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Organylthio(silyl)carbenes

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Dedicated to Professor Armin de Meijere on the occasion of his 70th birthday

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The title carbenes **5** can be generated either from diazo compounds **9** by copper-catalyzed catalysis or from chloro(organylthio)methylsilanes **12** by base-induced α-elimination. This is confirmed by [2+1] cycloadditions with alkenes to give the cyclopropanes **4a–d** and **14**. Product **4a** is identical with the product obtained from carbanion **1c**, phenyloxirane, and styrene, for which a carbene intermediate **5a** had been invoked. On heating in the presence of copper triflate, cyclopropane **4a** undergoes ring enlargement to the thiochroman **11**. With (*Z*)- or (*E*)-alkenes **20**, carbene **5a** gives stereospecific cyclopropane formation, although maleate turns out not to be a suitable indicator for a stereospecific cycloaddition. The suggested singlet character of **5** is confirmed by DFT calculations (B3LYP/cc-pVTZ). The structures of cyclopropanes **4a** and **23**, as well as those of thiochroman **11** and carbene dimer **15**, were confirmed by single-crystal X-ray investigations.

Introduction

Since their discovery almost 100 years ago, carbenes have continued to fascinate chemists because of the unusual nature of their bonding.[1,2] Although most carbenes are only transient species, it has recently been shown that nucleophilic carbenes may be stable, as in the cases of the imidazole-derived Arduengo carbenes[3,4] or the phosphorus/silicon-substituted Bertrand carbenes.[5–8] Indeed, even optically pure phosphanyl(silyl)carbenes are available.[9] However, only limited stability at 0 °C was found for amino(silyl)-carbenes.[10]

The variable effect of silyl substitution on carbene stability calls for studies of combinations of silylcarbenes additionally containing other heteroatom substituents. Here, we had previously invoked phenylthio(trimethylsilyl)carbene as an intermediate in the domino reaction of the deprotonated silylthioacetal **1c** and the silyloxirane **2** (Scheme 1).[11] This reaction may be regarded as a homo-Peterson reaction,[12,13] which should give a cyclopropanone dithioacetal of type **3**, as is the case for the reactions between carbanions **1a** or **1b** and oxirane **2**. In striking contrast, however, the phenylthio-substituted carbanion **1c** and **2** yield the isomeric cyclopropane **4f**. To account for this unusual change in the product, we postulated an equilibrium between carbanion ("carbenoid") **1c** and phenylthio(trimethylsilyl)carbene (**5a**) plus thiophenoxide (Scheme 1). NMR studies of similar carbanions do not confirm such an equilibrium,[14] so the equilibrium may be essentially on the carbenoid side, but once the oxirane is added, thiophenoxide is removed from the equilibrium at the same time, liberating carbene **5**. In the putative mechanism (Scheme 1), this is followed by nucleophilic attack of thiophenoxide on the silyloxirane **2**, which would be expected to occur in the usual contrasteric fashion[15] to give the alkoxide **6**. This is identical with the intermediate of a Peterson olefination[16] of formaldehyde by the anion of silylated thioanisole. Consequently, the olefination product **7** is formed and offers a chance for [2+1] cycloaddition with the carbene **5a**.

The credibility of this mechanism would definitely be enhanced if carbene **5a** could be generated independently and found to react as claimed. In addition, although silyl-[7,10,17] and organylthiocarbenes[18] are well documented, there is no literature report on any organylthio(silyl)carbene, and so a comprehensive study of the properties and the reactivity of this type of carbene seems highly desirable.

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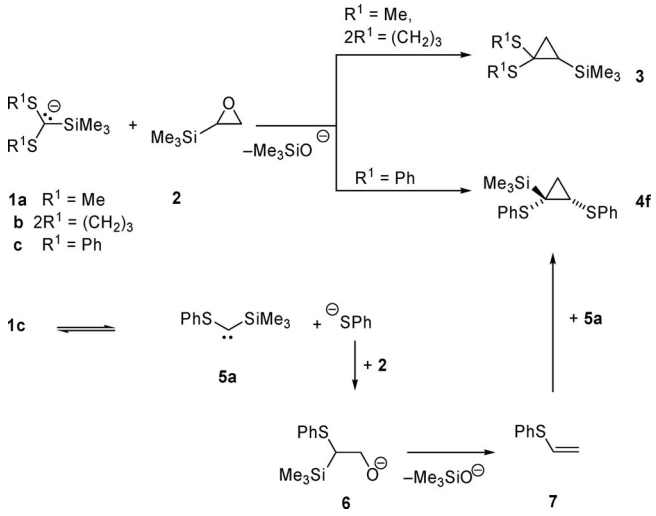
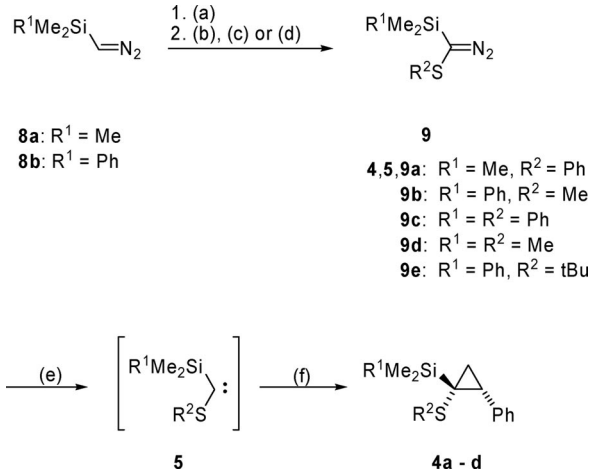


Scheme 1. Regular and irregular homo-Peterson products and the mechanism of "rearrangement".

Results and Discussion

Carbene Generation from Diazo Compounds

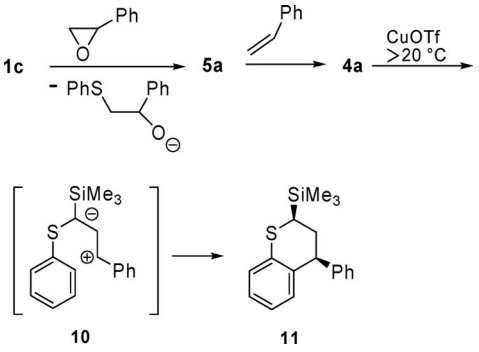
For an independent synthesis of carbene **5a** and congeners, the thermal decomposition of silyldiazomethanes **9** (Scheme 2) was envisaged. The starting materials would thus be (trimethylsilyl)-[19–21] or [dimethyl(phenyl)silyl]diazomethane (**8a** or **8b**).[20] These compounds are known to be CH-acidic, and their carbanions readily undergo addition of electrophiles.[22,23] We were pleased to see that this also holds for sulfur electrophiles such as sulfenyl chlorides or methyl methanemonothiosulfonate to give the Si/S-substituted diazo compounds **9a**/**9c**/**9e** and **9b**/**9d**, respectively (Scheme 2). The transition from a diazo compound **8** to a sulfur-containing diazo compound **9** can be conveniently monitored through a shift of the diazo stretch vibration in the IR spectrum from 2067 to 2045 cm^{-1}. Products **9** are



Scheme 2. Reactions and conditions: (a) BuLi, –78 °C → room temp.; (b) $MeSSO_2Me$, –78 °C (for **9b**, **9d**), (c) *t*BuSCl, –78 °C (for **9e**); (d) PhSCl, –78 °C (for **9a**, **9c**); (e) CuOTf, room temp.; (f) $PhCH{=}CH_2$, room temp.

thermally labile; however, in particular, the methylthio derivatives **9b** and **9d** are already starting to decompose on warming of their reaction mixtures to room temperature. The other examples can be kept in solution at room temperature, but do not survive removal of the solvent. Only diazo compound **9c** can be short-path-distilled, but the distillate again deteriorates on standing at room temperature, as shown by gas evolution and a color change.

On addition of copper(I) triflate at room temperature, the decomposing diazo compounds **9** immediately give gas evolution. No characterizable products were identified from these mixtures, but the generation of carbenes **5** was confirmed by their trapping as their [1+2] cycloadducts **4a**–**d** in the presence of styrene. Only the *tert*-butylthio-substituted carbene **5e** failed to give a cycloadduct but rather an intractable reaction mixture, probably due to steric hindrance. In the other cases, for a good yield of **4** it is advisable to add styrene shortly after the addition of the sulfur electrophile to deprotonated **8**. Product **4a** had been obtained before in a reaction similar to that shown in Scheme 1 when thiophenoxide was removed from the carbenoid/carbene equilibrium by addition of styrene oxide, followed by addition of styrene to trap the simultaneously formed carbene (Scheme 3).[11] The claimed 1α,2α configuration shown in Schemes 1 and 2 was confirmed by NOE measurements and



Scheme 3. Independent formation and isomerization of cyclopropane **4a**.

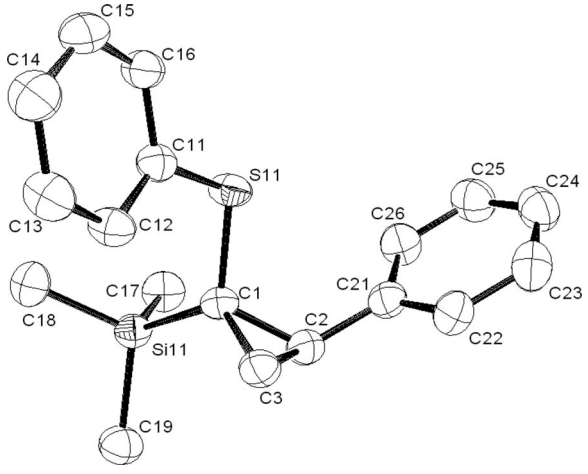


Figure 1. Crystal structure of cyclopropane **4a** (ORTEP plot).

finally by a single-crystal X-ray study of cyclopropane **4a** (Figure 1). This configuration is sterically favored, but may also be preferred because of a favorable secondary orbital interaction, because phenylthiocarbene and styrene give the analogous *cis*-cyclopropane.[24]

Isomerization of Cyclopropane 4a

If the reaction between diazo compound **9a**, copper(I) triflate, and styrene is run above room temperature, the yield of cyclopropane **4a** goes down, but another product – compound **11** – is formed in increasing amounts. With **9a** at 120 °C, no cyclopropane **4a** is found at all, but only product **11**. A control experiment showed that product **11** is also formed in very high yield from the primary three-membered-ring compound **4a**, which therefore is obviously an intermediate in the formation of **11**, but this process requires the presence of copper(I) triflate to open the cyclopropane ring. The thiochroman structure **11** is suggested by the spectroscopic evidence and was unambiguously corroborated by an X-ray structure analysis (Figure 2). A possible mechanism (Scheme 3) involves opening of the C1–C2 bond of **4a** under the influence of the copper catalyst to give the 1,3-zwitterion **10**; the subsequent cyclization to **11** follows the route of an intramolecular Friedel–Crafts alkylation. Interestingly, only the shown 2α,4α diastereomer is formed.

Carbene Generation by Dehydrochlorination

A third pathway to carbenes **5** should be opened up by the dehydrochlorination of chloro/silyl sulfides **12** (Scheme 4). Here, the initial formation of the carbenoids **13** can be expected and from there the formation of the carbenes **5**. In the trapping reaction with styrene, an AE mechanism via **13** may compete with the [1+2] cycloadditions involving the finally generated carbene **5** to give the three-membered-ring compounds **4**. In fact, the isolated cyclopropanes **4a**, **4c**, and **4d** are in all respects, including configuration, identical with the products **4** formed from the diazo compounds **9** via carbenes **5**, so it seems probable that the reacting species involved when precursors **12** are used are also carbenes **5** rather than carbenoids **13**.

As with styrene, carbenes **5a** and **5b** can also be trapped by cyclohexene, to give the norcarane derivatives **14** (Scheme 4), but for **5c** the reaction failed, and with **5a** the yield is low. The reactions are highly diastereoselective, each giving one isomer with >90% excess. From the reaction giving **14a**, a considerable amount (25%) of the formal carbene dimer **15** was isolated. The (*E*) configuration of this alkene was verified by an X-ray structure investigation (Figure 3).

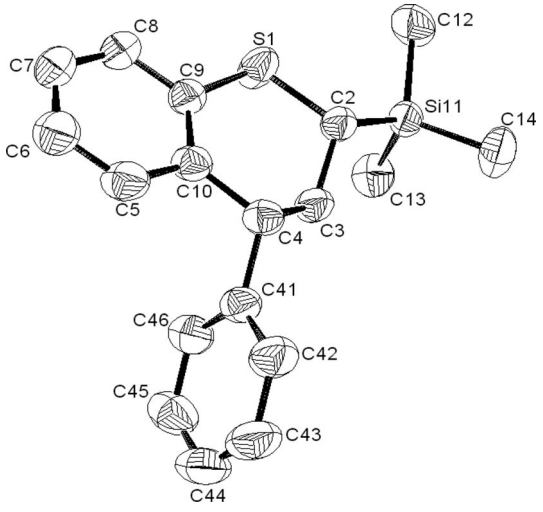


Figure 2. Crystal structure of thiochroman **11** (ORTEP plot).

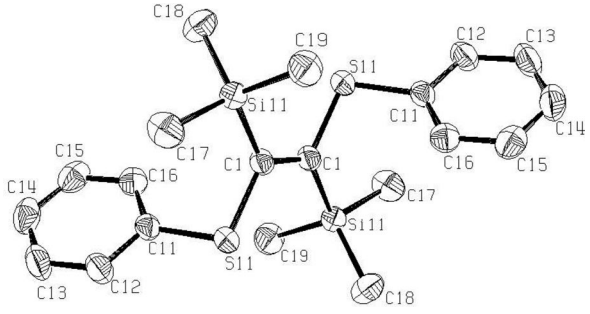
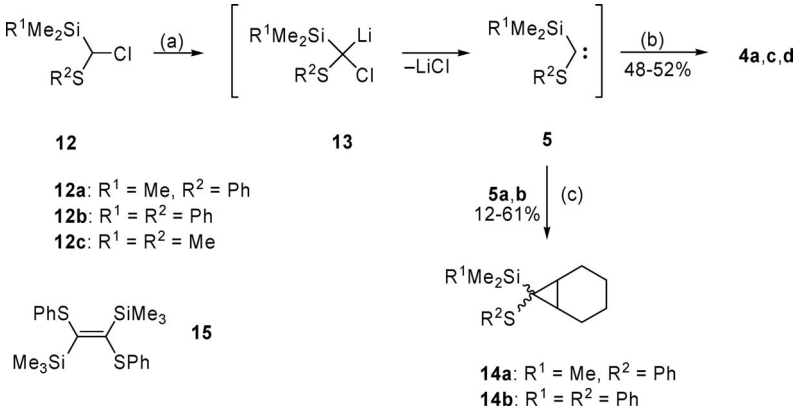


Figure 3. Crystal structure of **15** (ORTEP plot).

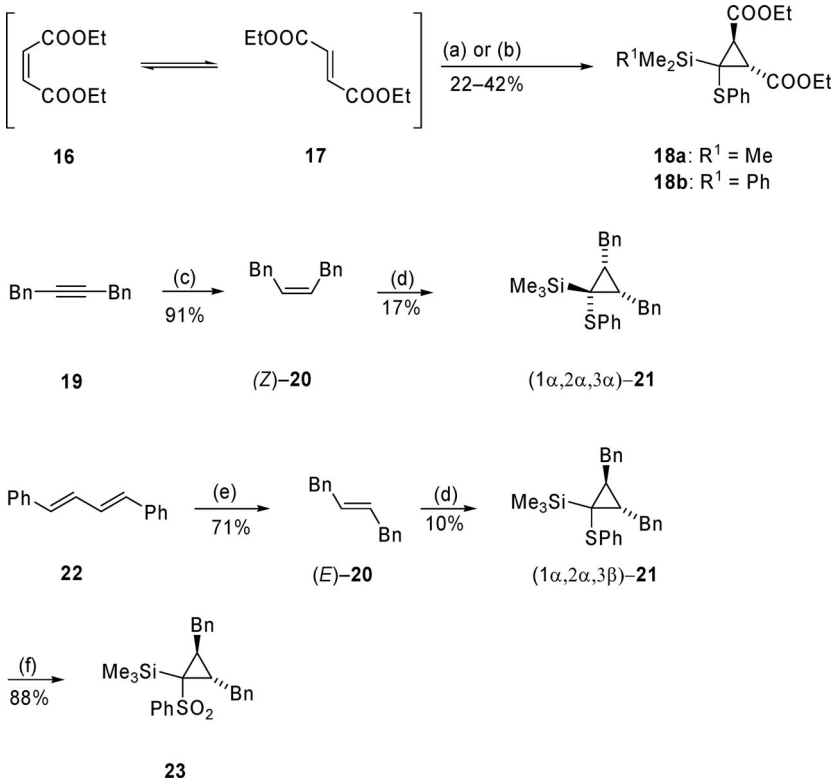


Scheme 4. Reactions and conditions: (a) BuLi, Et_2O, –78 °C; (b) $PhCH{=}CH_2$, 20 °C; (c) cyclohexene.

Diastereoselectivity of Carbene Trapping

Use of maleate to trap carbenes **5** should in principle have provided a tool to check on the diastereoselectivities of the [2+1] cycloadditions. Actually, by Skell's rule,[25] information on the multiplicities of the carbenes should be possible; this principle was very recently successfully applied to confirm the singlet natures of phosphanyl(silyl)carbenes.[26–28] Generation of carbenes **5a** or **5b** from chloro sulfides **12** as before (Scheme 4) but with trapping with diethyl maleate (**16**) in each case gives a [1+2] cycloadduct for which the NMR evidence, in particular a $^3J_{H,H}$ coupling constant of 6.3 Hz, suggests the *trans* arrangement of ester groups. The switch of configuration relative to the employed *cis*-ester **16** might indicate a reaction involving a carbenoid **13** rather than a carbene **5** to give an intermediate that would allow rotation around the original C=C bond. The same product was also obtained, however, both when the carbene **5a** was generated from the diazo compound **9a** in our one-pot approach to give an authentic carbene and when the *trans*-ester **17** was used as cycloaddition partner. To account for these results, a triplet character of carbene **5**, giving a cycloaddition via a 1,3-diradical, might be considered. However, when maleate **16** was used in excess and the unreacted, reisolated ester was analyzed after the reaction, it was found to be mostly fumarate **17**, so maleate is obviously configurationally unstable under the reaction conditions and may well isomerize prior to the cycloaddition. Control experiments showed that a catalytic amount of butyllithium (3 mol-%) transforms maleate **16** into a 1:4 mixture with fumarate **17** at room temperature. Possibly, this is the effect of residual salt in commercial butyllithium. In the actual carbene-generating experiments, however, sulfur nucleophiles in the reaction mixture (e.g., benzenesulfenyl chloride contamination in **9a**) may well also lead to the observed change of configuration.

For an unambiguous application of Skell's rule, 1,4-diphenylbut-2-ene (**20**; Scheme 5) was chosen as an alkene that could be expected to be both configurationally stable and easy to handle. After some experimentation, efficient methods to obtain both diastereomers were found. DIBAL reduction of 1,4-diphenylbut-2-yne (**19**) gave the (*Z*)-alkene, and sodium-driven reduction of 1,4-diphenylbuta-1,3-diene (**22**) provided the (*E*) isomer (Scheme 5). Both isomers underwent slow [2+1] cycloaddition with carbene **5a** as generated from thioacetal anion **1c** and styrene oxide (cf. Scheme 1), and two different cycloadducts with complex AA′BB′XX′ ^{1}H NMR patterns were obtained. For unambiguous configuration assignment, we therefore oxidized the putative *trans* adduct (1α,2α,3β)-**21** to the crystalline sulfone **23**. A single-crystal X-ray study (Figure 4) now allowed the structure and the *trans* configuration of the benzyl groups to be confirmed and therefore implicitly also the *cis* configuration of the benzyl groups in the product **21** obtained from (*Z*)-**20**.



Scheme 5. Reactions and conditions: (a) **9a**, CuOTf, Et_2O, **16** or **17**. –78 °C → room temp.; (b) **12a** or **12b**, BuLi, Et_2O, –78 °C → room temp.; (c) DIBAL, toluene, 55 °C; (d) phenyloxirane, **1c**, –78 °C→0 °C, THF; (e) Na, Et_2O, room temp.; (f) *m*CPBA, CH_2Cl_2, –20 °C → room temp.

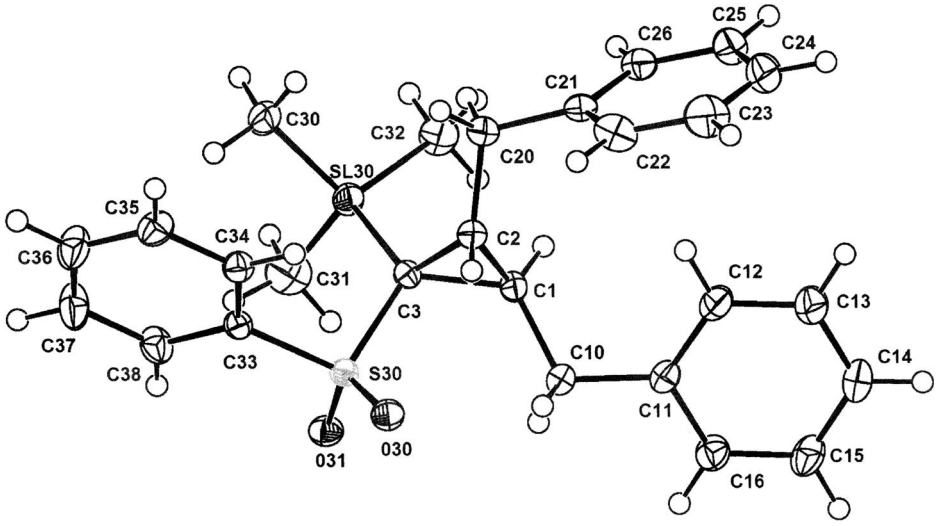


Figure 4. Crystal structure of **23** (ORTEP plot).

Physical and Theoretical Evidence for the Multiplicity

General expectations based on the heteroatom substitution[29] and the stereospecific course of the [2+1] cycloaddition with alkenes **20** both allow singlet character to be assigned to carbenes **5**. However, it seemed desirable to obtain additional evidence for this singlet nature. The diazo compound **9c** was thus irradiated with UV light, but the reaction product failed to give ESR signals. This indirect evidence of the singlet character of carbenes **5** was substantiated by DFT calculations for carbene **5d** at the B3LYP level.[30] These calculations gave optimized conformations of singlet and triplet carbenes (Figure 5) and a 13.14 kcal mol^{-1} higher stability of the singlet carbene.

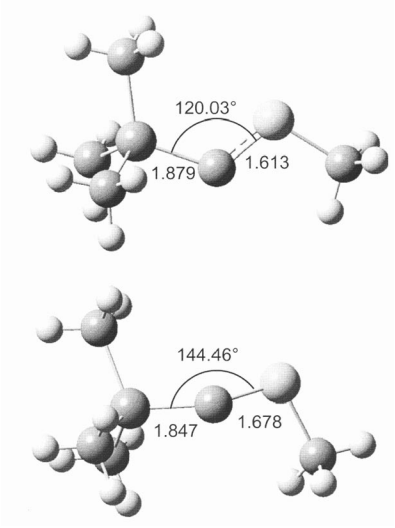


Figure 5. Calculated geometries of the singlet (top) and triplet forms (bottom) of methylthio(trimethylsilyl)carbene (**5d**; bond lengths in Å).

Conclusions

Previously, we had invoked organylthio(silyl)carbenes **5** only as intermediates in the reactions between silylthioacetal anion **1c** and oxiranes such as **2** (Scheme 1) or styrene oxide (Scheme 3). The current work shows that the carbene species generated either from diazo precursors **9** or from chloro sulfides **12** gives identical cycloaddition products with styrene, in terms both of structure and of configuration, so it can be deduced that the same carbenes **5** are intermediates in all three approaches. In no case was there any indication that a carbene **5** may be stable enough for isolation from the reaction mixture; not even a spectroscopic study in solution was feasible. These carbenes are therefore definitely less stable than the Bertrand carbenes,[5–8] indicating that the carbene-stabilizing effect of sulfur is much less pronounced than that of phosphorus. Nevertheless, with three convenient methods to generate carbene **5** now to hand, the synthetic value of the multifunctional organylthio(silyl)carbenes **5** should certainly be appreciated.

Experimental Section

General: Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded with Bruker AC 200 F or ARX 400 instruments in $CDCl_3$ as solvent. Chemical shifts (δ) were measured in ppm and coupling constants (J) in Hz. TMS or an internal TMS group was used as reference for ^{1}H NMR spectra (δ = 0.00 ppm). The solvent peak was used as reference for ^{13}C NMR spectra (δ = 77.00 ppm). For assignment of the number of substituents attached to the specified carbon atom, each carbon atom is described as p or t (primary or tertiary carbon atom), s (secondary carbon atom), or q (quaternary carbon atom), as determined by the DEPT method. When necessary, NMR spectroscopic data were assigned with the aid of H,H- and C,H-correlated spectra. MS data were recorded with a Varian Saturn 2100T or a Hewlett–Packard 5989B instrument; high-resolution MS (HRMS) measurements were carried out at the

Institut für Organische Chemie, Leibniz-Universität Hannover, or at the Institut für Organische Chemie, Universität Göttingen. IR spectra were recorded with a Bruker Vektor 22 FT-IR spectrometer. Elemental analyses were performed by the Institut für Pharmazeutische Chemie, Technische Universität Braunschweig. TLC was performed on Merck 60 F_{254} precoated silica plates, and spots were detected by UV fluorescence or by spraying with a solution of anisaldehyde/sulfuric acid in acetic acid/methanol (1:5:10:85) and subsequent heating. Flash chromatography was performed with silica gel 60 (Merck, 230–400 mesh). Petroleum ether (PE) with the boiling range 60–70 °C was used in the separations. All solvents were distilled before use. All reactions were carried out under nitrogen.

[Dimethyl(phenyl)silyl]diazomethane (8b): This compound was prepared analogously to **8a**.[20] Yellow liquid, yield 76% (ref.[20] 76%), b.p. 51 °C (2.3×10^{-1} mbar). ^{1}H NMR (200 MHz): δ = 0.00 (s, 6 H, $SiCH_3$), 2.37 (s, 1 H, CH), 6.95–7.16 (m, 5 H, aryl H) ppm. ^{13}C NMR (50 MHz): δ = –2.4 (p, 2 C, $SiCH_3$), 19.5 (t, 1 C, $–CN_2$), 127.9 (t, 2 C, aryl C), 129.5 (t, 1 C), 133.6 (t, 2 C, aryl C), 137.3 (q, 1 C, aryl C) ppm. IR (NaCl): $\tilde{\nu}$ = 3215, 3070, 3024, 2959, 2898, 2066, 1591, 1486, 1427, 1262, 1189, 1160, 1114, 1066, 817, 732, 698, 640 cm^{-1}.

General Procedure for the Preparation of Diazomethanes 9a–e: BuLi in hexanes (1.6 M, 0.75 mL, 1.2 mmol) was added dropwise at –78 °C to **8a**[20] or **8b** (1 mmol) in diethyl ether (10 mL). After the system had been stirred for 45 min, 1,1-dimethylethanesulfenyl chloride,[31] benzenesulfenyl chloride,[32] or *S*-methyl methanemonothiosulfonate[33] was added slowly, and stirring was continued for 10 min. For a good yield of cyclopropane **4**, styrene (0.57 mL, 5 mmol) was added at this point and the reaction mixture was allowed to warm to room temp., which for most diazo products **9** already leads to partial decomposition. The reaction mixture was then poured into water and the aqueous phase was extracted with diethyl ether (2×). The combined organic phases were dried (Na_2SO_4). Because of the thermal lability of the diazo products **9** the filtered solutions were used as such. These reactions led to a typical shift of the diazo absorption in the IR spectra from ca. 2067 cm^{-1} to ca. 2048 cm^{-1}. Because of ongoing decomposition no other reliable data could be obtained.

General Procedure for the Reactions between Diazo Compounds 9 and Styrene. Preparation of Cyclopropanes 4a–d: To complete each reaction with styrene, $CuSO_3CF_3$ (ca. 10 mg) was added, and the mixture was stirred at room temp. for 12 h. The cycloaddition can be monitored by IR spectroscopy by observing the disappearance of the absorption at ca. 2048 cm^{-1}. The reaction mixture was then washed with diluted HCl, and the aqueous phase was extracted with diethyl ether (2×). The combined organic phases were dried, and the solvent was evaporated in vacuo. After flash chromatography, products **4a**–**e** were obtained.

2α-Phenyl-1α-(phenylthio)-1β-(trimethylsilyl)cyclopropane (4a): This compound was prepared from **9a**. Yield 152 mg (51%). Colorless solid, m.p. 58 °C (ref.[11] 56–57 °C). ^{1}H NMR (400 MHz): δ = 0.00 (s, 9 H, $SiCH_3$), 1.47 (dd, J = 5.3, 6.7 Hz, 1 H, CH_2 cyclopropane), 1.60 (dd, J = 5.3, 8.2 Hz, 1 H, CH_2 cyclopropane), 2.43 (dd, J = 6.7, 8.2 Hz, CH cyclopropane), 7.08–7.31 (m, 10 H, aryl H) ppm. ^{13}C NMR (100 MHz): δ = –2.3 (p, 3 C, $SiCH_3$), 19.1 (s, 1 C, CH_2), 20.0 (q, 1 C, C cyclopropane), 28.2 (t, 1 C, C cyclopropane), 124.8, 126.4, 127.7, 127.9, 128.2 (each t, aryl C), 137.5, 138.4 (each q, 1 C, aryl C) ppm. GC-MS (70eV): m/z (%) = 298 (23.1) $[M]^+$. $C_{18}H_{22}SSi$ (298.52): calcd. C 72.42, H 7.43, S 10.74; found C 72.40, H 7.14, S 10.97.

1β-[Dimethyl(phenyl)silyl]-1α-(methylthio)-2α-phenylcyclopropane (4b): This compound was prepared from **9b**. Yield 182 mg (61%). Colorless oil. ^{1}H NMR (200 MHz): δ = 0.00, 0.02 (each s, 3 H, $SiCH_3$), 0.80 (dd, J = 5.1, 8.2 Hz, 1 H, CH_2 cyclopropane), 0.89 (dd, J = 5.1, 6.5 Hz, 1 H, CH_2 cyclopropane), 1.07 (s, 3 H, SCH_3), 1.93 (dd, J = 6.5, 8.2 Hz, 1 H, CH cyclopropane), 6.80–7.20 (m, 10 H, aryl H) ppm. ^{13}C NMR (50 MHz): δ = –3.9 (p, 2 C, $SiCH_3$), 15.7 (p, 1 C, SCH_3), 17.7 (s, 1 C, CH_2 cyclopropane), 19.8 (q, 1 C, CSSi cyclopropane), 28.8 (t, 1 C, CH cyclopropane), 126.2, 127.5, 127.8, 129.2, 129.3, 134.2 (each t, aryl C), 137.2, 137.5 (each q, aryl-C) ppm. IR (NaCl): $\tilde{\nu}$ = 3067, 3025, 2957, 2919, 1603, 1497, 1454, 1427, 1248, 1170, 1112, 1088, 1067, 1029, 834, 821, 774, 735, 697 cm^{-1}. GC-MS (70eV): m/z (%) = 298 (4.5) $[M]^+$. HR-EI-MS: calcd: 298.1211; found 298.1211.

1β-[Dimethyl(phenyl)silyl]-2α-phenyl-1α-(phenylthio)cyclopropane (4c): This compound was prepared from **8b**. Yield 274 mg (76%). Colorless oil. ^{1}H NMR (400 MHz): δ = 0.00, 0.07 (each s, 3 H, $SiCH_3$), 1.16 (dd, J = 5.3, 6.8 Hz, 1 H, CH_2 cyclopropane), 1.23 (dd, J = 5.3, 8.2 Hz, 1 H, CH_2 cyclopropane), 2.08 (dd, J = 6.8, 8.2 Hz, 1 H, CH cyclopropane), 6.71–7.27 (m, 15 H, aryl H) ppm. ^{13}C NMR (100 MHz): δ = –3.8 (p, $SiCH_3$), 19.2 (s, 1 C, CH_2 cyclopropane), 19.6 (q, CSSi), 28.5 (t, CHPh), 124.9, 126.4, 127.7, 127.8, 128.0, 128.2, 129.2, 129.4, 134.2 (each t, aryl CH), 136.6, 137.3, 138.2 (each q, aryl C) ppm. IR (NaCl): $\tilde{\nu}$ = 3065, 3025, 2957, 1582, 1497, 1477, 1454, 1438, 1427, 1249, 1112, 1090, 1068, 1026, 922, 821, 776, 736, 695, 651 cm^{-1}. GC-MS (70eV): m/z (%) = 360 (26.8) $[M]^+$. HR-EI-MS: calcd: 360.1368; found 360.1368.

1α-(Methylthio)-2α-phenyl-1β-(trimethylsilyl)cyclopropane (4d): This compound was prepared from **9a**. Yield 139 mg (59%). Colorless oil. ^{1}H NMR (200 MHz): δ = 0.00 (s, 9 H, $SiCH_3$), 1.13 (dd, J = 5.1, 8.1 Hz, 1 H, CH_2 cyclopropane), 1.20 (dd, J = 5.1, 6.4 Hz, 1 H, CH_2 cyclopropane), 1.58 (s, 3 H, SCH_3), 2.25 (dd, J = 6.4, 8.1 Hz, 1 H, CH cyclopropane), 7.07–7.15 (m, 5 H, aryl H) ppm. ^{13}C NMR (50 MHz): δ = –2.3 (p, 3 C, $SiCH_3$), 15.8 (p, 1 C, SCH_3), 17.7 (s, 1 C, CH_2 cyclopropane), 20.4 (q, 1 C, SCSi), 28.6 (t, 1 C, CH cyclopropane), 126.2, 127.5, 129.2 (each t, aryl C), 137.8 (q, aryl C) ppm. IR (NaCl): $\tilde{\nu}$ = 3060, 3028, 2954, 2920, 2897, 1604, 1497, 1454, 1247, 1170, 1087, 1065, 1030, 915, 837, 791, 754, 728, 694, 624 cm^{-1}. GC-MS (70eV): m/z (%) = 236 (7) $[M]^+$. HR-EI-MS: calcd. 236.1055; found 236.1055.

(2α,4α)-4-Phenyl-2-(trimethylsilyl)thiochroman (11) from Cyclopropane 4a: CuOTf (ca. 10 mg), toluene (5 mL), and **4a** (120 mg, 0.4 mmol) were heated at reflux for 18 h. After cooling, the reaction mixture was washed with diluted HCl, and the aqueous phase was extracted with diethyl ether (2×). The combined organic phases were dried (Na_2SO_4), and the solvents were evaporated in vacuo. Compound **11** was isolated by flash chromatography. Yield 108 mg (90%). Colorless solid, m.p. 102–105 °C. ^{1}H NMR (200 MHz): δ = 0.00 (s, 9 H, $SiCH_3$), 2.10 (ddd, J = 12.0, 12.5, 13.5 Hz, 1 H, ring CH_2), 2.42 (ddd, J = 2.3, 4.5, 13.5 Hz, 1 H, ring CH_2), 2.85 (dd, J = 2.3, 12.5 Hz, 1 H, ring CHSi), 4.04 (dd, J = 4.5, 12.0 Hz, 1 H, ring CHS), 6.53–7.24 (m, 9 H, aryl H) ppm. ^{13}C NMR (50 MHz): δ = –3.6 (p, 3 C, $SiCH_3$), 28.1 (t, 1 C, CHSSi), 34.9 (s, 1 C, CH_2), 47.6 (t, 1 C, CHPh), 123.7, 126.1, 126.3, 126.6, 128.7, 128.8, 130.2 (each t, 1 C, aryl CH), 134.2, 137.4, 145.7 (each q, 1 C, aryl C) ppm. IR (KBr): $\tilde{\nu}$ = 3054, 3025, 2953, 2927, 2901, 2856, 1600, 1586, 1561, 1492, 1471, 1451, 1431, 1247, 1180, 1154, 1133, 1072, 1046, 1030, 1015, 875, 839, 759, 746, 701 cm^{-1}. GC-MS (70eV): m/z (%) = 298 (11.4) $[M]^+$. $C_{18}H_{22}SSi$ (298.52): calcd. C 72.42, H 7.43, S 10.74; found C 72.40, H 7.14, S 10.97.

[Chloro(organylthio)methyl]silanes 12: The precursor (methylthio)-(trimethylsilyl)methane was obtained according to ref.,[34] and (phenylthio)(trimethylsilyl)methane according to ref.[35] (Phenylthio)(dimethylphenylsilyl)methane was prepared in a procedure

analogous to that described in ref.[34] to give a colorless oil (yield 71%). ^{1}H NMR (200 MHz): δ = 0.00 (s, 6 H, $SiCH_3$), 1.95 (s, 2 H, SCH_2Si), 6.64–7.14 (m, 10 H, aryl H) ppm. ^{13}C NMR (50 MHz): δ = –3.1 (p, 2 C, $SiCH_3$), 17.6 (t, 1 C, SCHSi), 124.7, 126.1, 128.0, 128.7, 129.6, 133.0 (each t, aryl CH), 137.3, 140.1 (each q, aryl C) ppm. GC-MS (70eV): *m*/*z* (%) = 258 (55.5) $[M]^+$. For chlorination, the corresponding precursor (2.0 mmol) in CCl_4 (10 mL) was stirred with NCS (267 mg, 2 mmol) for 1 d. The formed succinimide was removed by filtration, and the solvent was evaporated in vacuo. Products **12a** and **12c** were purified by Kugelrohr distillation; **12b** was used in crude form.

[Chloro(phenylthio)methyl]trimethylsilane (12a): Colorless liquid. Yield 450 mg (98%) (ref.[36] 96%). B.p. 90 °C (12 Torr). ^{1}H NMR (200 MHz): δ = 0.00 (s, 9 H, $SiCH_3$), 4.65 (s, 1 H, CHCl), 6.97–7.26 (m, 5 H, aryl H) ppm. GC-MS (70eV): *m*/*z* (%) = 230 (13.24) $[M]^+$.

[Chloro(phenylthio)methyl]dimethyl(phenyl)silane (12b): Colorless oil. Crude yield 537 mg (92%, GC purity 97%). ^{1}H NMR (200 MHz): δ = 0.00 (s, 6 H, $SiCH_3$), 4.85 (s, 1 H, SCHClSi), 7.02–7.20 (m, 10 H, aryl H) ppm. ^{13}C NMR (50 MHz): δ = –4.5, –4.3 (each p, 1 C, $SiCH_3$), 57.9 (t, 1 C, SCHClSi), 127.2, 127.9, 129.0, 129.6, 130.1 (each t, 1 C, aryl CH), 133.0 (q, 1 C, aryl C), 134.4 (t, 2 C, aryl CH), 135.5 (q, 1 C, aryl C) ppm. IR (NaCl): $\tilde{\nu}$ = 3070, 2960, 1717, 1583, 1480, 1438, 1427, 1252, 1170, 1116, 1091, 1067, 1025, 838, 788, 737, 697, 647 cm^{-1}. GC-MS (70eV): *m*/*z* (%) = 292 (14.12) $[M]^+$. HR-EI-MS: calcd: 292.0509; found 292.0508.

[Chloro(methylthio)methyl]trimethylsilane (12c): Colorless liquid. Yield 168 mg (50%) (ref.[37] 60%). B.p. 45 °C (2.3 mbar; ref.[37] 80–82 °C/28 Torr). ^{1}H NMR (200 MHz): δ = 0.00 (s, 9 H, $SiCH_3$), 2.06 (s, 3 H, SCH_3), 4.36 (s, 1 H, CHCl) ppm. ^{13}C NMR (50 MHz): δ = –2.8 (p, 3 C, $SiCH_3$), 17.2 (p, 1 C, SCH_3), 61.3 (t, 1 C, HCCl) ppm. GC-MS (70eV): *m*/*z* (%) = 168 (8.71) $[M]^+$, 169 (3.79) $[M + 1]^+$, 170 (3.78) $[M + 2]^+$.

Carbene Generation and Trapping from Silanes 12. General Procedure: Silane **12** (2 mmol) in diethyl ether (20 mL) was cooled to –78 °C, BuLi in hexanes (1.6 M, 1.5 mL, 2.4 mmol) was slowly added dropwise to the solution, and the mixture was stirred for 45 min. The yellow reaction mixture was then added by cannula at room temp. to styrene (4 mL, 35.1 mmol) or cyclohexene (4 mL, 39.5 mmol). After stirring at room temp. for 12 h, the reaction mixture was poured into water, and the aqueous phase was extracted with diethyl ether (2×). The combined organic phases were dried (Na_2SO_4), and the solvents were evaporated in vacuo. The following products were obtained after flash chromatography. With styrene, **4a** (52%), **4c** (48%), or **4d** (49%) was obtained; in the synthesis of **4a** side products were (phenylthio)(trimethylsilyl)methane[35] (12%) and bis(phenylthio)(trimethylsilyl)methane[38] (16%). With cyclohexene, **14a** of uncertain configuration was isolated along with (*E*)-1,2-bis(phenylthio)-1,2-bis(trimethylsilyl)ethene (**15**, 25%), (phenylthio)(trimethylsilyl)methane[35] (11%), and bis(phenylthio)(trimethylsilyl)methane[38] (39%), whereas **14b** was isolated along with [dimethyl(phenyl)silyl](phenylthio)methane (29%).

***endo*- or -*exo*-7-(Phenylthio)-*exo*- or -*endo*-7-(trimethylsilyl)bicyclo[4.1.0]heptane (14a):** Colorless solid, m.p. 80 °C. Yield 66 mg (12%). ^{1}H NMR (200 MHz): δ = 0.00 (s, 9 H, $SiCH_3$), 1.36–1.69 (m, 8 H, CH_2 groups), 2.0–2.07 (m, 2 H, CH groups), 7.10–7.38 (m, 5 H, aryl H) ppm. ^{13}C NMR (50 MHz): δ = –2.2 (p, 3 C, $SiCH_3$), 19.3 (q, 1 C, CSSi), 19.3 (t, 2 C, bridgehead C), 20.5, 22.0 (each s, 2 C, CH_2), 123.9, 126.2, 128.1 (each t, 2 C, aryl CH), 138.5 (q, 1 C, aryl C) ppm. IR (KBr): $\tilde{\nu}$ = 3004, 2930, 2852, 1580, 1477, 1436, 1251, 1172, 1095, 1071, 1025, 963, 922, 866, 833, 737, 691 cm^{-1}. GC-MS (70eV): *m*/*z* (%) = 276 (39.67) $[M]^+$. HR-EI-MS: calcd. 276.1368; found 276.1368.

***endo*- or -*exo*-7-(Phenylthio)-*exo*- or -*endo*-7-[dimethyl(phenyl)silyl]-bicyclo[4.1.0]heptane (14b):** Yellow oil. Yield 412 mg (61%). ^{1}H NMR (200 MHz): δ = 0.00 (s, 9 H, $SiCH_3$), 0.96–1.38 (m, 8 H, CH_2 groups), 1.65–1.76 (m, 2 H, CH groups), 6.82–7.32 (m, 10 H, aryl H) ppm. ^{13}C NMR (50 MHz): δ = –3.5 (p, 2 C, $SiCH_3$), 18.5 (q, 1 C, CSSi), 19.5 (t, 2 C, bridgehead C), 20.4, 21.9 (each s, 2 C, CH_2), 124.0, 126.1, 127.6, 127.7, 129.0, 134.2 (each t, aryl CH), 137.3, 138.1 (each q, 1 C, aryl C) ppm. IR (NaCl): $\tilde{\nu}$ = 3068, 2934, 2853, 1584, 1477, 1439, 1427, 1252, 1115, 1069, 1025, 959, 916, 853, 829, 797, 735, 699, 650 cm^{-1}. GC-MS (70eV): *m*/*z* (%) = 338 (50.15) $[M]^+$. HR-EI-MS: calcd. 338.1524; found 338.1524.

(*E*)-1,2-Bis(phenylthio)-1,2-bis(trimethylsilyl)ethene (15): Colorless solid, m.p. 131 °C. Yield 97 mg (25%). ^{1}H NMR (200 MHz): δ = 0.00 (s, 18 H, $SiCH_3$), 7.07–7.23 (m, 10 H, aryl H) ppm. ^{13}C NMR (50 MHz): δ = 1.5 (p, 6 C, $SiCH_3$), 125.6, 127.7, 128.9 (each t, aryl CH), 138.6 (q, 2 C, aryl C), 160.6 (q, 2 C, C=C) ppm. IR (KBr): $\tilde{\nu}$ = 3052, 2946, 2890, 1579, 1473, 1435, 1402, 1245, 1091, 1023, 843, 757, 740, 689 cm^{-1}. GC-MS (70eV): *m*/*z* (%) = 388 (13.6) $[M]^+$. HR-EI-MS: calcd. 388.1171; found 388.1171.

Cyclopropanedicarboxylates 18 from Chlorides 12. General Procedure: The procedure for the synthesis of **4a/4c/4d** and **14a/14b** given above was applied, but diethyl maleate (**16**; 4 mL, 24.7 mmol) or fumarate (**17**; 4 mL, 24.7 mmol) was used as C=C component. From **12a** and **16**, diester **18a** (yield 26%) was isolated along with (phenylthio)(trimethylsilyl)methane[37] (10%), bis(phenylthio)trimethylsilylmethane[38] (43%), and **15** (20%). Chloride **12a** and **17** gave diester **18a** (yield 25%) along with bis(phenylthio)(trimethylsilyl)methane[38] (36%).

Diethyl 3-(Phenylthio)-3-(trimethylsilyl)cyclopropane-*trans*-1,2-dicarboxylate (18a): Colorless oil. ^{1}H NMR (200 MHz): δ = 0.00 (s, 9 H, $SiCH_3$), 1.13, 1.19 (each t, J = 7.1 Hz, 3 H, OCH_2CH_3), 2.62, 2.63 (each d, J = 6.3 Hz, 1 H, CH cyclopropane), 3.96–4.16 (m, 4 H, OCH_2CH_3), 7.03–7.28 (m, 5 H, aryl H) ppm. ^{13}C NMR (50 MHz): δ = –0.8 (p, 3 C, $SiCH_3$), 14.1, 14.2 (each p, 1 C, OCH_2CH_3), 28.1 (q, 1 C, SCSi), 32.7, 32.4 (each t, 1 C, CH cyclopropane), 61.3, 61.4 (each s, 1 C, OCH_2CH_3), 125.9, 128.6, 128.8 (each t, aryl CH), 136.4 (q, 1 C, aryl C), 168.1, 169.7 (each q, 1 C, CO_2CH_2) ppm. IR (NaCl): $\tilde{\nu}$ = 3059, 2981, 2958, 2934, 2905, 1730, 1583, 1478, 1439, 1389, 1369, 1317, 1251, 1180, 1095, 1035, 842, 742, 697 cm^{-1}. GC-MS (70eV): *m*/*z* (%) = 366 (10.4) $[M]^+$. HR-EI-MS: calcd. 366.1321; found 366.1321.

Diethyl 3-[Dimethyl(phenyl)silyl]-3-(phenylthio)cyclopropane-*trans*-1,2-dicarboxylate (18b): Colorless oil. Yield 188 mg (22%) from **16**. ^{1}H NMR (200 MHz): δ = 0.00, 0.13 (each s, 3 H, $SiCH_3$), 0.77, 0.88 (each t, J = 7.1 Hz, 3 H, OCH_2CH_3), 2.30, 2.46 (each d, J = 6.3 Hz, 1 H, CH cyclopropane), 3.51, 3.76 (each q, J = 7.1 Hz, 2 H, OCH_2CH_3) 6.74–7.21 (m, 10 H, aryl H) ppm. ^{13}C NMR (50 MHz): δ = –2.8, –1.5 (each p, 1 C, $SiCH_3$), 13.9, 14.3 (each p, 1 C, OCH_2CH_3), 27.7 (q, 1 C, SCSi), 33.4, 34.9 (each t, 1 C, CH cyclopropane), 61.2, 61.3 (each s, 1 C, OCH_2CH_3), 125.9, 127.5, 128.5, 129.1, 129.3, 134.3 (each t, aryl CH), 136.2, 136.5 (each q, 1 C, aryl C), 167.9, 169.3 (each q, 1 C, CO_2CH_2) ppm. IR (NaCl): $\tilde{\nu}$ = 2980, 2905, 1730, 1583, 1478, 1439, 1428, 1388, 1368, 1318, 1251, 1182, 1113, 1035, 837, 817, 779, 737, 700 cm^{-1}. GC-MS (70eV): *m*/*z* (%) = 383 (16.6) $[M – 45]^+$. HR-EI-MS: calcd. for $[M – OEt]^+$: 383.1137; found 383.1137.

Cyclopropanedicarboxylate 18a from Diazo Compound 9a and Maleate 16: BuLi in hexanes (1.6 M, 3.2 mL, 5.1 mmol) was added dropwise at –78 °C to **8a** (0.23 g, 4.25 mmol) in diethyl ether (20 mL).

After the mixture had been stirred for 45 min, benzenesulfenyl chloride[32] (0.8 g, 5.5 mmol) was added slowly, and stirring was continued for 10 min. Ester **16** (4 mL, 24.7 mmol) was added, and the reaction mixture was allowed to warm to room temp., which was accompanied by considerable nitrogen evolution. The reaction mixture was then poured into water, and the aqueous phase was extracted with diethyl ether (2×). The combined organic phases were dried (Na_2SO_4), and the solvent was removed in vacuo. The product isolated by flash chromatography was in all respects identical with cyclopropanedicarboxylate **18a** obtained above from **12a** and **16**. Yield 42%.

(*Z*)-1,4-Diphenylbut-2-ene [(*Z*)-20]: This compound was prepared according to a procedure analogous to that described in ref.[39] DIBAL-H in toluene (20% by weight, 18.16 mL, 21.57 mmol) was added dropwise at –20 °C to alkyne **19** (2.670 g, 12.92 mmol). The reaction mixture was then kept at 55 °C for 16 h. After the mixture had been cooled to 0 °C, methanol (2.5 mL) was added carefully, followed by diluted H_2SO_4 (2 mL). This resulted in solidification of the reaction mixture. The product was thoroughly extracted with diethyl ether, and the organic phase was washed with water, saturated aqueous $NaHCO_3$, and again with water. The combined organic phases were dried (Na_2SO_4), and the solvents were evaporated in vacuo to give a colorless liquid (2.462 g, 91%). ^{1}H NMR (200 MHz): δ = 3.52 (d, J = 5.5 Hz, 4 H, CH_2), 5.71 (ddd, J = 5.8, 4.6, 1.2 Hz, 2 H, CH=CH), 7.15–7.34 (m, 10 H, H aryl) ppm. ^{13}C NMR (50 MHz): δ = 33.5 (s, 2 C, CH_2), 126.0 (t, 2 C, CH=CH), 128.4, 128.5, 129.1 (each t, aryl CH), 140.8 (q, 2 C, aryl C) ppm. IR (NaCl): $\tilde{\nu}$ = 3084, 3062, 3026, 2910, 2844, 1945, 1601, 1494, 1453, 1396, 1287, 1182, 1155, 1109, 1074, 1030, 901, 834, 736, 697 cm^{-1}.

(*E*)-1,4-Diphenylbut-2-ene [(*E*)-20]: This compound was obtained from diene **22** by reduction with sodium essentially as described in ref.[40] Yield 2.15 g (71%; ref.[40] 92%) from 3.00 g (14.54 mmol) of **22**. M.p. 41 °C (ref.[40] 43–45 °C).

Epimeric 2,3-Dibenzyl-1-(phenylthio)-1-(trimethylsilyl)cyclopropanes (21) from Carbanion 1c. General Procedure: BuLi in hexanes (1.6 M, 2.3 mL, 3.68 mmol) was added dropwise at –78 °C to protonated **1c** (1.000 g, 3.28 mmol) in absolute THF (10 mL), and the mixture was stirred for 40 min. It was then allowed to warm to 0 °C over 1 h and kept at this temperature for another 30 min. Phenyloxirane (0.39 mL, 3.41 mmol) and (*Z*)- or (*E*)-**20** (1.60 g, 7.68 mmol) were then added. After having been stirred at room temp. for 2 d, the reaction mixture was diluted with diethyl ether (50 mL) and washed with water (4×25 mL). The organic phase was dried (Na_2SO_4), and the solvents were removed in vacuo. Flash chromatography gave the following products.

(1α,2α,3α)-2,3-Dibenzyl-1-(phenylthio)-1-(trimethylsilyl)cyclopropane from (*Z*)-20: Yield 224 mg (17%). Colorless oil. The same product was obtained from chloromethylsilane **12a** (138.5 mg, 0.6 mmol) and (*Z*)-**20** (250 mg, 1.2 mmol) by the general procedure of Scheme 4, but with lithium tetramethylpiperidide as base at room temp. Yield 24 mg (10%). ^{1}H NMR (400 MHz): δ = 0 (s, 9 H, $SiCH_3$), 1.82 (ddd, J = 6.7, 4.6, 2.2 Hz, 2 H, CH cyclopropane), 3.19 (ddd, J = 15.2, 4.6, 2.2 Hz, 4 H, CH_2Ph), 7.21–7.45 (m, 15 H, aryl H) ppm. ^{13}C NMR (100 MHz): δ = –2.3 (p, 3 C, $SiCH_3$), 19.0 (q, 1 C, C cyclopropane), 27.4 (t, 2 C, CH cyclopropane), 30.7 (s, 2 C, CH_2Ph), 124.4, 125.9, 126.7, 128.2, 128.3, 128.7 (each t, aryl CH), 138.2, 141.2 (each q, aryl C) ppm. IR (NaCl): $\tilde{\nu}$ = 3061, 3027, 2954, 2898, 1602, 1583, 1495, 1478, 1454, 1439, 1250, 1085, 1073, 1026, 980, 879, 837, 737, 697 cm^{-1}. GC-MS (70eV): *m*/*z* (%) = 402 (3) $[M]^+$, 311 (100) $[M - Bn]^+$, 237 (11), 219 (59), 91 (30) $[Bn]^+$, 73 (77) $[SiCH_3]^+$, 65 (12) $[C_5H_5]^+$. HR-EI-MS: calcd: 402.1837; found 402.1836.

(1α,2α,3β)-2,3-Dibenzyl-1-(phenylthio)-1-(trimethylsilyl)cyclopropane from (*E*)-20: Yellow oil. Crude yield 180 mg (GC purity 73%, yield 10%). For full characterization the product was oxidized to the sulfone **23**.

(1α,2α,3β)-2,3-Dibenzyl-1-(phenylsulfonyl)-1-(trimethylsilyl)cyclopropane (23): *m*-CPBA (170 mg, 0.99 mmol) in CH_2Cl_2 (2 mL) was added dropwise at –20 °C to (1α,2α,3β)-**21** (104 mg, 0.26 mmol) in CH_2Cl_2 (2 mL). The mixture was allowed to warm slowly to room temp. and stirred for 1 d. It was then washed with saturated aque-

Table 1. X-ray data for compounds **4a**, **11a**, **15**, and **23**.

Parameter	**4a**	**11a**	**15**	**23**
Empirical formula	$C_{18}H_{22}SSi$	$C_{18}H_{22}SSi$	$C_{20}H_{28}S_2Si_2$	$C_{26}H_{30}O_2SSi$
Formula mass	298.51	298.51	388.72	434.65
Crystal system	orthorhombic	triclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P1$	$P2_1/c$	$P2_1/c$
Temperature [K]	223(2)	293	223(2)	153
Absorption coefficient μ [mm^{-1}]	0.25	0.248	0.356	0.208
Crystal size [mm]	0.5×0.3×0.25	0.38×0.27×0.19	0.4×0.4×0.15	0.45×0.24×0.22
Angle range [°]	2.60–26.37	1.73–27.53	2.56–26.36	1.95–28.02
Lattice parameters				
a [Å]	6.3186(5)	6.403(10)	6.4989(4)	7.5703(5)
b [Å]	14.4362(9)	11.775(10)	19.079(1)	27.540(2)
c [Å]	18.613(2)	12.280(10)	9.0728(6)	11.3397(7)
α [°]	90	74.14	90	90
β [°]	90	80.96	105.258(5)	94.213(1)
γ [°]	90	75.29	90	90
Cell volume V [Å^3]	1697.9(2)	857.58(10)	1085.3(1)	2357.8(3)
Formula units Z	4	2	2	4
Calculated density [g cm^{-3}]	1.168	1.156	1.189	1.224
Measured reflections	16152	9835	10951	5561
Independent reflections	3469	3932	2203	4466
$R1$ [$I > 2\sigma(I)$]	0.027	0.0458	0.0324	0.0366
$wR2$ [$I > 2\sigma(I)$]	0.060	0.1236	0.0717	0.0955
Goodness of fit on F^2	1.041	0.961	1.128	0.995
CCDC-	713344	713435	713345	714156

ous $NaHCO_3$ (3×) and dried ($MgSO_4$). The solvent was evaporated in vacuo, and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 50:1) to give a colorless solid (100 mg, 88%). M.p. 138 °C. ^{1}H NMR (400 MHz): δ = –0.07 (s, 9 H, $SiCH_3$), 1.76 (ddd, J = 8.8, 7.4, 4.9 Hz, 1 H, CH cyclopropane), 2.55 (dd, J = 14.0, 9.5 Hz, 1 H, CH_2Ph), 2.68 (ddd, J = 9.4, 7.3, 5.2 Hz, 1 H, CH cyclopropane), 2.98 (dd, J = 13.9, 5.1 Hz, 1 H, CH_2Ph), 3.26 (dd, J = 14.6, 8.9 Hz, 1 H, CH_2Ph), 3.35 (dd, J = 14.7, 4.9 Hz, 1 H, CH_2Ph), 7.04–7.23 (m, 10 H, aryl H), 7.44–7.50 (m, 2 H, aryl H), 7.53–7.59 (m, 1 H, aryl H), 7.80–7.84 (m, 2 H, aryl H) ppm. ^{13}C NMR (100 MHz): δ = 0.78 (p, 3 C, $SiCH_3$), 34.1 (s, 1 C, CH_2Ph), 35.0, 35.6 (each t, 1 C, CH cyclopropane), 35.7 (s, 1 C, CH_2Ph), 41.3 (q, 1 C, C cyclopropane), 126.0, 126.5, 127.8, 128.4, 128.6, 128.9, 133.0 (each t, aryl CH), 139.7, 141.1, 143.2 (each q, 1 C, aryl C) ppm. IR (KBr): $\tilde{\nu}$ = 3026, 2965, 2908, 1600, 1494, 1455, 1444, 1411, 1283, 1253, 1145, 1098, 1083, 1014, 969, 921, 903, 843, 800, 751, 736, 725, 700, 689, 646, 625 cm^{-1}. MS (70eV): *m/z* (%) = 343 (73) $[M – Bn]^+$, 327 (88), 199 (35), 183 (27), 135 (85), 104 (70) $[C_8H_8]^+$, 91 (63) $[Bn]^+$, 73 (100) $[SiCH_3]^+$. HR-ESI-MS: calcd. 498.1899 $[M + Na + CH_3CN]^+$; found 498.1902.

X-ray Structural Investigation of Products 4a, 11a, 15, and 23: A suitable single crystal of each of the title compounds was selected under a polarization microscope and mounted in a glass capillary (d = 0.5 mm). The crystal structures were determined by X-ray diffraction analysis. Single-crystal intensity data were collected for **4a** and **15** by use of a STOE IPDS II instrument and for **11a** and **23** by use of an Enraf–Nonius Kappa CCD fitted with a rotating anode (Mo-K_α radiation, λ = 0.71073 Å) [T as given in Table 1]. The crystal structures were solved by direct methods by use of SHELXS-97 and refined by use of alternating cycles of least-squares refinements against F^2 (SHELXL-97).[41] All non-H atoms were located in difference Fourier maps and were refined with anisotropic displacement parameters. The H positions were determined by a final difference Fourier synthesis. The resulting parameters are reported in Table 1. CCDC-713344 (**4a**), -713345 (**15**), -713435 (**11a**), and -714156 (**23**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Calculations: Optimized geometries of singlet and triplet **5d** were calculated at the B3LYP level[30,42,43] with employment of Dunning's cc-pVTZ basis set.[44] A spin-unrestricted formalism was used. All DFT calculations were carried out with Gaussian 03.[45] The natures of the stationary points were assessed by means of vibrational frequency analysis.

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