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(2+1) CYCLOADDITION OF CHLORO(PHENYLTHIO)CARBENE TO VINYL SILANES. A FACILE SYNTHESIS OF HIGHLY FUNCTIONALIZED CYCLOPROPANES

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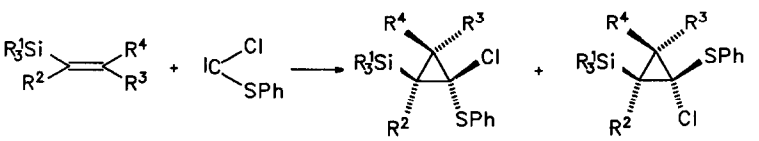
Abstract - Vinylsilanes **1d-h** react with chloro(phenylthio)carbene **2** to give functionalized silylcyclopropanes **3** with high *Z*-stereoselectivity. For **3g**, the relative configuration was proven by an X-ray structural analysis. Synthetic modifications of **3** include elimination, oxidation, and substitution to give products **5**, **6**, and **7a-f**, respectively.

Silylcyclopropanes are receiving increasing interest as synthetic building-blocks.[1] Obviously, additional functionality on the cyclopropane ring would further enhance the utility of these compounds. In this respect, a sulfide group seems particularly promising as it provides a flexible handle for subsequent synthetic elaboration.[2] A (2+1) cycloaddition between a vinylsilane **1** and a sulfur-substituted carbene should be a convenient route to these target molecules. However, phenylthio[3] and bis(phenylthio)carbene[4] are known to be only moderately reactive. Therefore we focused our attention on chloro(phenylthio)carbene **2**. This species[5,6], as well as the corresponding methylthio compound[7], gives a smooth (2+1) cycloaddition to various C=C systems.

(2+1) Cycloadditions

Chloro(phenylthio)carbene **2** was generated from dichloromethyl(phenyl)sulfide under phase-transfer conditions using a modification of Makosza's procedure.[6] The (2+1) cycloaddition to vinylsilanes **1** yielding cyclopropanes **3** (Scheme 1) occurs with variable efficiency. Good yields in the 60% range are obtained starting from 2-silylpropene **1d** and silylstyrenes **1g,h**. However, yields are lower for **3e** and



1 **2** ***Z*-3** ***E*-3**

1, 3a: R^1 = Me, R^2 = R^3 = R^4 = H
b: R^1 = Et, R^2 = R^3 = R^4 = H
c: R^1_3Si = *t*BuMe$_2$Si, R^2 = R^3 = R^4 = H
d: R^1 = Me, R^2 = Me, R^3 = R^4 = H
e: R^1 = Me, R^2 = R^4 = H, R^3 = Me
f: R^1 = Me, R^2 = R^3 = H, R^4 = Me
g: R^1 = Me, R^2 = Ph, R^3 = R^4 = H
h: R^1 = Me, R^2 = R^4 = H, R^3 = Ph
i: R^1 = Me, R^2 = R^3 = H, R^4 = Ph
j: R^1 = Me, R^2 + R^3 = $(CH_2)_4$, R^4 = H

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Scheme 1.

particularly **3f** and the approach fails to provide silylcyclopropanes **3a–c,i,j.** Some trisubstituted cyclopropane **3a** could be detected in the reaction mixture by ^{1}H NMR spectroscopy, but the compound decomposed on attempted isolation by chromatography. Similarly, the low yields of **3e,f** are due to limited stability of the products under the strongly basic conditions of synthesis. In contrast, vinylsilanes **1b,c** give no cycloadduct **3** with carbene **2** obviously for steric reasons. Also the failure of **1i** to react with **2** appears to be a consequence of steric screening, here by a perpendicular arrangement of the phenyl substituent to the plane of the C=C bond. For **1j**, trisubstitution of the C=C bond makes the cycloaddition sterically impossible.

Vinylsilanes **1e,f,h** were employed as pure stereoisomers and, as expected for a concerted (2+1) cycloaddition, the relative orientation of the substituents is maintained in the corresponding cycloadducts **3**. However, for **3d,h** the ^{1}H NMR spectra reveal the presence of two diastereomers *Z*-**3** and *E*-**3**, i. e. of epimers at the chlorine-substituted carbon. Because of the bulky silyl residue, a *cis*-arrangement of this group and the chlorine substituent should be favored and leads to the assigment of the preponderant isomers *as Z*-**3d** (84%) and *Z*-**3h** (94%), respectively. Products **3e–g** are isolated as pure diastereomers; assuming that 5% of the other isomer could be detected by ^{1}H NMR, the diastereoselectivity of the cycloaddition is at least 95%.

The assumption that *Z*-**3** is the favored isomer is confirmed by the X-ray structural analysis of **3g** (Fig. 1, Table 1). A striking feature of the structure is the comparatively long Si - cyclopropane bond of 190.5 pm which may be due to steric effects. An inspection of the other bond lengths (Table 1) reveals only minor differences from related other molecules.[8]

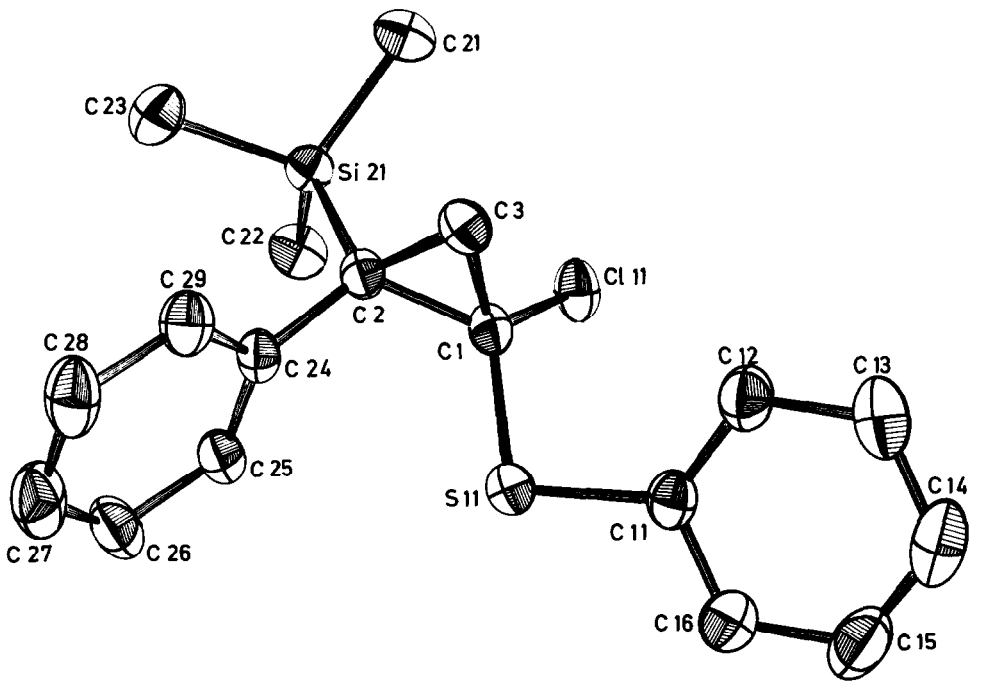


Fig. 1. ORTEP presentation of the molecular structure of **3g** showing 50% ellipsoids.

Table 1. Bond lengths [pm] and angles [°] with least-squares estimated standard deviations in parentheses for non-hydrogen atoms in **3g**. For numbering of atoms see Fig. 1

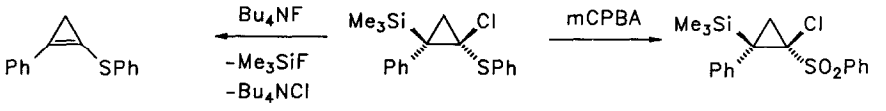
Bond lengths [pm]		Bond angles [°]	
Cl11 - C1	178.9(3)	C1 - S11 - C11	103.8(1)
S11 - C1	177.3(3)	C2 - Si21 - C21	112.4(2)
S11 - C11	176.8(3)	C2 - Si21 - C22	110.1(2)
Si21 - C2	**190.5(3)**	C2 - Si21 - C23	105.5(2)
Si21 - C21	185.8(3)	C21 - Si21 - C22	111.4(2)
Si21 - C22	185.7(3)	C21 - Si21 - C23	108.3(2)
Si21 - C23	186.2(4)	C22 - Si21 - C23	108.8(2)
C1 - C2	**151.2(3)**	Cl11 - C1 - S11	113.1(1)
C1 - C3	**148.4(4)**	Cl11 - C1 - C2	117.8(2)
C2 - C3	**151.3(3)**	Cl11 - C1 - C2	117.7(2)
C2 - C24	150.2(3)	S11 - C1 - C2	117.6(2)
C11 - C12	137.3(4)	S11 - C1 - C3	120.5(2)
C11 - C16	138.0(4)	**C2 - C1 - C3**	**60.6(2)**
C12 - C13	139.1(4)	Si21 - C2 - C1	121.7(2)
C13 - C14	137.0(6)	Si21 - C2 - C3	118.6(2)
C14 - C15	135.0(6)	Si21 - C2 - C24	111.5(2)
C15 - C16	138.2(5)	**C1 - C2 - C3**	**58.8(2)**
C24 - C25	138.5(4)	C1 - C2 - C24	117.8(2)
C24 - C29	138.3(4)	C3 - C2 - C24	119.2(2)
C25 - C26	138.4(4)	**C1 - C3 - C2**	**60.6(2)**
C26 - C27	137.5(5)	S11 - C11 - C12	124.8(2)
C27 - C28	137.0(5)	S11 - C11 - C16	116.1(2)
C28 - C29	138.7(4)	C12 - C12 - C16	119.0(3)
		C11 - C12 - C13	119.8(3)
		C12 - C13 - C14	120.4(4)
		C13 - C14 - C15	119.8(4)
		C14 - C15 - C16	120.6(4)
		C11 - C16 - C15	120.4(4)
		C2 - C24 - C25	120.1(2)
		C2 - C24 - C29	121.1(2)
		C25 - C24 - C29	118.6(3)
		C24 - C25 - C26	120.8(3)
		C25 - C26 - C27	119.8(3)
		C26 - C27 - C28	120.3(3)
		C27 - C28 - C29	119.9(3)
		C24 - C29 - C28	120.7(3)

Interestingly, allyl(trimethyl)silane also gives a smooth reaction with carbene **2** to yield cyclopropane **4** as a mixture of stereoisomers.

Synthetic Modifications of Cyclopropanes 3

Preliminary experiments prove that the vicinal substitution of **3** by silicon and sulfur allows various synthetic transformations. Thus, tetrabutylammonium fluoride induces a clean and smooth elimination in **3g** to give cyclopropenylsulfide **5** (Scheme 2). The ß-elimination of the elements of trimethylsilyl halide by fluoride had previously been carried out for 1,1-dihalo-2-silyl-substituted cyclopropanes,[9] where information on the stereochemistry of the halodesilylation is not accessible. In contrast, based on the known *Z*-configuration of **3g** (Fig. 1), the reaction to give **5** is a formal *cis*-elimination. However, the

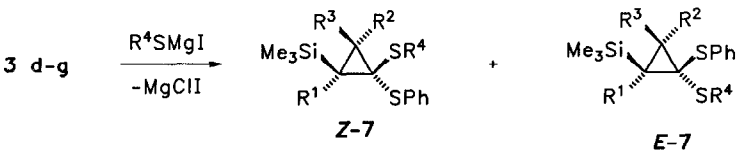
available evidence does not yet allow differentiation between an E1cB mechanism and a concerted E2 elimination. In any case, the reaction of **3** to give cyclopropene **5** provides a convenient access to this interesting class of reactive vinyl sulfides.[10]



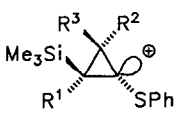
5 **3g** **6**

Scheme 2.

Nucleophilic substitution reactions on cyclopropanes are notoriously difficult, though a sulfur residue in the geminal position to the leaving-group facilitates the process.[5b,11a] However, additional substituents on the three-membered ring favor ring-opening on attempted S_N reactions[11b] and thiolate nucleophiles give competing redox reactions.[11c] Contrary to these reports, we observed a clean displacement of the chlorine in **3** by thiophenolate (Scheme 3) with (phenylthio)magnesium iodide in ether. The presence of a silyl group on the neighboring carbon apparently favors the displacement reaction.[12] Taken together, the experimental evidence points toward an S_N1 mechanism, where the positive charge in the intermediate is efficiently stabilized by the donor effect of the sulfur and by the well-established ß-effect[13] of the silicon.



7a: R^1 = Me, R^2 = R^3 = H, R^4 = Ph
b: R^1 = R^3 = H, R^2 = Me, R^4 = Ph
c: R^1 = R^2 = H, R^3 = Me, R^4 = Ph
d: R^1 = R^4 = Ph, R^2 = R^3 = H
e: R^1 = R^3 = H, R^2 = R^4 = Ph
***E/Z*-7f**: R^1 = Ph, R^2 = R^3 = H, R^4 = 4-MeC_6H_4



8

Scheme 3.

In order to gain some insight into the stereochemistry of the displacement, we looked at the reaction of ***Z*-3g** with 4-(methyl)thiophenolate as nucleophile. Here, a 2:1 mixture of the diastereomers of **7f** results. These isomers could not be separated by chromatography, and spectroscopic methods do not allow unambiguous assigment of configuration. However, the formation of diastereomers in unequal quantitity can be understood in terms of a non-planar arrangement of substituents around the cationic carbon in the intemediate.[5b] Thus, the most favorable conformation of the cation should be **8** with the phenylthio substituent being bent away from the voluminous silyl group. On the other hand, attack of the incoming nucleophile on the face of the silyl residue will be sterically hindered in **8**, but will be comparatively easy in the epimeric cation. In conclusion, the stereochemical evidence is in line with the assumed S_N1 mechanism for the displacement of chlorine in **3** to give **7**.

The transformation of 2-chloro-substituted silylcyclopropanes into thioacetals **7** represents a novel route to the latter which are usually made via a ring-closure method.[14] The present approach is particularly interesting for examples with an additional 3-substituent as this substitution pattern is not accessible in a sequence of nucleophilic addition/elimination.[15] Thus, the two methods nicely complement one another.

In another modification of silylcyclopropanes **3**, we looked at the possibility to oxidize the sulfide group in order to increase its electron-withdrawing effect. In fact, treatment of **3g** with two equivalents of *m*-chloroperbenzoic acid smoothly yields sulfone **6**. Interestingly, the silyl substituent is not affected by the reaction.

Further transformations of cyclopropanes **3** as well as the chemistry of **5–7** are presently under study.[16]

Acknowledgement - We are grateful for support of this work by Fonds der Chemischen Industrie, Frankfurt.

Experimental

M.ps were determined with a Leitz hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 297 spectrometer in KBr unless otherwise noted. ^{1}H NMR spectra were measured on a Varian T60, Bruker WH-270, or WM-400 spectrometer, and ^{13}C NMR spectra with a Bruker WM-400 instrument, using TMS as an internal standard in all NMR experiments and $CDCl_3$ as solvent unless otherwise noted; the symbols given in parentheses with ^{13}C chemical shifts designate primary or tertiary (+), secondary (-), and quaternary carbon atoms (o), respectively, as indicated by the DEPT method. Mass spectra were obtained on a Varian CH 7 mass spectrometer.

Cyclopropanes **3d–f**, **4** *from Vinylsilanes* **1d–f** *or an Allylsilane.* To a *vigorously* stirred emulsion of vinylsilane **1d**, **e**, or **f** or of allyl(trimethyl)silane (80.0 mmol), sodium hydroxide (13.0g, 325 mmol), water (75 ml), dichloromethane (75 ml), and cetrimide (250 mg), a soln of dichloromethyl phenyl sulfide (7.72 g, 40 mmol) in dichloromethane (25 ml) was added dropwise at 55–60°C over a period of 20 min. Stirring was continued for 15 min and the reaction mixture allowed to cool to room temp. Then the mixture was extracted with water six to eight times, dried (Na_2SO_4) and concentrated. Distillation *in vacuuo* provided products **3d–f**, **4**. Starting from **1a**, a complex mixture of products was isolated, whereas vinylsilanes **1b,c,j** were recovered unchanged under these conditions.

E/Z-1-Chloro-2-methyl-2-trimethylsilyl-cyclopropyl phenyl sulfide (**3d**): Bp. 95°C/0.25 mmHg; yield 63%; IR (film): 1250 ($SiMe_3$), 840 ($SiMe_3$); ^{1}H-NMR (Z/E = 5.4), ***E*-3d**: 0.16 (s, 9 H, $SiMe_3$), 1.21 (d, *J* = 5.4 Hz, 1H, cyclopropyl), 1.42 (s, 3 H, CH_3), 1.43 (d, *J* = 5.4 Hz, 1H, cyclopropyl); 7.15 - 7.6 (m, br, 5 H, aryl-H); ***Z*-3d**: 0.22 (s, 9 H, $SiMe_3$), 1.14 (d, *J* = 5.4 Hz, 1 H, cyclopropyl), 1.33 (s, 3 H, CH_3), 1.60 (d, *J* = 5.4 Hz, 1 H, cyclopropyl), 7.15 - 7.6 (m, br, 5 H, aryl-H); ^{13}C-NMR, **Z-3d**: -0.96 (+), 20.00 (+), 22.74 (o), 29.29 (-), 57.46 (o), 126.23 (+), 128.14 (+), 128.75 (+), 135.2 (o).

Anal. for $C_{13}H_{19}ClSSi$ (270.9): Calcd C 57.64 H 7.07 Cl 13.09 S 11.84
Found C 57.42 H 6.85 Cl 12.81 S 11.65

r-1-Chloro-t-3-methyl-c-2-trimethylsilyl-cyclopropyl phenyl sulfide (**Z-3e**): Bp. 100°C/0.3 mmHg; yield 31%; IR (film): 1240 ($SiMe_3$), 835 ($SiMe_3$); ^{1}H-NMR: 0.14 (s, 9 H, $SiMe_3$), 0.27 (d, *J* = 9.4 Hz, 1 H, cyclopropyl), 1.38 (d, *J* = 6.2 Hz, CH_3), 1.78 (d+q, *J* = 6.2 Hz, *J* = 9.4 Hz, 1 H, cyclopropyl), 7.2 - 7.9 (m, br, 5 H, aryl-H); ^{13}C-NMR: -0.92 (+), 16.77 (+), 26.98 (+), 31.0 (+), 58.21 (o), 126.59 (+), 128.77 (+), 129.20 (+), 134.9 (o).

Anal. for $C_{13}H_{19}ClSSi$ (270.9): Calcd C 57.64 H 7.07 Cl 13.09 S 11.84
Found C 56.44 H 6.92 Cl - S 11.88

r-1-Chloro-c-3-methyl-c-2-trimethylsilyl-cyclopropyl phenyl sulfide (***Z*-3f**): Bp. 92°C/0.15 mmHg; yield 18%; IR (film): 1240 ($SiMe_3$), 840 ($SiMe_3$); ^{1}H-NMR: 0.11 (s, 9 H, $SiMe_3$), 0.70 (d, *J* = 12 Hz, 1 H, cyclopropyl), 1.38 (d, *J* = 6.4 Hz, 3 H, CH_3), 1.87 (d+q, *J* = 6.4 Hz, *J* = 12 Hz, 1 H, cyclopropyl), 7.2 - 7.6 (m, br, 5 H, aryl-H); ^{13}C-NMR: 0.34 (+), 13.66 (+), 25.04 (+), 29.08 (+), 58.90 (o), 127.15 (+), 128.05 (+), 130.2 (+), 134.99 (o).

Anal. for $C_{13}H_{19}ClSSi$ (270.9): Calcd C 57.64 H 7.07 Cl 13.09 S 11.84
Found C 56.62 H 6.78 Cl 14.10 S 11.98

(E/Z)-1-Chloro-2-(trimethylsilylmethyl)cyclopropyl phenyl sulfide (**4**): B.p. 100°C/0.1 mmHg; yield 55%; IR (film): 1240, 835 cm^{-1}; ^{1}H-NMR (*E/Z* = 4.0), ***Z*-4**: 0.1 (s, 9H, $SiMe_3$), 0.63 (dd, *J* = 14.5 Hz, *J* =

Hz, 1H, Me_3SiCH_2), 0.98 (dd, J = 7.4 Hz, J = 5.8 Hz, 1H, cyclopropyl), 1.20 (dd, J = 14.5 Hz, J = 4.0 Hz, 1H, Me_3SiCH_2), 1.72 (dd, J = 9.7 Hz, J = 5.8 Hz, 1H, cyclopropyl), 1.86 (dddd, J = 11 Hz, J = 9.7 Hz, J = 7.4 Hz, J = 4.0 Hz, 1H, cyclopropyl), 7.2-7.6 (m, br, 5H, phenyl-H); *E*-**4**: 0.1 (s, 9H, $SiMe_3$), 0.72 (dd, 1H), 1.04 (m, 1H), 1.09 (m, 1H), 1.56 (m, 2H), 7.2-7.6 (m, br, 5H, phenyl-H); ^{13}C-NMR (*Z*-**4**): -1.43 (+), 18.11 (-), 27.78 (-), 29.83 (+), 52.10 (o), 126.44 (+), 128.74 (+), 128.87 (+), 134.91 (o); (*E*-**4**): -1.47 (+), 18.28 (-), 27.46 (-), 27.86 (+), 53.26 (o), 126.82 (+), 129.20 (+), 129.33 (+), 137.26 (o).

Anal. for $C_{13}H_{19}ClSSi$ (270.9): Calcd C 57.64 H 7.07 Cl 13.09 S 11.84
Found C 56.97 H 6.85 Cl 12.93 S 11.97

Cyclopropanes **3g,h** *from Vinylsilanes* **1g,h**. To a *vigorously* stirred emulsion of vinylsilane **1g** or **h** (110.0 mmol), sodium hydroxide (16.0g, 400 mmol), water (100 ml), dichloromethane (100 ml), and cetrimide (300 mg) a soln of dichloromethyl(phenyl)sulfide (19.3g, 100 mmol) in dichloromethane (100 ml) was added dropwise at 55-60°C over a period of 1.5 hrs. Stirring was continued for 1.5 hrs and the reaction mixture allowed to cool to room temp. Subsequent work-up followed the procedure given above except for the final purification steps: removal of unreacted starting-material by Kugelrohr distillation at 55-60°C/0.0006 mmHg and subsequent recrystallization of the residue from ether. Starting from **1i**, no reaction was observed.

Z-1-Chloro-2-phenyl-2-trimethylsilyl-cyclopropyl phenyl sulfide (**3g**): Mp. 87°C; yield 64%; IR: 1245 ($SiMe_3$), 850 ($SiMe_3$). ^{1}H-NMR: 0.20 (s, 9 H, $SiMe_3$), 2.04 (d, J = 5 Hz, 1 H, cyclopropyl), 2.14 (d, J = 5 Hz, 1 H, cyclopropyl), 7.10 - 7.8 (m, br, 10 H, aryl-H); ^{13}C-NMR: -0.86 (+), 31.19 (-), 34.06 (o), 57.18 (o), 126.11 (+), 126.91 (+), 127.79 (+), 127.86 (+), 128.70 (+), 129.29 (+), 130.25 (+), 134.64 (o), 141.33 (o).

Anal. for $C_{18}H_{21}ClSSi$ (332.96): Calcd C 64.93 H 6.36 Cl 10.65 S 9.63
Found C 64.88 H 6.31 Cl 10.70 S 9.74

r-1-Chloro-c/t-3-phenyl-2-trimethylsilyl-cyclopropyl phenyl sulfide (**3h**): M.p. 86-87°C; yield 60%; IR: 1240 ($SiMe_3$), 850, 840 ($SiMe_3$); ^{1}H-NMR (*Z/E*) = 17), *E*-**3h**: 0.3 (s, 9 H, $SiMe_3$), 1.41 (d, J = 10 Hz, 1 H, cyclopropyl), 2.73 (d, J = 10 Hz, 1 H, cyclopropyl), 7.2 - 7.5 (m, br, 10 H, aryl-H), *Z*-**3h**: 0.25 (s, 9 H, $SiMe_3$), 1.27 (d, J = 10 Hz, 1 H, cyclopropyl), 3.03 (d, J = 10 Hz, 1 H, cyclopropyl), 7.2 - 7.5 (m, br, 10 H, aryl-H); ^{13}C-NMR, *Z*-**3h**: -1.03 (+), 25.76 (+), 40.29 (+), 59.36 (o), 127.18 (+), 127.28 (+), 128.0 (+), 128.58 (+), 128.66 (+), 130.93 (+), 133.91 (o), 136.44 (o).

Anal. for $C_{18}H_{21}ClSSi$ (332.96): Calcd C 64.93 H 6.36 Cl 10.65 S 9.63
Found C 64.80 H 6.36 Cl 10.66 S 9.56

X-ray structural analysis. Appropriate crystals of **3g** were obtained by recrystallization from diethyl ether. Rotating-crystal, Weissenberg and precession photographs gave approximate lattice constants and suggested space group $P2_1/c$. Refinement of the lattice constants led to the following cell dimensions:

a = 1894.4(2) ppm	V = $1.809 \cdot 10^9$ pm^3
b = 777.1(1) pm	Z = 4
c = 1233.9(1) pm	d_{calc} = 1.22 g · cm^{-3}
ß = 95.28(1)°	

Intensity data were collected on a CAD4-SDP single-crystal diffractometer using CuK_α radiation. The final refinement was based on 2782 symmetry-independent reflexions with $I > 3\sigma$. The structure was solved by the direct-methods program MULTAN.[17] The *E* map revealed the positions of all the heavy atoms. After the refinement of these positions, the H atoms were found from a difference Fourier synthesis.[18] Convergence was achieved at R 0.033 (R_w 0.032). Fractional atomic coordinates, tables of bond lengths and angles as well as of anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

Elimination reaction of **3g** *to give* **5**. To a soln of **3g** (0.66g, 2.0 mmol) in THF (15 ml) tetrabutylammonium fluoride (2.0 mmol) in THF (6 ml) was added dropwise at -20°C during 20 min. Subsequently, the mixture was stirred at room temp. for 15 min and extracted eight times with pentane-water (1:1). After drying the organic phase (Na_2SO_4), the mixture was stirred twice with 5 g each of neutral alumina. THF was removed at 0°C/0.01 mmHg. The residual oil of **5** could be studied

immediately by spectroscopy, but began to show appreciable decomposition after 15 min. It could be stored at -15°C in pentane soln for some time.

2-Phenyl-cyclopropenyl phenyl sulfide (**5**): IR (film): 1780 (C=C); ^{1}H-NMR (C_6D_6): 1.68 (s, 2 H, CH_2), 7.15 - 7.6 (m, br, 10 H, aryl-H); MS: 224 (M^+, 36.95%). The product proved to be too unstable for elemental analysis.

Oxidation of **3g**. A soln of *m*-chloroperbenzoic acid (50.0 mmol) in dichloromethane (100 ml) was added dropwise at -20°C to a soln of **3g** (25.0 mmol) in dichloromethane (50 ml). After stirring at room temp. for 10 hrs, the mixture was extracted 10 to 15 times with saturated sodium bicarbonate for complete removal of the acid, dried (Na_2SO_4), and concentrated *in vacuuo*. The residual solid was dried *in vacuuo* and may be recrystallized from chloroform for improved purity.

Z-1-Chloro-2-phenyl-2-trimethylsilylcyclopropyl phenyl sulfone (**6**): M.p. 170-171°C (from $CHCl_3$); yield 92%; IR: 1305 (SO_2), 1240 ($SiMe_3$), 1140 (SO_2), 835 ($SiMe_3$); ^{1}H-NMR: 0.1 (s, 9 H, $SiMe_3$), 1.85 (d, J = 5.7 Hz, 1 H, cyclopropyl), 2.62 (d, J = 5.7 Hz, 1 H, cyclopropyl), 7.08 - 7.98 (m, br, 10 H, aryl-H); ^{13}C-NMR: -1.23 (+), 24.93 (-), 34.16 (o), 64.23 (o), 126.33 (+), 127.47 (+), 127.65 (+), 128.31 (+), 128.56 (+), 129.55 (+), 130.11 (+), 133.61 (+), 137.5 (o), 138.32 (o); MS: 364 (M^+, 0.6%), 73 (M^+-291, $SiMe_3$, 100%).

Anal. for $C_{18}H_{21}O_2ClSSi$ (364.96): Calcd C 59.24 H 5.80 Cl 9.71 S 8.79
Found C 59.17 H 5.76 Cl 9.72 S 8.77

Thioacetals **7** *from cyclopropanes* **3d-h**. Magnesium (1.8g, 75 mol) was suspended in ether (200 ml) and activated by addition of 1,2-dibromoethane (1 ml). Then methyl iodide (3.55g, 25 mmol) in ether (25 ml) was added at a rate sufficient to maintain gentle refluxing. The mixture was heated under reflux for 1 hr. To the solution which was obtained by decanting, thiophenol (2.63g, 23.75 mmol) or 4-methylthiophenol (2.95 g, 23.75 mmol) in ether (5 ml) was added slowly. After gas evolution had ceased, the resulting grey suspension was treated dropwise with a soln of **3** (10.0 mmol) in ether (50 ml) at room temp. After 36 hrs, the precipitate was removed by filtration and the filtrate washed with four portions of water. The organic phase was dried (Na_2SO_4) and concentrated with a rotary evaporator. Products **7a-f** were purified by column chromatography using the eluents given below in parentheses (PE = petroleum ether).

1,1-Bis(phenylthio)-2-methyl-2-trimethylsilylcyclopropane (**7a**): PE/ethyl acetate (14:1); m.p. 73-74°C; yield: 74%; IR: 1240 ($SiMe_3$), 840 ($SiMe_3$); ^{1}H-NMR: 0.27 (s, 9 H, $SiMe_3$), 1.14 (d, J = 4.8 Hz, 1 H, cyclopropyl), 1.41 (s, 3 H, CH_3), 1.45 (d, J = 4.8 Hz, 1 H, cyclopropyl), 7.09 - 7.6 (m, br, 10 H, phenyl-H); ^{13}C-NMR: -0.23 (+), 19.44 (+), 24.47 (o), 28.47 (-), 42.76 (o), 125.51 (+), 126.53 (+), 127.92 (+), 128.55 (+), 128.59 (+), 130.03 (+), 136.21 (o), 136.45 (o).

Anal. for $C_{19}H_{24}S_2Si$ (344.6): Calcd C 66.22 H 7.02 S 18.61
Found C 66.19 H 7.20 S 18.63

E-1,1-Bis(phenylthio)-3-methyl-2-trimethylsilylcyclopropane (**7b**): PE/toluene (5:1); yield: 36%; IR (film): 1240 ($SiMe_3$), 840 ($SiMe_3$); ^{1}H-NMR: 0.1 (s, 9H, $SiMe_3$), 0.41 (d, J = 8.7 Hz, 1 H, cyclopropyl), 1.54 (d, J = 5.6 Hz, 3 H, CH_3), 1.63 (d+q, J = 5.6 Hz, J = 8.7 Hz, 1 H, cyclopropyl), 7.1 - 7.6 (m, br, 10 H, phenyl-H); ^{13}C-NMR: -0.37 (+), 17.34 (+), 29.94 (+), 32.19 (+), 44.25 (o), 125.95 (+), 126.95 (+), 128.59 (+), 128.67 (+), 128.89 (+), 131.33 (+), 136.04 (o), 137.05 (o).

Anal. for $C_{19}H_{24}S_2Si$ (344.6): Calcd C 66.22 H 7.02 S 18.61
Found C 66.15 H 7.04 S 18.67

Z-1,1-Bis(phenylthio)-3-methyl-2-trimethylsilylcyclopropane (**7c**): PE/toluene (5:1); yield: 34%; IR (film): 1240 ($SiMe_3$), 835 ($SiMe_3$); ^{1}H-NMR: 0.09 (s, 9 H, $SiMe_3$), 0.77 (d, J = 11 Hz, 1 H, cyclopropyl), 1.38 (d, J = 6.4 Hz, 3 H, CH_3), 2.17 (d+q, J = 6.4 Hz, J = 11 Hz, 1 H, cyclopropyl), 7.15 - 7.63 (m, br, 10 H, phenyl-H); ^{13}C-NMR: 0.78 (+), 13.71 (+), 25.23 (+), 30.60 (+), 43.25 (o), 125.41 (+), 127.28 (+), 127.86 (+), 128.51 (+), 128.57 (+), 131.9 (+), 135.64 (o), 136.39 (o).

Anal. for $C_{19}H_{24}S_2Si$ (344.6): Calcd C 66.22 H 7.02 S 18.61
Found C 66.42 H 7.18 S 18.53

1,1-Bis(phenylthio)-2-phenyl-2-trimethylsilylcyclopropane (**7d**): PE/toluene (5:1); yield: 89%; IR (film): 1240 ($SiMe_3$), 830 ($SiMe_3$); ^{1}H-NMR: 0.3 (s, 9 H, $SiMe_3$), 1.86 (d, J = 5.3 Hz, 1 H, cyclopropyl), 1.9 (d, J = 5.3 Hz, 1 H, cyclopropyl), 7.0 - 7.6 (m, br, 15 H, phenyl-H); ^{13}C-NMR: -0.17 (+), 28.55 (-), 36.98

(o), 43.68 (o), 125.90 (+), 126.39 (+), 126.77 (+), 127.52 (+), 128.23 (+), 128.30 (+), 128.61 (+), 129.05 (+), 129.55 (+), 130.23 (+), 131.66 (+), 135.09 (o), 136.53 (o), 141.51 (o).

Anal. for $C_{24}H_{26}S_2Si$ (406.7): Calcd C 70.90 H 6.40 S 15.80
Found C 70.77 H 6.49 S 15.89

E-1,1-Bis(phenylthio)-3-phenyl-2-trimethylsilylcyclopropane (**7e**): PE/toluene (10:1); m.p. 75–77°C; yield: 32%; IR: 1240 ($SiMe_3$), 840 ($SiMe_3$); ^{1}H-NMR: 0.4 (s, 9 H, $SiMe_3$), 1.56 (d, J = 9.4 Hz, 1 H, cyclopropyl), 3.08 (d, J = 9.4 Hz, 1 H, cyclopropyl), 7.21 – 7.78 (m, br, 15 H, phenyl-H); ^{13}C-NMR: -0.42 (+), 27.83 (+), 40.90 (+), 46.58 (o), 126.57 (+), 126.91 (+), 127.09 (+), 127.91 (+), 128.77 (+), 128.90 (+), 129.06 (+), 130.67 (+), 131.01 (+), 135.83 (o), 136.09 (o), 137.05 (o).

Anal. for $C_{24}H_{26}S_2Si$ (406.7): Calcd C 70.90 H 6.40 S 15.80
Found C 71.10 H 6.31 S 15.64

E/Z-1-Phenylthio-1-(4-methyl)phenylthio-2-phenyl-2-trimethylsilyl-cyclopropane (**7f**): PE/toluene (5:1); yield: 90%; IR (film): 1240 ($SiMe_3$), 830 ($SiMe_3$); ^{1}H-NMR (two diastereomers, ratio 2:1, more intense signals are labeled by *): 0.05 (s, 9 H, $SiMe_3$)*, 0.1 (s, 9 H, $SiMe_3$), 1.86 (d, J = 4.8 Hz, 1 H, cyclopropyl)*, 1.87 (d, J = 4.8 Hz, 1 H, cyclopropyl), 1.89 (d, J = 4.8 Hz, 1 H, cyclopropyl), 1.91 (d, J = 4.8 Hz, 1 H, cyclopropyl)*, 2.35 (s, 3 H, CH_3)*, 2.40 (s, 3 H, CH_3), 6.98-7.66 (m, br, 28 H, aryl-H).

Anal. for $C_{25}H_{28}S_2Si$ (420.72): Calcd C 71.37 H 6.71 S 15.24
Found C 71.50 H 6.74 S 15.13

References

[1] L. A. Paquette, *Isr. J. Chem.* **21**, 128 (1981); *Chem. Rev.* **86**, 733 (1986).

[2] E. Block, M. Aslam, *Tetrahedron* **44**, 281 (1988).

[3] G. Boche, D. R. Schneider, *Tetrahedron Lett.* **1975**, 4247; M. Saquet, M. G. Champetier, *C. R. Acad. Sci.* **C275**, 283 (1972); D. B. Reddy, C. G. Reddy, V. Padmauithi, *Sulfur Lett.* **5**, 123 (1987); M. Bhupathy, T. Cohen, *Tetrahedron Lett.* **28**, 4797 (1987).

[4] D. Seebach, *Chem. Ber.* **105**, 487 (1972).

[5a] U. Schöllkopf, F. P. Woerner and E. Wiskott, *Chem. Ber.* **99**, 806 (1966). – [5b] B. Riefling, Ph. D. thesis, Univ. Göttingen (1975).

[6] M. Makosza and E. Bialecka, *Tetrahedron Lett.* **1971**, 4517.

[7] R. A. Moss and F. G. Pilkiewicz, *Synthesis* **1973**, 209.

[8] G. Maas, *Phosphorus Sulfur* **14**, 143 (1983).

[9] T. H. Chan, D. Massuda, *Tetrahedron Lett.* **1975**, 3383; W. E. Billups, E. W. Casserly, B. E. Arney, Jr., *J. Am. Chem. Soc.* **106**, 440 (1984); I. J. Anthony, D. Wege, *Tetrahedron Lett.* **28**, 4217 (1987).

[10] H. Yoshida, M. Kato, T. Ogata and M. Matsumoto, *J. Org. Chem.* **50**, 1145 (1985); M. A. Kirms, H. Primke, M. Stohlmeier and A. de Meijere, *Recl Trav. Chim. Pays-Bas* **105**, 462 (1986).

[11a] R. Jorritsma, H. Steinberg and Th. J. de Boer, *Recl Trav. Chim. Pays-Bas* **100**, 184 (1981). – [11b] *Ibid.* p. 194. – [11c] *Ibid.* **101**, 288 (1982).

[12] Cf.: T. Ishihara, T. Kudaka and T. Ando, *Tetrahedron Lett.* **25**, 4765 (1984).

[13] S. G. Wierschke, J. Chandrasekhar, W. L. Jorgensen, *J. Am. Chem. Soc.* **107**, 1496 (1985); J. B. Lambert, G. Wang, R. B. Finzel, and D. H. Teramura, *ibid.* **109**, 7838 (1987).

[14] T. Cohen, J. P. Sherbine, S. A. Mendelson, M. Myers, *Tetrahedron Lett.* **26**, 2965 (1985); E. Schaumann, C. Friese and C. Spanka, *Synthesis* **1986**, 1035.

[15] C. Friese, Ph. D. thesis, Univ. Hamburg (1988).

[16] K. Timm, Diplom thesis, Univ. Hamburg (1988).

[17] G. Germain, P. Main and M. M. Woolfson, *Acta Crystallogr.* **A27**, 368 (1971).

[18] B. A. Franz, *Structure Determination Package (SDP)*, College Station, Texas 77840.