mmol) in THF (20 mL) was stirred at ambient temperature for 10 min and then at reflux for 40 min. The progress of the reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95), showing a yellow-green spot, **14**/**15** at R_f 0.10. Chromatography on alumina gel (eluent, ether/hexane, 20/80) yielded dark green crystals, **14**/**15** (0.1368 g, 0.12 mmol, 61%): decomp pt 118–120 °C; ^{13}C NMR (CD_2Cl_2) δ 211 (br, exchanging molybdenum and cobalt carbonyls), 181.8 (ester carbonyl), 141–124 (phenyls and indenyl aromatic CH's), 94.2/93.7 (indenyl C-2), 84.7/84.5, 82.5/82.3 (indenyl C-1, C-3), 75.2 (C-3), 47.6/47.1 (C-4), 41.5/41.1 (C-2), 34.8 (C-6), 32.0 (C-1), 26.0/25.9 (C-8), 25.4 (CH_2P), 23.7 (CH_2As), 23.2 (C-5), 22.3 (C-7), 20.8 (C-10), 16.3 (C-9); ^{31}P NMR (CD_2Cl_2, 300 K) 43.5 and 42.0 ppm; IR (CH_2Cl_2) ν_{CO} 2030 (w), 2010 (m), 1985 (vs), 1975 (vs), 1945 (m), 1910 (m), 1740 (sh), 1720 (s), 1635 (ester) cm^{-1}; FAB mass spectrum, m/z (relative intensity) 1052 (37, $(M - 3CO)^+$), 1024 (100, $(M - 4CO)^+$), 996 (7, $(M - 5CO)^+$), 968 (6, $(M - 6CO)^+$). Anal. Calcd for $C_{53}H_{50}O_8Co_2MoAsP$: C, 56.10; H, 4.44. Found: C, 56.36; H, 4.48.

$CpMoCo_2(CO)_7(P(OMe)_3)CCO_2$(menthyl) (16). A solution of **10** (0.184 g, 0.26 mmol) and trimethyl phosphite (0.032 mL, 0.26 mmol) was stirred together in THF (20 mL) for 47 h at room temperature. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 12/88) showing two spots: dark green **16**, R_f 0.29; green **10**, R_f 0.14. The solvent was removed and the resulting green oil separated by flash chromatography on silica gel (eluent, ether/hexane, 22/78). The product was obtained as a green oil, **16** (0.0836 g, 0.11 mmol, 42%): ^{31}P NMR (CD_2Cl_2, 300 K) 162.4 and 157.4 ppm; IR (CH_2Cl_2) ν_{CO} 2055 (s), 2000 (vs), 1990 (sh), 1970 (sh), 1920 (m), 1865 (m), 1655 (ester) cm^{-1}. The FAB mass spectrum indicates the presence of a very small amount of disubstituted product. FAB mass spectrum: m/z (relative intensity) 797 (12) $(M + 1)^+$), 768 (10, $(M - CO)^+$); 740 (14, $(M - 2CO)^+$); 712 (44, $(M - 3CO)^+$), 684 (71, $(M - 4CO)^+$), 656 (19, $(M - 5CO)^+$), 628 (65, $(M - 6CO)^+$), 600 (25, $(M - 7CO)^+$). $CpMoCo_2(CO)_6(P(OMe)_3)_2CCO_2$(menthyl): FAB mass spectrum, m/z (relative intensity) 836 (5, $(M - 2CO)^+$), 808 (7, $(M - 3CO)^+$), 780 (25, $(M - 4CO)^+$), 752 (4, $(M - 5CO)^+$), 724 (11, $(M - 6CO)^+$).

$CpMoCo_2(CO)_7(P(C_6H_{11})_3)CCO_2$(menthyl) (17). Tricyclohexylphosphine (0.0780 g, 0.28 mmol) and **10** (0.1825 g, 0.26 mmol) were stirred together in THF (20 mL) at ambient temperature for 38 h. The progress of the reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 16/84) showing three spots: yellow-green, **17**, R_f 0.65; UV visible, $P(C_6H_{11})_3$, R_f 0.40; dark green, **10**, R_f 0.25. Flash chromatography on silica (eluent, ether/hexane, 7/93) was used to separate the product from the starting materials. A dark green solid, **17**, was obtained (0.1436 g, 0.15 mmol, 58%): mp 62–64 °C; ^{31}P NMR (CD_2Cl_2, 300 K) 52.0 and 50.9 ppm; IR (CH_2Cl_2) ν_{CO} 2090 (w), 2075 (w), 2050 (s), 2025 (s), 2000 (s), 1970 (m), 1930 (m), 1855 (w), 1725 (sh), 1645 (ester) cm^{-1}; FAB mass spectrum: m/z (relative intensity) 896 (5, $(M - 2CO)^+$), 840 (8, $(M - 4CO)^+$), 784 (71, $(M - 6CO)^+$), 758 (100, $(M - 7CO)^+$, 728 (5, $(M - 5CO - C_6H_{11})^+$), 702 (89, $(M - 6CO - C_6H_{11})^+$), 676 (27, $(M - 7CO - C_6H_{11})^+$), 648 (38, $(M - 5CO - 2C_6H_{11})^+$). Anal. Calcd for $C_{42}H_{57}O_9Co_2MoP$: C, 53.06; H, 6.04. Found: C, 52.94; H, 6.28.

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Registry No. **7**, 117707-13-8; **8**, 117627-32-4; **9a**, 117708-19-7; **9b**, 117627-38-0; **10**, 117707-15-0; **11**, 117627-33-5; **12** (isomer 1), 117627-34-6; **12** (isomer 2), 117707-16-1; **13**, 117627-35-7; **14**, 117627-36-8; **15**, 117707-14-9; **16** (isomer 1), 117627-37-9; **16** (isomer 2), 117707-17-2; **17** (isomer 1), 117627-39-1; **17** (isomer 2), 117707-18-3; $[Mo(CO)_3(i\text{-}PrCp)]_2$, 105046-06-8; $[Mo(CO)_3(C_9H_7)]_2$, 12098-65-6; Co, 7440-48-4; Mo, 7439-98-7; ((+)-methyl)-O_2CCl_3, 117652-31-0; $Co_2(CO)_8$, 10210-68-1; (+)-menthol, 15356-60-2.

Synthesis and Chemistry of Thiagermiranes

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Dimethylgermylene (1) reacts with thioketones **3** and **9** to give 1,3,2,4-dithiadigermolanes **4** and **10**, the ultimate products of formation of thiagermiranes **6** and **11** and subsequent addition of dimethylgermanethione (**7**). Dimesitylgermylene (**16**) reacts with adamantanethione (**3**) to give 3-(2-adamantyl)-2,2-dimesityl-1,2-thiagermirane (**18**). Photolysis of thiagermirane **18** yields dimesitylgermylene (**16**) and adamantanethione (**3**) derived from germathiocarbonyl ylide **22**. Oxidation of thiagermirane **18** by mCPBA gives 3-(2-adamantyl)-4,4-dimesityl-1,2,4-oxathiagermetane *S*-oxide (**27**). X-ray analyses were done for thiagermirane **18** and 1,2,4-oxathiagermetane *S*-oxide **27**.

Introduction

A great deal of attention both experimental and theoretical has been devoted to cyclic compounds containing metal and hetero atoms, most particularly cyclopropane and cyclobutane systems and their derivatives.[2-7] Since the introduction of strained rings into a molecular environment can have a profound efect on the chemistry of the

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[1] (a) The University of Tsukuba. (b) Sankyo Co., Ltd.

[2] (a) Gordon, M. S.; George, C. *J. Am. Chem. Soc.* **1984**, *106*, 609. (b) Grev, R. S.; Schaefer, H. F. *J. Am. Chem. Soc.* **1987**, *109*, 6577.

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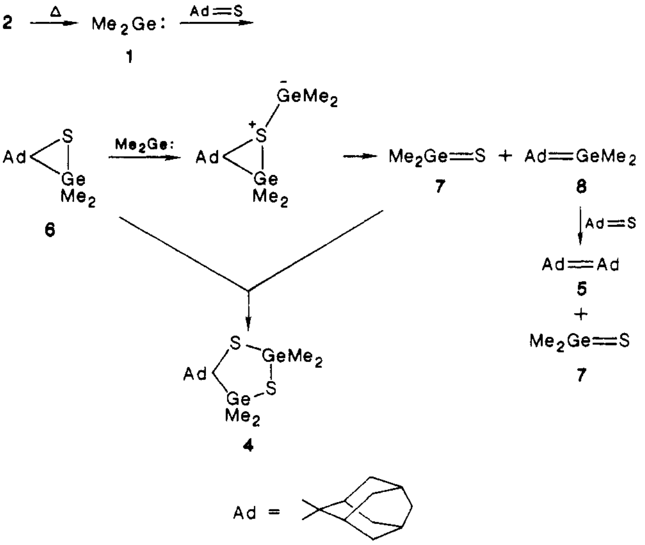
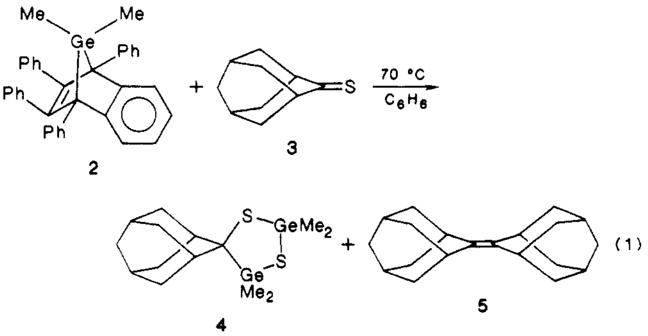
Scheme I



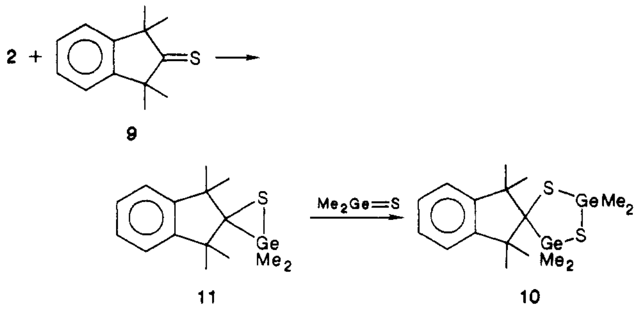
overall system, interest in strained cyclic compounds in which one or more carbons is replaced by metal and hetero atoms is likely to increase. Recently we prepared several strained cyclic molecules containing one or more silicon or germanium atoms with hetero atoms in the ring.[3c,d,5e,6] In this paper, we report the first synthesis of thiagermiranes from the reactions of germylenes with thioketones.

Results and Discussion

Reactions of Dimethylgermylene (1) with Thioketones.[6a] When 7,7-dimethyl-7-germanorbornadiene 2[8] (1 mmol) was decomposed in the presence of adamantanethione (3)[9] (2 mmol) in benzene at 70 °C, a major product was 1,3,2,4-dithiadigermolane 4 (38%), along with adamantylideneadamantane (5)[10] (4%) and 1,2,3,4-tetraphenylnaphthalene (eq 1). Most of this reaction can be explained in quite conventional fashion: dimethylgermylene (1) adds to adamantanethione (3) to form thiagermirane 6, which reacts with another molecule of germylene to eliminate sulfur to form dimethylgermanethione (7). 7 reacts with 6 to give 4 (Scheme I).[11,12] Adamantylideneadamantane (5) is probably derived from pseudo Wittig-type reaction of 3 and germaethene 8.[13]



Scheme II



Scheme III

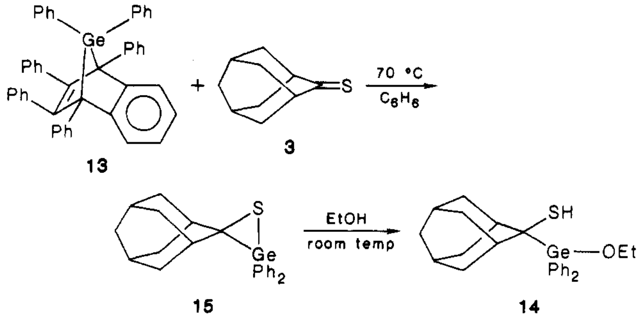
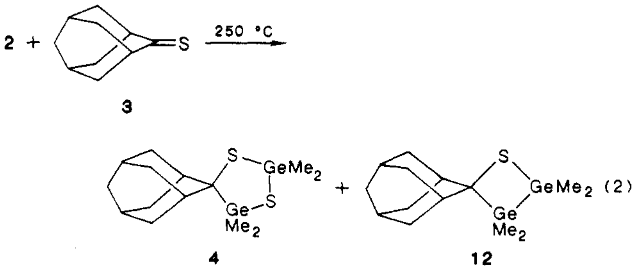


Table I. Yield of the Products in Thermolysis of 3 and 2

mole ratio (3/2)	yield (%)		
	12	4	5
0.46	52	5	
1.2	60	6	
4.4	12	33	5

The results obtained in the reaction of dimethylgermylene (1) with 1,1,3,3-tetramethyl-2-indanthione (9)[14] were similar to those with adamantanethione (3). The main product was 1,3,2,4-dithiadigermolane 10 (11%), presumably derived from the reaction of dimethylgermanethione (7) and thiagermirane 11 (Scheme II).

Although dimethylgermylene (1) gives a significant amount of polymeric products under the reaction conditions,[15] 2 was copyrolyzed with adamantanethione (3) at 250 °C to give 1,2,3-thiadigermetane 12 along with 1,3,2,4-dithiadigermolane 4 (eq 2). The yield of 12 was



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(11) Reaction of thiirane with germylene was reported to yield the similar insertion product: Barrau, J.; Bouchaut, M.; Lavayssiere, H.; Dousse, G.; Satgé, J. *J. Organomet. Chem.* **1983**, *243*, 281.

(12) It is well-known that dimethylgermanethione (7) trimerizes very quickly to $(Me_2GeS)_3$, but we could not detect this trimer.

(13) Barrau, J.; Hamida, N. B.; Satgé, J. *J. Organomet. Chem.* **1985**, *282*, 315.

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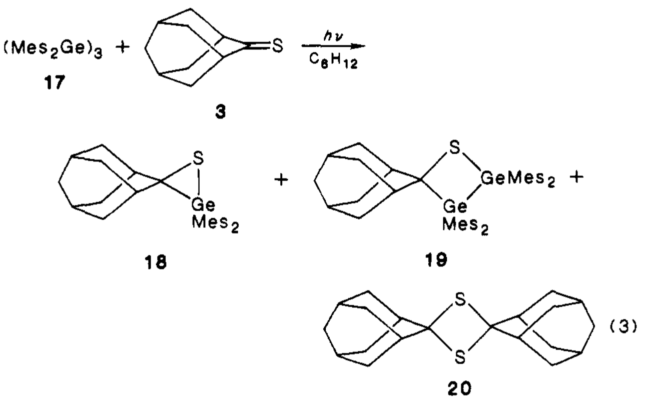
maximum at equal mole ratio of **2** and **3** but decreased with increasing concentration of **3** as shown in Table I. In this system dimethylgermylene (**1**) dimerizes to form tetramethyldigermene which is captured by adamantanethione (**3**) to give **12**. Another conceivable route is germylene insertion into thiagermirane intermediate **6**.[16]

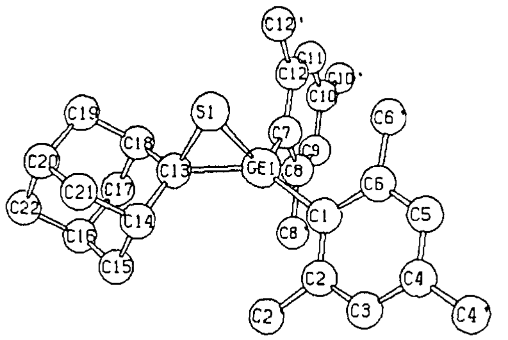
Reactions of Diarylgermylenes with Adamantanethione (3).[6b] Thermolysis of a benzene solution of 7,7-diphenyl-7-germanorbornadiene **13** (0.6 mmol) and adamantanethione (**3**) (2 mmol) at 70 °C gave ethoxygermane **14**, a product of the addition of ethanol to thiagermirane **15** in 50% yield after treatment by ethanol at room temperature (Scheme III). These results suggest that thiagermirane **15** is stable at room temperature in the absence of alcohols. However the isolation of **15** failed probably because it was unstable toward moisture or oxygen.

We next tried the reaction of a bulky substituted germylene: dimesitylgermylene (**16**) with adamantanethione (**3**). When a cyclohexane solution of hexamesitylcyclotrigermane (**17**)[7] (0.4 mmol) and adamantanethione (**3**) (1.2 mmol) in a quartz tube was irradiated at room temperature with a low-pressure mercury lamp for 2.5 h, the major products were 3-(2-adamantyl)-2,2-dimesityl-1,2-thiagermirane (**18**) (53%), 1,2,3-thiadigermetane **19** (11%), adamantanethione dimer **20** (37%), and unreacted **17** (35%) (eq 3). The structure of **18** was confirmed by ^{1}H and ^{13}C NMR and mass spectroscopic analyses and elemental analysis. It is noted that the chemical shift attributed to the ring carbon (56.3 ppm) is similar to that of the corresponding thiasilirane (53.6 ppm). Thiagermirane **18** is stable in an atmosphere containing oxygen or moisture and does not decompose even when heated to its melting point (mp 208–209 °C).

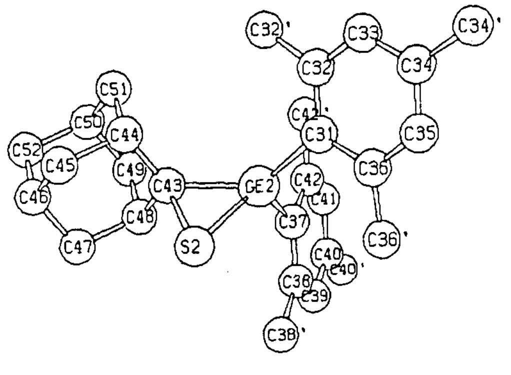


Compound **18** presumably arises from the direct reaction of dimesitylgermylene (**16**) with adamantanethione (**3**). Tetramesityldigermene generated in the photolysis of cyclotrigermane **17** reacted with adamantanethione (**3**) to yield 1,2,3-thiadigermetane **19** as the [2 + 2] addition product. In a separate experiment tetramesityldigermene, prepared from the photolysis of cyclotrigermane **17**, reacted with adamantanethione at room temperature to yield 1,2,3-thiadigermetane **19**.

A single-crystal X-ray diffraction study of **18** confirmed the proposed structure. The asymmetric unit contains two crystallographically independent molecules (molecules A and B), and they were quite similar in conformation, bond angles, and bond lengths. Their molecular structure with atomic labeling schemes are shown in Figure 1.



Molecule A



Molecule B

Figure 1. Molecular conformation and atomic labeling of **18**.

The bond lengths in the three-membered rings are 2.222 (1) Å for Ge–S bonds, 1.973 (5) and 1.970 (5) Å for Ge–C bonds, and 1.880 (5) and 1.877 (5) Å for S–C bonds. The endocyclic bond angles of Ge, C, S are 52.9 (1), 70.4 (1), and 56.8 (1)° for molecule A and 52.8 (1), 70.5 (1), and 56.7 (1)° for molecule B, respectively. The two aryl substituents form dihedral angles of 107.7 (1) and 66.2 (2)° for molecule A and 104.7 (2) and 65.4 (1)° for molecule B with the central thiagermirane ring. The dihedral angles between mesityl rings are 77.3 (2) and 73.1 (2)° for molecules A and B. The independent Ge–C$_{\mathrm{Ar}}$ bond lengths are 1.956 (4) and 1.958 (4) Å for molecule A and 1.954 (5) and 1.969 (5) Å for molecule B. Other bond lengths and significant bond angles for **18** are listed in Tables II and III.

Photolysis and Pyrolysis of Thiagermirane 18. Irradiation of a cyclohexane solution of **18** (0.2 mmol) and 2,3-dimethyl-1,3-butadiene (2 mmol) with a low-pressure mercury lamp at room temperature produced germacyclopentene **21**[17] and adamantanethione dimer **20**, both in 37% yield. Decomposition of **18** at 495 °C under flowing nitrogen yielded **21** (34%) and adamantanethione (**3**) (29%).

Since **21** appears to be derived from the addition of dimesitylgermylene (**16**) to 2,3-dimethyl-1,3-butadiene, it is clear that **18** undergoes cycloelimination on photolysis or pyrolysis to produce dimesitylgermylene (**16**) and adamantanethione (**3**) either via the simultaneous cleavage of both the Ge–C and Ge–S bonds or via the germathiocarbonyl ylide **22** (Scheme IV).

Since the matrix-isolation technique has been used widely for the observation of the reactive species,[18] we tried

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Table II. Bond Lengths (Å) in 18 (Esd's in Parentheses)

molecule A		molecule B	
Ge(1)–S(1)	2.222 (1)	Ge(2)–S(2)	2.222 (1)
Ge(1)–C(1)	1.956 (4)	Ge(2)–C(31)	1.954 (5)
Ge(1)–C(7)	1.958 (4)	Ge(2)–C(37)	1.969 (5)
Ge(1)–C(13)	1.973 (5)	Ge(2)–C(43)	1.970 (5)
S(1)–C(13)	1.880 (5)	S(2)–C(43)	1.877 (5)
C(1)–C(2)	1.387 (6)	C(31)–C(32)	1.395 (7)
C(1)–C(6)	1.425 (7)	C(31)–C(36)	1.430 (7)
C(2)–C(3)	1.385 (6)	C(32)–C(33)	1.372 (7)
C(2)–C(2′)	1.516 (7)	C(32)–C(32′)	1.515 (8)
C(3)–C(4)	1.389 (8)	C(33)–C(34)	1.394 (8)
C(4)–C(5)	1.381 (7)	C(34)–C(35)	1.374 (8)
C(4)–C(4′)	1.522 (7)	C(34)–C(34′)	1.511 (8)
C(5)–C(6)	1.391 (6)	C(35)–C(36)	1.380 (7)
C(6)–C(6′)	1.509 (7)	C(36)–C(36′)	1.504 (7)
C(7)–C(8)	1.409 (7)	C(37)–C(38)	1.385 (7)
C(7)–C(12)	1.407 (6)	C(37)–C(42)	1.414 (7)
C(8)–C(9)	1.403 (7)	C(38)–C(39)	1.397 (8)
C(8)–C(8′)	1.513 (7)	C(38)–C(38′)	1.526 (8)
C(9)–C(10)	1.383 (7)	C(39)–C(40)	1.398 (9)
C(10)–C(11)	1.378 (8)	C(40)–C(41)	1.356 (8)
C(10)–C(10′)	1.522 (8)	C(40)–C(40′)	1.519 (9)
C(11)–C(12)	1.401 (7)	C(41)–C(42)	1.403 (8)
C(12)–C(12′)	1.521 (7)	C(42)–C(42′)	1.510 (8)
C(13)–C(14)	1.523 (7)	C(43)–C(44)	1.509 (7)
C(13)–C(18)	1.523 (6)	C(43)–C(48)	1.529 (7)
C(14)–C(15)	1.553 (8)	C(44)–C(45)	1.537 (8)
C(14)–C(21)	1.545 (8)	C(44)–C(51)	1.540 (8)
C(15)–C(16)	1.525 (7)	C(45)–C(46)	1.519 (8)
C(16)–C(17)	1.527 (8)	C(46)–C(47)	1.522 (8)
C(16)–C(22)	1.526 (8)	C(46)–C(52)	1.544 (9)
C(17)–C(18)	1.533 (7)	C(47)–C(48)	1.550 (8)
C(18)–C(19)	1.539 (8)	C(48)–C(49)	1.545 (8)
C(19)–C(20)	1.547 (8)	C(49)–C(50)	1.517 (9)
C(20)–C(21)	1.535 (7)	C(50)–C(51)	1.531 (8)
C(20)–C(22)	1.527 (8)	C(50)–C(52)	1.532 (9)

Table III. Significant Bond Angles (deg) in 18 (Esd's in Parentheses)

molecule A		molecule B	
S(1)–Ge(1)–C(1)	110.1 (1)	S(2)–Ge(2)–C(31)	112.2 (1)
S(1)–Ge(1)–C(7)	119.1 (1)	S(2)–Ge(2)–C(37)	118.6 (1)
S(1)–Ge(1)–C(13)	52.9 (1)	S(2)–Ge(2)–C(43)	52.8 (1)
C(1)–Ge(1)–C(7)	115.1 (1)	C(31)–Ge(2)–C(37)	115.4 (1)
C(1)–Ge(1)–C(13)	126.2 (1)	C(31)–Ge(2)–C(43)	128.6 (1)
C(7)–Ge(1)–C(13)	116.9 (1)	C(37)–Ge(2)–C(43)	113.4 (1)
Ge(1)–S(1)–C(13)	56.8 (1)	Ge(2)–S(2)–C(43)	56.7 (1)
Ge(1)–C(1)–C(6)	116.7 (2)	Ge(2)–C(31)–C(36)	115.8 (2)
Ge(1)–C(1)–C(2)	124.6 (3)	Ge(2)–C(31)–C(32)	126.3 (3)
C(2)–C(1)–C(6)	118.5 (2)	C(32)–C(31)–C(36)	117.9 (3)
Ge(1)–C(7)–C(8)	115.0 (2)	Ge(2)–C(37)–C(38)	126.7 (2)
Ge(1)–C(7)–C(12)	126.1 (2)	Ge(2)–C(37)–C(42)	114.0 (2)
C(8)–C(7)–C(12)	118.9 (3)	C(38)–C(37)–C(42)	119.2 (2)
C(13)–C(18)–C(17)	109.4 (2)	C(43)–C(48)–C(47)	108.8 (2)
C(13)–C(18)–C(19)	109.1 (2)	C(43)–C(48)–C(49)	109.1 (2)
C(17)–C(18)–C(19)	109.5 (3)	C(47)–C(48)–C(49)	108.6 (3)
Ge(1)–C(13)–C(14)	126.6 (2)	S(2)–C(43)–C(44)	114.8 (1)
Ge(1)–C(13)–C(18)	116.1 (2)	S(2)–C(43)–C(48)	111.5 (2)
S(1)–C(13)–C(14)	113.4 (1)	Ge(2)–C(43)–S(2)	70.5 (1)
S(1)–C(13)–C(18)	112.3 (2)	Ge(2)–C(43)–C(44)	126.4 (2)
Ge(1)–C(13)–S(1)	70.4 (1)	Ge(2)–C(43)–C(48)	115.1 (2)
C(14)–C(13)–C(18)	110.8 (3)	C(44)–C(43)–C(48)	111.3 (3)
C(13)–C(14)–C(15)	110.0 (2)	C(43)–C(44)–C(45)	108.5 (2)
C(13)–C(14)–C(21)	108.0 (2)	C(43)–C(44)–C(51)	109.4 (2)
C(15)–C(14)–C(21)	108.2 (3)	C(45)–C(44)–C(51)	107.9 (3)

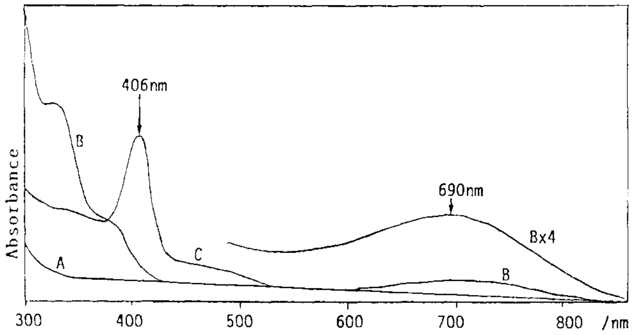
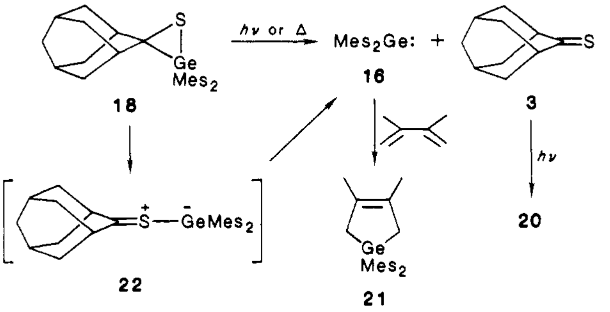
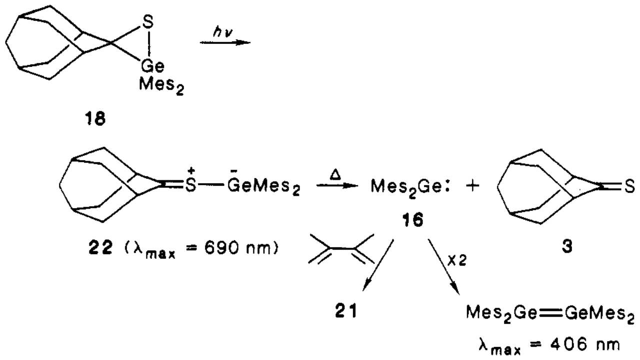


Figure 2. UV–vis spectrum in 3-MP at 77 K: (A) prior photolysis of 18; (B) after photolysis with 254 nm for 30 min, 77 K; (C) after annealing and recooling to 77 K.

Scheme IV



Scheme V



the photochemical decomposition of 18 in a hydrocarbon matrix at 77 K. Irradiation of thiagermirane 18 in 3-methylpentane (3-MP) matrix at 77 K with a low-pressure mercury lamp led to the appearance of a new band at 690 nm in the UV–vis spectrum, and the matrix became blue in color (Figure 2). This absorption band was indefinitely stable at 77 K.

After careful annealing of the matrix and recooling, this band diminished and a new band was formed with λ_{max} at 406 nm, which was assigned to tetramesityldigermene.[19] Complete warming to room temperature resulted in disappearance of this band. Tetramesityldigermene probably reacted with adamantanethione at room temperature to yield 19. In the presence of 2,3-dimethyl-1,3-butadiene in 3-MP glass, melting of the matrix gave addition product 21.

Recently, silacarbonyl or silathiocarbonyl ylides 23 or 24 have been detected spectroscopically from the photolysis of oxasilirane 25 or thiasilirane 26 in a hydrocarbon matrix at 77 K.[20] On the basis of these results, it is quite reasonable to assume that the blue intermediate is most

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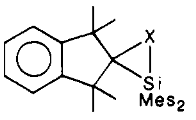
(18) (a) Chapman, O. L. *Pure Appl. Chem.* **1974**, *40*, 511. (b) Dunkin, I. R. *Chem. Soc. Rev.* **1980**, *9*, 1.

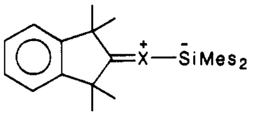
(19) Dimesitylgermylene shows an absorption band at 550 nm in 3-MP matrix at 77 K and dimerizes to tetramesityldigermene (λ_{max} 406 nm at 77 K) on annealing the matrix: Ando, W.; Tsumuraya, T.; Sekiguchi, A. *Chem. Lett.* **1987**, 317.

(20) Ando, W.; Hagiwara, K.; Sekiguchi, A. *Organometallics* **1987**, *6*, 2270.

(21) Gray, M. D. M.; Russel, D. D. R.; Smith, D. J. H.; Durst, T.; Gimbarzevsky, B. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1826.



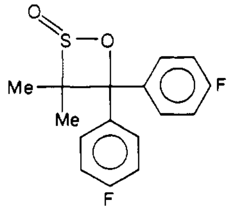
25 (X = O)
26 (X = S)



23 (X = O)
24 (X = S)

probably germathiocarbonyl ylide **22**, which decomposes thermally to dimesitylgermylene (**16**) and adamantanethione (**3**) as shown in Scheme V.

Oxidation of 18 by *m*-Chloroperbenzoic Acid. Thiagermirane **18** is fairly air-stable but is easily oxidized by treatment with *m*-chloroperbenzoic acid (mCPBA). The reaction of **18** with 1 equiv of mCPBA in dichloromethane at 0 °C gave a colorless crystalline compound, 3-(2-adamantyl)-4,4-dimesityl-1,2,4-oxathiagermetane *S*-oxide (**27**), in 50% yield, along with a 50% yield of unreacted **18**. When 2 equiv of mCPBA were used under the same conditions, **18** was completely consumed and quantitative yield of **27** was obtained. **27** was further oxidized by the treatment with mCPBA to afford 3-(2-adamantyl)-4,4-dimesityl-1,2,4-oxathiagermetane *S*,*S*-dioxide (**28**). Although thiagermirane *S*-oxide **29** was not isolated, the formation of compound **27** can be explained by either direct oxidation of **29** or oxidation of its rearrangement product **30** (Scheme VI). The structure of compound **27** was confirmed by an X-ray diffraction study, and the molecular structure with an atomic labeling scheme is shown in Figure 3. The four-membered ring consisting of O1, S, C, and Ge has a puckered structure in which the dihedral angle formed by plane Ge, S, C and plane Ge, S, O1 is 24.3 (3)°. The bond lengths in the four-membered ring are 1.876 (3) Å for the Ge–O1 bond, 2.033 (5) Å for the Ge–C bond, 1.844 (4) Å for the S–C bond, and 1.603 (4) Å for the S–O1 bond. The slightly long Ge–C bond length is probably due to the steric repulsion of bulky adamantyl and mesityl groups. The S–O2 bond length (1.461 (5) Å) is consistent with that of 1,2-oxathietane *S*-oxide **31** (1.466 Å).[21] The endo cyclic bond angles of Ge, S, C, and O1 atoms are 77.9 (1), 90.8 (1), 86.7 (1), and 99.7 (1)°, respectively. Other bond lengths and angles for **27** are listed in Tables IV and V.



31

Experimental Section

General Procedure. All reactions were carried out under an atmosphere of dry argon. The ^{1}H NMR spectra were recorded on Varian EM 360A and JEOL PMX 60 SI spectrometers. ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer. Mass spectra were obtained on a Hitachi RMU-6M mass spectrometer. UV spectra were measured in cyclohexane on a Shimazu UV-365 spectrometer. IR spectra were recorded on a Hitachi 260–50 spectrometer. Preparative HPLC was carried out on a LC–08 (Japan Analytical Ind. Co., Ltd.). Preparative gas chromatographic separations were carried out on a Ohkura gas chromatograph with a 8 mm × 1.5 m glass column of 10% SF-96 on Celite 545. All melting points were uncorrected.

Materials. 2,3-Benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorborna-2,5-diene (**2**) was prepared according to the literature procedures.[8] 2,3-Benzo-1,4,5,6,7,7-hexaphenyl-7-germanorborna-2,5-diene (**13**) was synthesized by the reaction of 1,1,2,3,4,5-hexaphenylgermole and benzyne generated by 1-

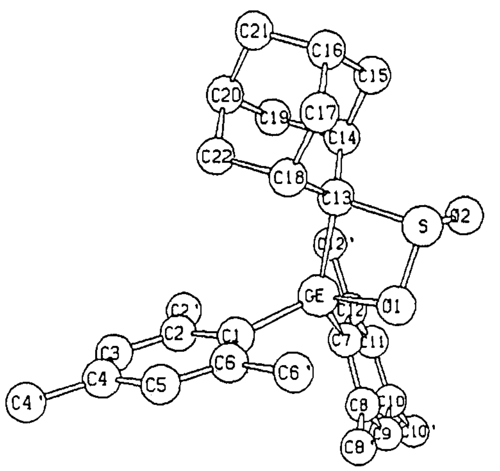


Figure 3. Molecular conformation and atomic labeling of **27**.

Scheme VI

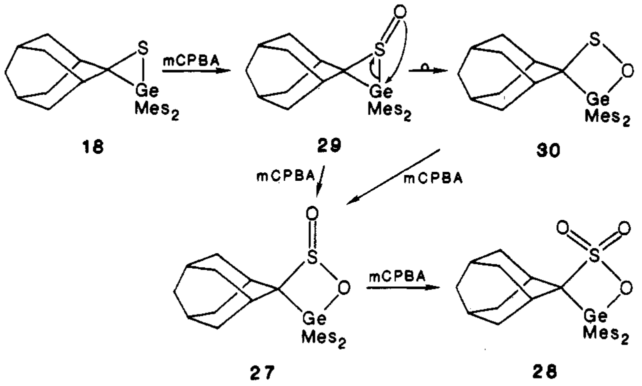


Table IV. Bond Lengths (Å) in 27 (Esd's in Parentheses)

Ge–O(1)	1.876 (3)	C(8)–C(8′)	1.505 (8)
Ge–C(1)	1.959 (5)	C(9)–C(10)	1.399 (9)
Ge–C(7)	1.971 (5)	C(10)–C(11)	1.369 (7)
Ge–C(13)	2.033 (5)	C(10)–C(10′)	1.512 (8)
S–O(1)	1.603 (4)	C(11)–C(12)	1.390 (7)
S–O(2)	1.461 (5)	C(12)–C(12′)	1.513 (7)
S–C(13)	1.844 (4)	C(13)–C(14)	1.542 (8)
C(1)–C(2)	1.405 (7)	C(13)–C(18)	1.551 (7)
C(1)–C(6)	1.427 (8)	C(14)–C(15)	1.531 (8)
C(2)–C(3)	1.390 (7)	C(14)–C(19)	1.537 (7)
C(2)–C(2′)	1.506 (8)	C(15)–C(16)	1.534 (8)
C(3)–C(4)	1.382 (9)	C(16)–C(17)	1.521 (9)
C(4)–C(5)	1.378 (8)	C(16)–C(21)	1.531 (8)
C(4)–C(4′)	1.507 (8)	C(17)–C(18)	1.535 (8)
C(5)–C(6)	1.385 (7)	C(18)–C(22)	1.557 (7)
C(6)–C(6′)	1.513 (7)	C(19)–C(20)	1.526 (8)
C(7)–C(8)	1.395 (7)	C(20)–C(21)	1.534 (9)
C(7)–C(12)	1.398 (8)	C(20)–C(22)	1.530 (9)
C(8)–C(9)	1.399 (7)		

Table V. Significant Bond Angles (deg) in 27 (Esd's in Parentheses)

O(1)–Ge–C(1)	111.3 (1)	Ge–C(7)–C(8)	116.0 (1)
O(1)–Ge–C(7)	102.6 (1)	C(8)–C(7)–C(12)	119.8 (3)
O(1)–Ge–C(13)	77.9 (1)	Ge–C(13)–C(18)	108.5 (3)
C(1)–Ge–C(7)	113.4 (1)	S–C(13)–C(14)	111.6 (3)
C(1)–Ge–C(13)	112.8 (1)	S–C(13)–C(18)	110.3 (1)
C(7)–Ge–C(13)	129.8 (1)	Ge–C(13)–S	86.7 (1)
O(1)–S–O(2)	109.3 (1)	Ge–C(13)–C(14)	128.8 (2)
O(1)–S–C(13)	90.8 (1)	C(14)–C(13)–C(18)	108.6 (3)
O(2)–S–C(13)	105.1 (1)	C(13)–C(14)–C(15)	108.4 (2)
Ge–O(1)–S	99.7 (1)	C(13)–C(14)–C(19)	110.0 (4)
Ge–C(1)–C(2)	117.2 (2)	C(15)–C(14)–C(19)	107.9 (3)
Ge–C(1)–C(6)	123.9 (4)	C(13)–C(18)–C(17)	110.6 (4)
C(2)–C(1)–C(6)	118.6 (5)	C(13)–C(18)–C(22)	109.1 (2)
Ge–C(7)–C(12)	124.1 (3)	C(17)–C(18)–C(22)	108.2 (3)

aminobenzotriazole and $Pb(OAc)_4$.[22] Hexamesitylcyclotrigermane (17) was prepared by reductive coupling of Mes_2GeCl_2 with Mg and $MgBr_2$ in THF as reported previously.[7] Adamantanethione (3)[9] and 1,1,3,3-tetramethyl-2-indanthione (9)[14] were synthesized according to the literature procedures. Benzene, cyclohexane, and 3-methylpentane used as solvents were dried over lithium aluminium hydride and distilled before use. Dichloromethane was dried over calcium chloride and then distilled.

Thermolysis of 2,3-Benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorborna-2,5-diene (2) with Adamantanethione (3). A solution of 2 (535 mg, 1 mmol), 3 (332 mg, 2 mmol), and benzene (7 mL) was heated at 70 °C for 3 h. Separation of the reaction mixture by preparative GLC gave 4 (38%) and 5 (4%). 4: colorless oil; ^1H NMR (CCl_4) δ 0.72 (s, 6 H), 0.82 (s, 6 H), 1.3–2.9 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 5.9 (q), 9.0 (q), 27.1 (d), 27.9 (d), 34.3 (t), 36.7 (d), 36.8 (t), 38.9 (t), 63.4 (s); MS, *m/e* (relative intensity) 404 (22, M^+), 389 (50, $M^+ - 15$), 223 ($M^+ -$ Ad=S $-$ 15), 119 (98, Me_3Ge). HR-MS Calcd for $C_{14}H_{26}S_2{}^{72}Ge^{74}Ge$: 403.9909. Found: 403.9920.

All spectral data obtained for 5 were identical with those of an authentic sample.[10]

Thermolysis of 2 with 1,1,3,3-Tetramethyl-2-indanthione (9). A solution of 2 (535 mg, 1 mmol), 9 (408 mg, 2 mmol), and benzene (7 mL) was heated at 70 °C for 3 h. Separation of the reaction mixture by preparative GLC gave 10 in 11% yield. 10: mp 144.5–145.5 °C; ^1H NMR (CCl_4) δ 0.78 (s, 6 H), 0.92 (s, 6 H), 1.56 (s, 12 H), 7.20 (s, 4 H); MS, *m/e* (relative intensity) 442 (40, M^+), 427 (29, $M^+ - 15$), 255 (21, $M^+ - C_{13}H_{16} - 15$), 238 (43, $M^+ - C_{13}H_{16}S$), 223 (59, $M^+ - C_{13}H_{16}S - 15$), 119 (100, Me_3Ge). Anal. Calcd for $C_{17}H_{28}S_2Ge_2$: C, 46.22; H, 6.38. Found: C, 46.23; H, 6.40.

Flow Pyrolysis of 2 with 3. The pyrolysis apparatus consisted of a 28 cm × 1 cm Pyrex tube packed with Pyrex chips. The upper end of the tube was equipped with a rubber cap for syringe introduction of the sample and a nitrogen inlet. The pyrolysis tube was maintained at 250 °C, and the nitrogen flow was ca. 10 mL/min. The sample was introduced drop by drop using a syringe. The pyrolysates were trapped in a receiver cooled by dry ice–MeOH. A solution of 2 (53.5 mg, 0.1 mmol), 3 (7.6 mg, 0.046 mmol), and benzene (0.7 mL) was pyrolyzed at 250 °C under flowing nitrogen. Separation of the reaction mixture by preparative gas chromatography to give 12 (52%) and 4 (5%). The same reactions were carried out for 2 (0.1 mmol)/3 (0.44 mmol) and 2 (0.1 mmol)/3 (0.12 mmol). 12: colorless oil; ^1H NMR (CCl_4) δ 0.60 (s, 6 H), 0.70 (s, 6 H), 1.2–2.6 (m, 14 H); MS, *m/e* (relative intensity) 372 (16, M^+), 357 (42, $M^+ - 15$), 238 (16, Ad=$GeMe_2$), 223 (14, $M^+ -$ Ad $-$ 15), 206 (9, $Me_2Ge{=}GeMe_2$), 166 (25, Ad=S), 119 (100, Me_3Ge). Elemental analysis could not be achieved since compound 12 rapidly decomposed under air. The reaction of 12 and sulfur in benzene at 80 °C gave 4, an insertion product of sulfur into a Ge–Ge bond of 12.

Thermolysis of 2,3-Benzo-1,4,5,6,7,7-hexaphenyl-7-germanorborna-2,5-diene (13) with Adamantanethione (3). A solution of 13 (395 mg, 0.6 mmol), 3 (332 mg, 2 mmol), and benzene (5 mL) was heated at 70 °C for 3 h. Addition of ethanol at room temperature and separation by preparative HPLC gave colorless crystals of 14 in 50% yield. 14: mp 151–152 °C; ^1H NMR ($CDCl_3$) δ 1.14 (t, 3 H), 1.3–3.2 (m, 14 H), 1.40 (s, 1 H), 3.60 (q, 2 H), 7.6–8.3 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 19.1 (q), 27.1 (d), 27.9 (d), 32.4 (t), 35.9 (t), 37.1 (d), 39.2 (t), 52.0 (s), 61.4 (t), 128.0 (d), 131.2 (d), 134.5 (s), 135.4 (d); MS, *m/e* (relative intensity) 394 (25, $M^+ - EtOH$), 260 (6, $Ph_2Ge{=}S$), 228 (20, Ph_2Ge), 166 (100, Ad=S). Anal. Calcd for $C_{24}H_{30}OSGe$: C, 65.64; H, 6.88. Found: C, 65.42; H, 6.98.

Photolysis of Hexamesitylcyclotrigermane (17) with 3. A solution of 17 (373 mg, 0.4 mmol), 3 (199 mg, 1.2 mmol), and cyclohexane (5 mL) in a quartz tube was irradiated with a low-pressure mercury lamp at room temperature for 2.5 h. The resulting reaction mixture was concentrated and separated by preparative HPLC to give 18 (53%), 19 (11%), 20 (37%), and unreacted 17 (35%). 18; mp 208–209 °C; ^1H NMR ($CDCl_3$) δ 1.5–2.5 (m, 14 H), 2.23 (s, 6 H), 2.60 (s, 12 H), 6.87 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 20.9 (q), 24.5 (q), 27.1 (d), 28.0 (d), 35.6 (t), 38.2 (t), 39.1 (t), 39.1 (d), 56.3 (s), 128.8 (d), 132.5 (s), 139.1 (s), 143.1 (s); MS, *m/e* (relative intensity) 478 (5, M^+), 344 (17, $Mes_2Ge{=}S$), 312 (29, Mes_2Ge), 166 (100, Ad=S). Anal. Calcd for $C_{28}H_{36}SGe$: C, 70.46; H, 7.60. Found: C, 70.67; H, 7.77. 19; mp 187–189 °C; ^1H NMR ($CDCl_3$) δ 1.2–2.0 (m, 14 H), 2.20 (s, 12 H), 2.40 (s, 24 H), 6.80 (s, 8 H); ^{13}C NMR ($CDCl_3$) δ 20.8 (q), 26.0 (q), 27.1 (d), 28.0 (d), 37.1 (t), 38.2 (t), 39.4 (t), 40.0 (d), 66.2 (s), 129.2 (d), 137.1 (s), 137.9 (s), 138.6 (s), 141.5 (s), 143.8 (s), 145.5 (s); MS *m/e* (relative intensity) 431 (21, Mes_3Ge), 334 (9, $Mes_2Ge{=}S$), 312 (100, Mes_2Ge). Anal. Calcd for $C_{46}H_{58}SGe_2$: C, 70.09; H, 7.41. Found: C, 69.98; H, 7.48.

All spectral data obtained for 20[9] and 17[7] were identical with those of authentic samples.

Photolysis of 18 with 2,3-Dimethyl-1,3-butadiene. A solution of 18 (100 mg, 0.2 mmol), 2,3-dimethyl-1,3-butadiene (164 mg, 2 mmol), and cyclohexane (5 mL) was irradiated with a low-pressure mercury lamp at room temperature for 5 h. Separation of the reaction mixture by preparative HPLC gave 21 (39%) and 20 (39%). All spectral data obtained for 21[17] and 20 were identical with those of authentic samples.

Pyrolysis of 18 with 2,3-Dimethyl-1,3-butadiene under Flowing Nitrogen. The pyrolysis was carried out by the same procedure used for flow pyrolysis of 2 and 3. A solution of 18 (47.7 mg, 0.1 mmol), 2,3-dimethyl-1,3-butadiene (410 mg, 5 mmol), and benzene (1 mL) was pyrolyzed at 495 °C under flowing nitrogen. Separation of the reaction mixture by preparative TLC (silica gel, benzene/hexane = 1/3) gave 21 (25%), 3 (21%), and unreacted 18 (27%).

All spectral data obtained for 21, 3, and 18 were identical with those of authentic samples.

Photolysis of 18 in 3-MP Matrix at 77 K. A mixture of 18 (ca. 1 mg) and 3-MP (5 mL) was placed in a quartz UV cell and degassed for several times. The mixture was cooled to 77 K, and the resulting matrix was irradiated with a low-pressure mercury lamp. The UV–vis absorptions were taken at periodic intervals. An absorption band with a maximum at 690 nm appeared and grew on irradiation as shown in Figure 2. On annealing the matrix this band immediately disappeared with concurrent formation of a new band with λ_{max} = 406 nm.

Photolysis of 18 with 2,3-Dimethyl-1,3-butadiene in 3-MP Matrix at 77 K. A mixture of 18 (ca. 5 mg), 2,3-dimethyl-1,3-butadiene (0.5 mg), and 3-MP (5 mL) was placed in a quartz tube and degassed several times. The mixture was irradiated with a low-pressure mercury lamp for 10 min. The matrix turned to blue, and a broad band with λ_{max} = 690 nm was observed. When matrix was warmed to melt, the color disappeared, and 21 was detected by GLC-mass spectrometry.

Oxidation of 18 with mCPBA. To a mixture of 18 (47.7 mg, 0.1 mmol) and dichloromethane (3 mL) was added *m*-chloroperbenzoic acid (mCPBA) (0.1 mmol) at 0 °C. The reaction mixture was separated by preparative HPLC to give 27 (50%) and unreacted 18 (50%). Similar reaction of 18 (47.7 mg, 0.1 mmol) and mCPBA (0.2 mmol) gave quantitative yield of 27. 27 was further oxidized to 28 by the treatment with mCPBA at room temperature. 27: mp 225.5–227 °C; ^1H NMR ($CDCl_3$) δ 1.1–2.1 (m, 12 H), 2.1–2.6 (m, 18 H), 2.6–3.3 (m, 2 H), 6.88 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.0 (q), 23.0 (q), 26.4 (d), 26.8 (d), 30.6 (d), 32.1 (d), 35.0 (t), 35.1 (t), 35.8 (t), 36.0 (t), 36.8 (t), 96.8 (s), 129.0 (d), 129.6 (d), 133.5 (s), 138.8 (s), 140.0 (s), 140.1 (s), 140.8 (s), 142.3 (s); IR ($CDCl_3$) 1120 cm^{-1} (–SO–O–); MS, *m/e* (relative intensity) 446 (14, $M^+ - SO_2$), 312 (100, Mes_2Ge). Anal. Calcd for $C_{28}H_{36}SO_2Ge$: C, 66.04; H, 7.12. Found; C, 66.08; H, 7.29. 28: mp >300 °C; ^1H NMR ($CDCl_3$) δ 1.5–3.0 (m, 14 H), 2.27 (s, 6 H), 2.45 (s, 12 H), 6.90 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.0 (q), 23.3 (q), 26.5 (d), 33.0 (d), 34.6 (t), 37.0 (t), 37.3 (t), 94.9 (s), 129.7 (d), 132.6 (s), 140.8 (s), 142.1 (s); IR ($CDCl_3$) 1305, 1155 cm^{-1} (–SO_2–O–); MS, *m/e* (relative intensity) 526 (10, M^+), 312 (100, Mes_2Ge). Anal. Calcd for $C_{28}H_{36}SO_3Ge$: C, 64.02; H, 6.90. Found: C, 63.77; H, 6.96.

X-ray Crystallography of 18 and 27. Crystals of dimensions 0.4 × 0.4 × 0.15 mm for 18 and 0.4 × 0.3 × 0.2 mm for 27, obtained from hexane, were used for the X-ray analysis. Lattice constants were determined by least-squares fit of angular settings of 20 reflections within range $30 < 2\theta < 50°$. Intensity data were obtained on a Rigaku AFC-5R equipped with graphite-monochromatized Cu Kα radiation and using the θ–2θ scan technique

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[22] Campbell, C. D.; Rees, C. W. *J. Chem. Soc.* **1969**, 742.

Table VI. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($Å^2$) for 18 (Esd's in Parentheses)

atom	x	y	z	B_{eq}
		Molecule A		
Ge(1)	1705.5 (2)	1204.7 (5)	3668.1 (3)	2.79
S(1)	1498 (1)	1654 (1)	2507 (1)	4.32
C(1)	2484 (2)	680 (5)	3892 (2)	2.86
C(2)	2915 (2)	1426 (5)	4214 (3)	3.26
C(3)	3463 (2)	1040 (5)	4254 (3)	3.81
C(4)	3594 (2)	−111 (5)	3996 (3)	4.16
C(5)	3167 (2)	−897 (5)	3713 (3)	3.98
C(6)	2613 (2)	−526 (5)	3659 (3)	3.27
C(2′)	2816 (2)	2682 (5)	4532 (3)	4.16
C(4′)	4198 (2)	−502 (7)	4017 (4)	6.11
C(6′)	2165 (2)	−1420 (5)	3340 (3)	4.18
C(7)	1178 (2)	229 (4)	4128 (2)	2.74
C(8)	1253 (2)	302 (4)	4883 (3)	3.18
C(9)	910 (2)	−393 (5)	5268 (3)	3.79
C(10)	501 (2)	−1168 (5)	4922 (3)	4.07
C(11)	426 (2)	−1229 (5)	4183 (3)	4.04
C(12)	755 (2)	−542 (5)	3776 (3)	3.40
C(8′)	1697 (2)	1107 (5)	5306 (3)	4.35
C(10′)	139 (2)	−1929 (6)	5352 (3)	5.34
C(12′)	634 (2)	−685 (5)	2963 (3)	4.31
C(13)	1436 (2)	2804 (4)	3241 (2)	3.05
C(14)	1780 (2)	3972 (5)	3193 (3)	3.74
C(15)	1742 (2)	4823 (5)	3848 (3)	4.53
C(16)	1134 (2)	5156 (5)	3872 (3)	4.62
C(17)	811 (2)	3961 (5)	3943 (3)	4.25
C(18)	832 (2)	3129 (5)	3288 (3)	3.54
C(19)	580 (2)	3824 (5)	2602 (3)	4.69
C(20)	923 (2)	5017 (5)	2538 (3)	5.00
C(21)	1532 (3)	4678 (5)	2505 (3)	5.15
C(22)	889 (3)	5443 (5)	3188 (3)	5.39
		Molecule B		
Ge(2)	1866.2 (3)	1487.4 (5)	8558.6 (3)	3.47
S(2)	1602 (1)	1142 (1)	7394 (1)	4.48
C(31)	2630 (2)	2104 (5)	8766 (3)	3.54
C(32)	3097 (2)	1428 (5)	9070 (3)	4.18
C(33)	3618 (2)	1954 (5)	9156 (3)	4.64
C(34)	3704 (2)	3170 (6)	8947 (3)	4.80
C(35)	3245 (2)	3840 (5)	8650 (3)	4.34
C(36)	2712 (2)	3361 (5)	8566 (3)	3.67
C(32′)	3049 (3)	108 (5)	9328 (3)	5.57
C(34′)	4276 (3)	3752 (7)	9039 (4)	6.80
C(36′)	2233 (2)	4182 (5)	8263 (3)	4.46
C(37)	1332 (2)	2267 (5)	9111 (3)	3.50
C(38)	864 (2)	2944 (5)	8836 (3)	3.98
C(39)	498 (3)	3355 (6)	9291 (3)	5.20
C(40)	594 (3)	3078 (6)	10025 (3)	5.84
C(41)	1056 (3)	2425 (6)	10294 (3)	5.33
C(42)	1437 (2)	2010 (5)	9855 (3)	4.28
C(38′)	707 (2)	3290 (6)	8046 (3)	4.82
C(40′)	188 (3)	3481 (8)	10520 (4)	8.67
C(42′)	1945 (3)	1294 (7)	10189 (3)	6.12
C(43)	1596 (2)	−83 (5)	8100 (3)	3.45
C(44)	1943 (2)	−1214 (5)	8003 (3)	4.41
C(45)	1668 (3)	−1918 (6)	7333 (3)	5.59
C(46)	1079 (3)	−2303 (6)	7416 (3)	5.32
C(47)	731 (2)	−1160 (5)	7516 (3)	4.76
C(48)	1001 (2)	−440 (5)	8192 (3)	3.94
C(49)	1021 (3)	−1298 (6)	8852 (3)	5.75
C(50)	1356 (3)	−2451 (6)	8743 (3)	6.58
C(51)	1951 (3)	−2078 (5)	8655 (3)	5.85
C(52)	1089 (3)	−3160 (6)	8074 (4)	6.65

($2\theta < 128°$). During data collection three standards, measured before every 200 reflections, indicated no systematic variation of intensity with time. Of 8577 and 4171 independent reflections measured, only 7062 and 3687 for **18** and **27**, respectively, were considered as observed on the basis of the criterion $F_o > 2\sigma(F_o)$. All intensities were corrected for Lorentz and polarization effects but not for absorption.

Crystal data for **18**: $C_{28}H_{36}SGe$; mol wt 477.3; monoclinic; $P2_1/n$; $a = 24.277$ (5) Å, $b = 10.789$ (1) Å, $c = 18.832$ (2) Å, $\beta = 98.70$ (1)°; $U = 4875.9$ Å^3; $Z = 8$; $\rho = 1.30$ g cm^{-3}; μ(Cu K$_\alpha$) = 27 cm^{-1}; $F(000) = 2016$; $T = 297$ K.

Table VII. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($Å^2$) for 27 (Esd's in Parentheses)

atom	x	y	z	B_{eq}
Ge	228 (1)	6235.6 (2)	7405 (1)	2.76
S	−1142 (2)	5862 (1)	4960 (2)	2.92
O(1)	−1286 (4)	5796 (1)	6438 (4)	2.73
O(2)	−2183 (5)	6245 (2)	4256 (4)	4.79
C(1)	1743 (6)	5939 (2)	8993 (5)	2.25
C(2)	2913 (6)	6234 (2)	9837 (5)	2.78
C(3)	4140 (7)	6038 (2)	10879 (6)	3.02
C(4)	4239 (7)	5553 (2)	11121 (6)	3.42
C(5)	3063 (7)	5266 (2)	10321 (6)	3.18
C(6)	1821 (6)	5439 (2)	9256 (5)	2.48
C(7)	−1047 (6)	6734 (2)	7868 (6)	2.48
C(8)	−1992 (7)	6586 (2)	8613 (6)	3.10
C(9)	−3031 (7)	6909 (2)	8881 (6)	3.54
C(10)	−3123 (7)	7381 (2)	8428 (7)	3.77
C(11)	−2147 (7)	7519 (2)	7733 (6)	3.63
C(12)	−1108 (7)	7208 (2)	7435 (6)	3.04
C(13)	792 (6)	6145 (2)	5691 (5)	2.31
C(14)	1078 (7)	6527 (2)	4737 (6)	3.24
C(15)	1078 (8)	6283 (2)	3427 (6)	4.41
C(16)	2370 (8)	5906 (2)	3694 (6)	4.36
C(17)	2105 (7)	5529 (2)	4644 (6)	3.42
C(18)	2107 (7)	5766 (2)	5969 (6)	2.86
C(19)	2691 (8)	6758 (2)	5385 (7)	4.45
C(20)	3995 (8)	6388 (2)	5661 (7)	4.32
C(21)	3963 (8)	6144 (3)	4339 (7)	5.12
C(22)	3720 (7)	6012 (2)	6620 (6)	3.52
C(2′)	2872 (7)	6767 (2)	9647 (7)	3.64
C(4′)	5572 (8)	5342 (3)	12252 (7)	5.05
C(6′)	610 (7)	5084 (2)	8462 (6)	3.28
C(8′)	−1979 (8)	6087 (2)	9146 (7)	4.39
C(10′)	−4270 (8)	7723 (2)	8714 (8)	5.74
C(12′)	−63 (8)	7399 (2)	6680 (7)	4.35

Crystal data for **27**: $C_{28}H_{36}O_2SGe$; mol wt 509.3; monoclinic, $P2_1/c$; $a = 9.040$ (1) Å, $b = 28.061$ (3) Å, $c = 10.454$ (1) Å, $\beta = 109.02$ (1)°; $U = 2507.0$ Å^3; $Z = 4$; $\rho = 1.35$ g cm^{-3}; μ(Cu K$_\alpha$) = 27 cm^{-1}; $F(000) = 1072$; $T = 297$ K.

Both structures **18** and **27** were solved by MULTAN84[23] and refined by block-diagonal least-squares methods. Positions of the hydrogen atoms were estimated from standard geometry. The final refinements with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms lowered R values to 0.056 ($R_w = 0.063$, $W = 1/\sigma^2(F_o)$) and 0.061 ($R_w = 0.056$, $w = 1/\sigma^2(F_o)$), for **18** and **27**, respectively. The goodness of fit values were 3.45 and 2.32, and maximum and minimum heights in the final difference Fourier syntheses were +0.2, −0.2 and +0.2, −0.3 e Å^{-3} for **18** and **27**, respectively. The maximum and average shifts in the final cycle of refinements were 0.33, 0.05 and 0.21, 0.03 of the corresponding standard deviations for **18** and **27**, respectively. The molecular structures with atomic labeling schemes, the bond lengths, the selected bond angles, and atomic coordinates for the non-hydrogen atoms are given in Figure 1 and Tables II, III, and VI for **18** and in Figure 3 and Tables IV, V, and VII for **27**, respectively.

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Supplementary Material Available: Tables of bond angles, anisotropic thermal factors, and H-atom parameters for **18** and **27** (7 pages); listings of structure factors (43 pages). Ordering information is given on any current masthead page.

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(23) Main, P.; Germain, G.; Woolfson, M. M. MULTAN84: A System of Computer Programs for the Automatic Data; Universities of York: York, England, and Louvain: Louvain Belgium, 1984.