (d), 141.90 (s), 148.36 (s), 153.00 (s); mass spectrum, m/e (relative intensity) 769 (2, M^+), 678 (11, $M^+ - NPh$), 636 (2, $M^+ - Ar$), 473 (9, Ar_2Ge), 431 (24, $Ar_2Ge=NPh$), 340 (100, Ar_2Ge), 207 (59, $ArGe$); UV (hexane) λ_{max} 270 nm ($\log \epsilon$ 4.60). Anal. Calcd for $C_{46}H_{57}NGe_2$: C, 71.83; H, 7.47. Found: C, 71.65; H, 7.45.

(15) Compound **14**: mp 287–290 °C; 1H NMR ($CDCl_3$) δ 0.80 (t, $J = 7$ Hz, 24 H, CH_3), 2.60 (q, $J = 7$ Hz, 8 H, CH_2), 2.70 (q, $J = 7$ Hz, 8 H, CH_2), 6.5–7.4 (m, 17 H, Ar, Ph); mass spectrum, m/e (relative intensity) 785 (2, M^+), 694 (72, $M^+ - NPh$), 561 (100, $M^+ - NPh - Ar$), 431 (15, $Ar_2Ge=NPh$), 356 (12, $Ar_2Ge=O$), 340 (57, Ar_2Ge). Anal. Calcd for $C_{46}H_{57}NOGe_2$: C, 70.36; H, 7.31. Found: C, 70.36; H, 7.41.

(16) Compound **15**: mp 217–218 °C; 1H NMR ($CDCl_3$) δ 0.80 (t, $J = 7$ Hz, 24 H, CH_3), 2.65 (q, $J = 7$ Hz, 8 H, CH_2), 2.80 (q, $J = 7$ Hz, 8 H, CH_2), 6.5–7.4 (m, 17 H, Ar, Ph); mass spectrum, m/e (relative intensity) 801 (11, M^+), 710 (100, $M^+ - NPh$), 668 (67, $M^+ - Ar$). Anal. Calcd for $C_{46}H_{57}NSGe_2$: C, 68.96; H, 7.17. Found: C, 68.88; H, 7.22.

(17) Compound **16**: mp 201–203 °C; 1H NMR ($CDCl_3$) δ 0.80 (t, $J = 7$ Hz, 24 H, CH_3), 2.62 (q, $J = 7$ Hz, 8 H, CH_2), 2.75 (q, $J = 7$ Hz, 8 H, CH_2), 6.5–7.3 (m, 17 H, Ar, Ph); mass spectrum, m/e (relative intensity) 847 (2, M^+), 756 (25, $M^+ - NPh$), 431 (100, $Ar_2Ge=NPh$), 418 (51, $Ar_2Ge=Se$). Anal. Calcd for $C_{46}H_{57}NSeGe_2$: C, 65.14; H, 6.77. Found: C, 65.01; H, 6.84.