Synthesis of 1,3-Difunctionalized Cyclopentenes and 1,3,5-Trifunctionalized Cyclohexanes by Silicon-Induced Domino Reactions

Frank Tries[a] and Ernst Schaumann*[a]

Dedicated to Professor Lutz F. Tietze on the occasion of his 60th birthday

Keywords: Carbocycles / Domino reactions / Michael-type additions / Oxiranes / Silicon-stabilized carbanions

A novel domino process based on a 1,4-C→O shift of a silyl group (**4** → **3**) and a Michael-induced ring-closure reaction (**3** → **2**) is investigated. Specifically, attack of carbanions **5** on vinyloxiranes **6** usually occurs on the oxirane unit to give the desired silyl shift. When starting from vinyloxiranes **6a** and **6b**, however, the reaction stops at this stage to give silyl ethers **7**. Sulfur (**6c**) or silicon activation (**6d**–**f**) of the C=C unit is required to yield cyclopentenes **1a**–**d**. Analogously, carbanion **5a** and allyloxiranes **15** give cyclization products **19**–**22**, particularly if the ring-closure step is supported by silicon substitution.

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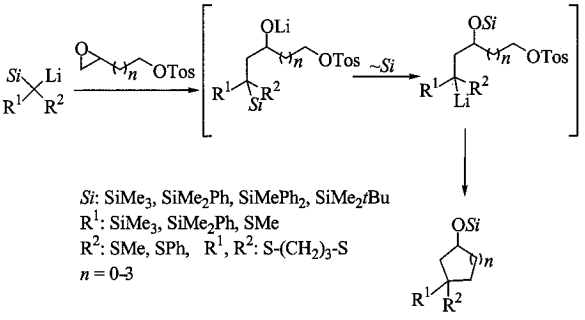
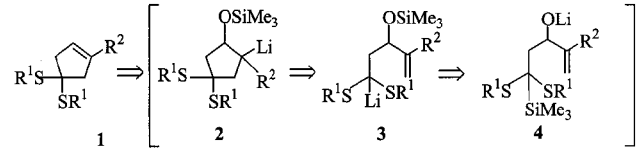
Introduction

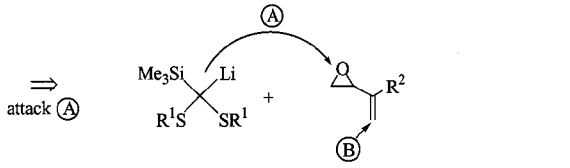
The reaction between silyl-stabilized carbanions and (ω,ω−1)-epoxyalkyl tosylates turned out to provide an elegant domino synthesis[1] of cyclobutanes,[2] cyclopentanes, and larger carbocycles (Scheme 1).[3] Similarly, bis(epoxides) can be employed as bis(electrophiles)[4] and ω-bromoalkyl isocyanates afford N-heterocycles.[5] This shows that both the *exo-tet* and *endo-tet* ring-closure modes are possible in the final cyclization step. We now report on a novel extension of the domino process in which the crucial cyclization step obeys the 5-*endo*-*trig* mode, as shown for the five-membered ring as target in Scheme 2. By analogy with the chemistry in Scheme 1, the idea was to use silylated thioacetals **5** as masked dianions, but to employ vinyloxiranes **6** as bis(electrophiles). Oxirane ring-opening to give **4** should be followed by 1,4-C→O silicon migration[6] to yield silyl ether **3**. The subsequent cyclization step, an intramolecular Michael-type addition, should provide cyclopentane **2**, which may be regarded as a formal intermediate of a Peterson olefination starting from a 5-silylalkanal.[7] Consequently, cyclopentenes **1** should be the final products. However, this reasoning is hampered by inherent questions. Is it possible to control the chemoselectivity of primary attack according to pathway A through a suitable choice of substituent R^2 (Scheme 2)? If so, will the



Scheme 1



(see Schemes 4,5)



Scheme 2

[a] Institut für Organische Chemie, Technischen Universität Clausthal,
Leibnizstraße 6, 38678 Clausthal-Zellerfeld, Germany
Fax: (internat.) + 49-5323/722858
E-mail: ernst.schaumann@tu-clausthal.de

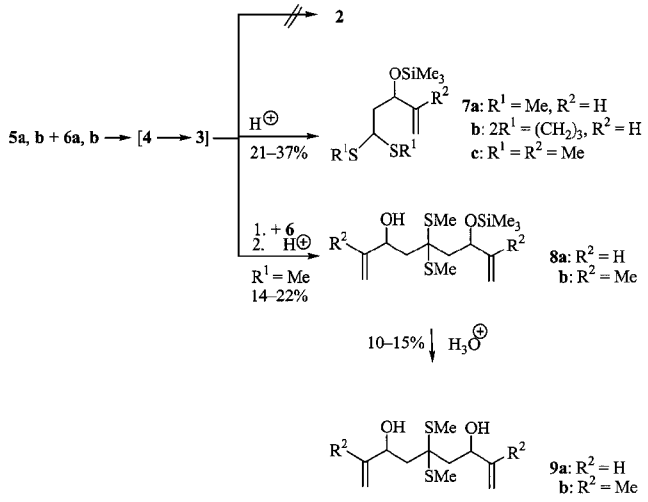
cyclization step **3** → **2** be possible, as it is generally considered a disfavored process for five-membered ring systems?[8] However, examples have been reported for a 5-*endo-trig* process occurring under surprisingly mild conditions.[8c,9]

Use of Non-Activated Vinyloxiranes 6a and 6b

The desired chemoselectivity (pathway A in Scheme 2) should be secured if the olefinic bond in **6** is not activated toward nucleophilic attack, as in the parent vinyloxirane **6a** and its homologue **6b**. Actually, oxiranes **6a** and **6b** undergo smooth reactions with carbanions **5a** and **5b**. Careful hydrolytic workup affords a product mixture in which silyl ether **7** predominates. This is the protonated form of intermediate **3**; the presence of **3** is also documented by isolation of bis-(adduct) **8** and its desilylated congener **9**, the result of addition of a second equivalent of oxirane **6** to carbanion **3**. It can therefore be concluded that the reaction course follows the desired pathway A (Scheme 2): exclusive attack of **5** on the oxirane unit in **6**. Moreover, by analogy with the chemistry in Scheme 1, the resulting intermediate **2** undergoes the 1,4-C→O silyl shift to silyl ether **3**. However, there is no trace of a product that could be derived from cyclization of **3** to a cyclopentene **2**. At this point it is an open question whether the failure of **3** with R^2 = H, Me to cyclize is due to a lack of activation of the C=C bond for an intramolecular Michael-type addition or to the inherent problem of a 5-*endo-trig* process. Further vinyloxiranes **6** with activating groups therefore had to be investigated.

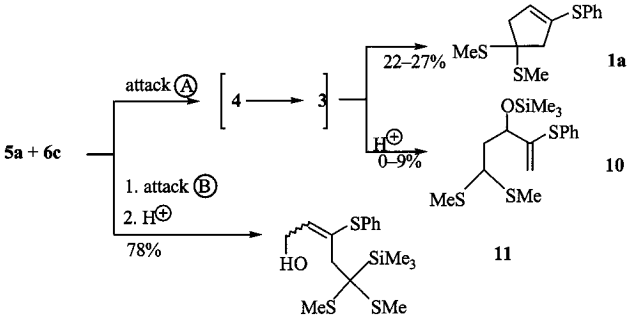
Use of Sulfur- or Silicon-Activated Vinyloxiranes 6c−f

Because of the required chemoselective attack on the oxirane unit in **6**, strongly electron-withdrawing groups R^2 have to be excluded. However, vinyloxiranes **6c−f** with phenylthio or silyl substituents in the R^2 position have recently become accessible[10] and appear to be ideally suited as building blocks in the novel domino process (Scheme 2).



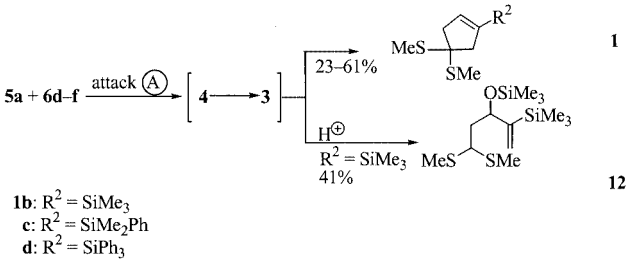
Scheme 3

The sulfur-substituted oxirane **6c** turned out to show moderate chemoselectivity in the reaction with carbanion **5a** (Scheme 4). The main product is alkenol **11**, obviously the result of primary attack on **6c** as in pathway B (cf. Scheme 2) and subsequent opening of the oxirane ring in the intermediate Michael-type adduct. However, the second product, cyclopentene **1a**, originates from the anticipated novel domino process and confirms the feasibility of the sequence of oxirane opening, silicon migration, Michael-induced ring-closure, and final Peterson olefination (cf. Scheme 2). As with oxiranes **6a** and **6b** as starting materials, a certain reluctance to undergo the final cyclization step can be seen in the detection of small amounts of silyl ether **10** in some experiments.



Scheme 4

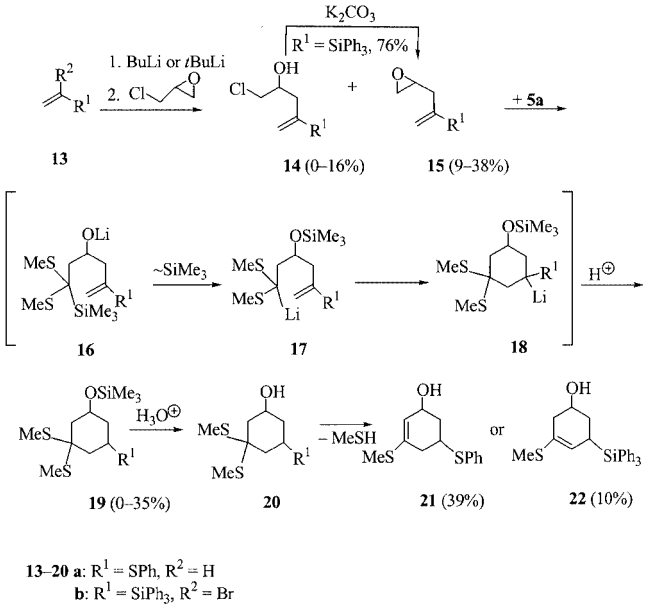
In contrast to sulfur derivative **6c**, the presence of a silicon substituent R^2 − as in **6d−f** − produces a complete shift of the reaction to pathway A (cf. Scheme 2). Cyclopentenes **1** are isolated in all cases; only for TMS derivative **6d** is the activation of the C=C unit for intramolecular nucleophilic attack so moderate that silyl ether **12** is isolated (cf. formation of **7** in Scheme 3). Thus, phenyl-substituted silyl groups R^2 offer the perfect solution for cyclopentene synthesis in the domino process (Scheme 5).



Scheme 5

Use of Allyloxiranes 15 To Give Cyclohexanes 19−22

The domino process should be amenable to the synthesis of other functionalized carbocycles. This was demonstrated by the extension of the approach to cyclohexane synthesis



Scheme 6

(Scheme 6). The required starting materials are allyloxiranes **15**, which can be obtained by a modification of a published procedure.[11] The key step is an alkylation of lithiated alkenes **13** by epichlorohydrin. In the silicon case, this produces a mixture of chloroalkanol **14b** and oxirane **15b**, but complete conversion into the oxirane can be achieved by treatment with potassium carbonate.

The silicon-substituted allyloxirane **15b** gives the desired domino process to afford functionalized cyclohexane **19b**. Thus, by analogy with cyclopentene synthesis (Scheme 2), the reaction with anion **5a** is initiated by chemoselective oxirane ring-opening to give **16b**, followed in situ by silyl migration to **17b** and intramolecular Michael addition to give **18b**. Workup gives cyclohexane **19b**, along with desilylated material **20b**; interestingly, partial loss of methanethiol is also observed and confirmed by isolation of cyclohexene **22**. Here, the regioselectivity of thiol elimination was determined by means of NMR experiments (cf. Exp. Sect.).

The reaction between the sulfur-substituted allyloxirane **15a** and carbanion **5a** gives a complex reaction mixture in which cyclohexane **19a** is probably present, but only elimination product **21** could be characterized. This result underlines the greater utility of the silicon-activated oxiranes also in cyclohexane synthesis, including the option of the use of optically active epichlorohydrins to give enantiopure **19b** and congeners.

Experimental Section

General: NMR: Bruker DPX 200 (200 MHz) or ARX 400 (400 MHz); solvent $CDCl_3$ unless stated otherwise, with TMS as internal standard; coupling constants *J* are given in Hz; assignments of ^{13}C NMR signals were supported by broadband-decoupled DEPT. IR: Bruker Vektor 22 or Pye-Unicam SP3-200 spectrometers. All experiments were performed under dry N_2. THF was distilled from sodium benzophenone ketyl prior to use. CH_2Cl_2 was distilled from CaH_2. Column chromatography: Merck silica gel (70−230 mesh). Petroleum ether (PE), boiling range 60−70 °C, was always used in the separations. Analytical TLC: Merck silica gel 60 PF_{254} plates (visualization with UV light or 4-methoxybenzaldehyde spray reagent). Melting points are uncorrected. Elemental analyses: Institut für Pharmazeutische Chemie, TU Braunschweig. Protonated **5a**, **5b**[12] vinyloxiranes **6b**,[13] **6c**−**f**,[10] and (1-bromovinyl)(triphenyl)silane (**13b**)[14] were prepared according to literature procedures. Vinyloxirane (**6a**) and vinyl sulfide **13a** were commercially available.

Synthesis of Carbocycles by the Silicon-Induced Domino Reaction. General Procedure: A solution of dithioacetal **5** (1.2 equiv.) in dry THF (3 mL/mmol) was cooled to −78 °C. *n*BuLi (1.6 M solution in hexane, 1.1 equiv.) and TMEDA (1.2 equiv.) were then added, and the solution was allowed to warm to 0 °C over 2 h. This temperature was maintained for 1 h, and the mixture was again cooled to −78 °C. To this mixture, **6** or **15** (1.0 equiv.) in dry THF (20 mL/mmol) was added dropwise. The yellow reaction mixture was allowed to warm to room temperature over 12 h. For workup, it was hydrolyzed with a mixture of diethyl ether/saturated NH_4Cl solution (1:1). The aqueous phase was separated and extracted twice with diethyl ether. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo.

Reaction of Dithioacetal 5a with Vinyloxirane (6a): Protonated **5a** (260 mg, 1.2 mmol) and vinyloxirane (**6a**; 70 mg, 1.0 mmol) gave three fractions after purification by flash chromatography (eluent PE → PE/ethyl acetate, 20:1 → 10:1 → 5:1 → 1:1).

First Fraction. 5,5-Bis(methylthio)-3-(trimethylsiloxy)pent-1-ene (7a): Yield 92 mg (37%), yellow oil. IR (film): $\tilde{\nu}$ = 1643 (C=C), 1423, 1251, 842 ($SiMe_3$), 1083, 1027, 926, 753 cm^{-1}. ^1H NMR (200 MHz): δ = 0.12 (s, 9 H, $SiMe_3$), 1.80 (dd, ^3J = 4.6, ^3J = 9.4, 1 H, CH_2), 1.91 (dd, ^3J = 5.4, ^3J = 8.6, 1 H, 4-CH_2), 2.08 (s, 3 H, SMe), 2.09 (s, 3 H, SMe), 3.73 [dd, ^3J = 5.4, ^3J = 9.4, 1 H, C*H*$(SMe)_2$], 4.41 (m, 1 H, CHOSi), 5.06 (dt, ^2J = 1.2, ^4J = 1.2, ^3J = 10.4, 1 H, olef. CH_2), 5.19 (dt, ^2J = 1.2, ^4J = 1.2, ^3J = 17.2, 1 H, olef. CH_2), 5.79 (ddd, ^3J = 6.4, ^3J = 10.4, ^3J = 17.2, 1 H, olef. CH) ppm. ^{13}C NMR (50 MHz): δ = 140.8 (olef. CH), 114.6 (olef. CH_2), 71.3 (CHOSi), 42.7 (4-CH_2), 50.5 [*C*H$(SMe)_2$], 12.5, 12.1 (2 SMe), 0.3 ($SiMe_3$) ppm.

Second Fraction. 5,5-Bis(methylthio)-7-(trimethylsiloxy)nona-1,8-dienol (8a): Yield 35 mg (14%), yellow oil. IR (film): $\tilde{\nu}$ = 3448 (OH), 1643 (C=C), 1422, 1252, 1083, 923, 842 ($SiMe_3$), 753, 676 cm^{-1}. ^1H NMR (200 MHz): δ = 0.1 (s, 9 H, $SiMe_3$), 1.75 (m, 1 H, CH_2), 1.86 (dd, ^3J = 9.6, ^2J = 15.2, 1 H, CH_2), 1.95 (s, 3 H, SMe), 2.10 (s, 3 H, SMe), 2.25 (dd, ^3J = 8.8, ^2J = 15.2, 2 H, CH_2), 4.02 (d, ^2J = 1.6, 1 H, OH), 4.65 (m, 2 H, C*H*OH, CHOSi), 5.04 (dd, ^4J = 1.2, ^3J = 10.0, 1 H, olef. CH_2), 5.08 (dd, ^4J = 1.2, ^3J = 9.2, 1 H, olef. CH_2), 5.15 (dt, ^4J = 1.2, ^3J = 17.2, 1 H, olef. CH_2), 5.29 (dt, ^4J = 1.6, ^3J = 17.2, 1 H, olef. CH_2), 5.82 (ddd, *J* = 5.2, ^3J = 10.0, *J* = 16.8, 1 H, olef. CH), 5.87 (ddd, *J* = 7.2, *J* = 10.2, *J* = 17.2, 1 H, olef. CH) ppm. ^{13}C NMR (50 MHz): δ = 142.0, 140.1 (olef. CH), 114.3, 114.1 (olef. CH_2), 72.3, 69.9 (CHO), 61.7 [*C*$(SMe)_2$], 42.7, 41.5 (CH_2), 11.9, 10.7 (SMe), 0.7 ($SiMe_3$) ppm.

Third Fraction. 5,5-Bis(methylthio)nona-1,8-diene-3,7-diol (9a): Yield 26 mg (10%), yellow oil. IR (film): $\tilde{\nu}$ = 3281 (OH), 1644 (C=C), 1423, 993, 922, 733 cm^{-1}. ^1H NMR (200 MHz): δ = 1.82 (d, ^2J = 15.6, 2 H, 2 CH_2), 2.01 (s, 6 H, 2 SMe) 2.27 (dd, ^3J = 9.4, ^2J = 15.6, 2 H, 2 CH_2), 3.76 (s, 2 H, 2OH), 4.60 (m, 2 H, 2 C*H*OH), 5.08 (dt, ^2J = 1.2, ^4J = 1.2, ^3J = 10.4, 2 H, 2 olef. CH_2), 5.86 (ddd, ^3J = 6.0, ^3J = 10.4, ^3J = 16.8, 2 H, 2 olef. CH_2) ppm. ^{13}C NMR

(50 MHz): δ = 141.0 (2 olef. CH), 114.3 (2 olef. CH_2), 70.0 (2 CHOH), 62.1 [*C*$(SMe)_2$], 41.9 (2 CH_2), 11.2 (2 SMe) ppm.

2-[2-(Trimethylsiloxy)but-3-enyl]-1,3-dithiane (7b): Yield 61 mg (23%) from the reaction between protonated **5b** (230 mg, 1.2 mmol) and oxirane **6a** (70 mg, 1.0 mmol) after purification by flash chromatography (eluent PE → PE/ethyl acetate stepwise to 1:1), yellow oil. IR (film): $\tilde{\nu}$ = 1644 (C=C), 1422, 1251, 1128, 1082, 1027, 994, 931, 883, 843 ($SiMe_3$), 754 cm^{-1}. ^1H NMR (200 MHz): δ = 0.13 (s, 9 H, $SiMe_3$), 1.80−1.92 (m, 2 H, CH_2), 2.72−2.90 [m, 6 H, $S(CH_2)_3S$], 4.04 (dd, ^3J = 6.0, ^3J = 8.6, 1 H, CHS), 4.38 (m, CHOSi), 5.06 (dt, $^2J = {}^4J$ = 1.4, ^3J = 10.4, 1 H, olef. CH_2), 5.20 (dt, $^2J = {}^4J$ = 1.4, ^3J = 17.2, 1 H, olef. CH_2), 5.79 (ddd, ^3J = 6.2, ^3J = 10.4, ^3J = 17.2, 1 H, olef. CH) ppm. ^{13}C NMR (50 MHz): δ = 140.6 (olef. CH), 114.6 (olef. CH_2), 70.1 (CHOSi), 43.5 (CHS), 43.2 (CH_2), 31.0, 30.2, 29.8 [$S(CH_2)_3S$] ppm.

Reaction between Thioacetal 5a and Oxirane 6b: Protonated **5a** (216 mg, 1.2 mmol) and **6b** (84 mg, 1.0 mmol) reacted to give three fractions after flash chromatography (eluent PE → PE/ethyl acetate, 40:1 → 20:1 → 10:1 → 5:1 → 1:1).

First Fraction. 2-Methyl-5,5-bis(methylthio)-3-(trimethylsiloxy)pent-1-ene (7c): Yield 55 mg (21%), yellow oil. IR (film): $\tilde{\nu}$ = 1650 (C=C), 1436, 1252, 842 ($SiMe_3$), 1087, 751 cm^{-1}. ^1H NMR (200 MHz): δ = 0.11 (s, 9 H, $SiMe_3$), 1.69 (s, 3 H, CCH_3), 1.81 (dd, ^3J = 4.4, ^3J = 9.4, 1 H, CH_2), 1.92 (dd, ^3J = 5.4, ^3J = 8.8, 1 H, CH_2), 2.07, 2.10 (s, 3H each, SMe), 3.71 [dd, ^3J = 5.4, ^3J = 9.4, 1 H, C*H*$(SMe)_2$], 4.39 (dd, ^3J = 4.4, ^3J = 8.8, 1 H, CHOSi), 4.80, 4.93 (each d, *J* = 1.4, 1 H, olef. CH_2) ppm. ^{13}C NMR (50 MHz): δ = 147.2 (olef. C), 111.3 (olef. CH_2), 74.0 (CHOSi), 50.9 [*C*H$(SMe)_2$], 41.2 (CH_2), 17.1 (CH_3), 12.8, 11.9 (SMe), 0.1 ($SiMe_3$) ppm.

Second Fraction. 2,8-Dimethyl-5,5-bis(methylthio)-7-(trimethylsiloxy)nona-1,8-dien-3-ol (8b): Yield 76 mg (22%), yellow oil. IR (film): $\tilde{\nu}$ = 3447 (OH), 1650 (C=C), 1438, 1372, 1252, 1091, 1010, 972, 947, 901, 842 ($SiMe_3$), 753, 689 cm^{-1}. ^1H NMR (200 MHz): δ = 0.07 (s, 9 H, $SiMe_3$), 1.66−1.78 (m, 1 H, CH_2), 1.72 (s, 3 H, CCH_3), 1.77 (s, 3 H, CCH_3), 1.95−2.01 (m, 1 H, CH_2), 1.98 (s, 3 H, SMe), 2.11 (dd, ^3J = 2.0, ^2J = 15.2, 1 H, CH_2), 2.12 (s, 3 H, SMe), 2.30 (dd, ^3J = 10.0, ^2J = 15.2, 1 H, CH_2), 3.90 (d, ^3J = 1.6, 1 H, OH), 4.60 (m, 2 H, C*H*OH, CHOSi), 4.77 (t, $^2J = {}^4J$ = 1.6, 1 H, olef. CH_2), 4.82 (t, *J* = 1.6 Hz, 1 H, olef. CH_2), 4.92 (t, *J* = 1.0 Hz, 1 H, olef. CH_2), 4.98 (t, *J* = 1.0 Hz, 1 H, olef. CH_2) ppm. ^{13}C NMR (50 MHz): δ = 148.6, 146.8 (olef. C), 111.3, 111.2 (olef. CH_2), 74.7, 73.0 (CHOH, CHOSi), 61.8 [*C*$(SMe)_2$], 41.8, 40.5 (CH_2), 18.0, 17.1 (CCH_3), 12.0, 10.9 (SMe), 0.3 ($SiMe_3$) ppm.

Third Fraction: 2,8-Dimethyl-5,5-bis(methylthio)nona-1,8-diene-3,7-diol (9b): Yield 40 mg (15%), yellow oil. IR (film): $\tilde{\nu}$ = 3281 (OH), 1644 (C=C), 1423, 993, 922, 733 cm^{-1}. ^1H NMR (200 MHz): δ = 1.74 (s, 6 H, 2 CCH_3), 1.77 (broad d, ^2J = 15.8, 1H of each CH_2), 2.0 (s, 6 H, 2 SMe), 2.31 (dd, ^3J = 9.6, ^2J = 15.8, 1 H of each CH_2), 3.90 (s, 2 H, 2OH), 4.57 (broad d, ^3J = 9.6, 2 H, 2 CHOH), 4.79 (t, $^2J = {}^4J$ = 1.4, 1 H of each olef. CH_2), 4.97 (broad s, 1 H of each olef. CH_2) ppm. ^{13}C NMR (50 MHz): δ = 147.9 (olef. C), 110.8 (olef. CH_2), 72.7 (CHOH), 62.9 [o, $C(SMe)_2$], 40.7 (CH_2), 17.7 (CCH_3), 11.2 (SMe) ppm.

Reaction between Thioacetal 5a and Oxirane 6c: The reaction between protonated **5a** (108 mg, 0.6 mmol) and **6c** (89 mg, 0.5 mmol) gave two fractions after flash chromatography (eluent PE → PE/ethyl acetate, 40:1 → 5:1).

First Fraction: 4,4-Bis(methylthio)-1-(phenylthio)cyclopent-1-ene (1a): Yield 30 mg (22%), yellow oil. IR (film): $\tilde{\nu}$ = 1607, 1582 (C=C), 1477, 1436, 1250, 1092, 746, 693 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.78 (s, 6 H, SMe), 2.59, 2.60, 2.80, 2.81 (m, 1 H each, 2 CH_2), 5.56 (m, 1 H, olef. CH), 6.90−7.06 (m, 3 H, SPh), 7.40−7.48 (m, 2 H, SPh) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 134.4, 133.7 (arom. C, olef. C), 131.1, 130.1, 129.3, 128.3, 127.1 (olef. CH, arom.CH), 63.1 (*C*SMe), 50.3, 48.4 (2 CH_2), 12.9 (2 SMe) ppm.

Second Fraction. 5,5-Bis(methylthio)-3-(phenylthio)-5-(trimethylsilyl)pent-2-en-1-ol (11): 140 mg (78%), yellow oil, isomer mixture (3.6:1*). Assignment to the *cis* and *trans* forms was not possible. IR (film): $\tilde{\nu}$ = 3365 (OH), 1623, 1582 (C=C), 1248, 843 ($SiMe_3$), 1022, 744, 693 (Ph) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.17 (s, 9 H, $SiMe_3$), 0.22* (s, 9 H, $SiMe_3$*), 2.03 (s, 6 H, SMe), 2.17* (s, 6 H, SMe*), 2.72 (s, 2 H, CH_2), 2.84* (s, 2 H, CH_2*), 4.16* (d, ^3J = 7.8*, 2 H, CH_2OH), 4.38 (d, ^3J = 5.8, 2 H, CH_2OH), 5.62* (t, ^3J = 7.8, 1 H, olef. CH), 6.43 (t, ^3J = 5.8, 1 H, olef. CH), 7.13−7.45 (m, 5 H, arom. CH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.9, 133.4, 133.3*, 129.3*, 129.1, 128.1*, 126.2 (arom. CH, olef. CH), 137.8*, 135.6, 131.3, 130.8* (arom. C, olef. C), 61.2, 59.0* (CH_2OH), 47.6, 45.8* (*C*SMe), 43.5, 39.0* (CH_2), 12.9*, 12.0 (SMe), −0.9, −1.5* ($SiMe_3$) ppm. $C_{16}H_{26}OS_3Si$ (358.6): calcd. C 53.62, H 7.32, S 26.79; found C 54.92, H 7.65, S 26.59.

Independent Experiment. 5,5-Bis(methylthio)-2-(phenylthio)-3-(trimethylsiloxy)pent-1-ene (10): Yield 14 mg (9%), yellow oil. IR (film): $\tilde{\nu}$ = 1607, 1582 (C=C), 1477, 1436, 1250, 1092, 844 ($SiMe_3$), 746, 693 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.08 (s, 9 H, $SiMe_3$), 1.94−2.08 (m, 2 H, CH_2), 1.99, 2.06 (each s, 3 H, SMe), 3.71 [dd, ^3J = 5.0, ^3J = 10.0, 1 H, C*H*$(SMe)_2$], 4.47 (dd, ^3J = 3.6, ^3J = 8.8, 1 H, CHOSi), 4.82 (s, 1 H, olef. CH_2), 5.40 (d, *J* = 0.8 Hz, 1 H, olef. CH_2), 7.15−7.45 (m, 5 H, arom. CH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 149.3 (olef. C), 132.4 (arom. C), 129.3, 129.2, 127.1 (arom. CH), 116.4 (olef. CH_2), 72.6 (CHOSi), 50.9 (CHS), 42.3 (CH_2), 13.1, (SMe), 0.1 ($SiMe_3$) ppm.

Reaction between Thioacetal 5a and Oxirane 6d: Compound **6d** (71 mg, 0.5 mmol) and protonated **5a** (108 mg, 0.6 mmol) gave a yellow oil (90 mg) as a mixture of **1b** (23%) and **12** (41%) after flash chromatography (eluent PE/EE, 5:1) and circular chromatography (chromatotron).

4,4-Bis(methylthio)-1-(trimethylsilyl)cyclopent-1-ene (1b): IR (film): $\tilde{\nu}$ = 1435, 1422, 1249 ($SiMe_3$), 1081, 933, 839 ($SiMe_3$), 756, 691 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.19 (s, 9 H, $SiMe_3$), 1.43 (s, 4 H, CH_2), 2.03 (s, 6 H, SMe), 6.71 (t, ^3J = 6.4, 1 H, olef. CH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 144.9 (olef. CH), 135.7 (olef. C), 42.2, 40.2 (CH_2), 12.9, 11.7 (SMe), 0.8 ($SiMe_3$) ppm. GC-MS: *m*/*z* = 232 (0.5) [M^+], 211 (12), 185 (11) [M − SMe], 106 (10), 105 (26), 91 (43), 73 ($SiMe_3$, 100), 59 (10).

5,5-Bis(methylthio)-3-(trimethylsiloxy)-2-(trimethylsilyl)pent-1-ene (12): IR (film): $\tilde{\nu}$ = 1435, 1422, 1249 ($SiMe_3$), 1081, 933, 839 ($SiMe_3$), 756, 691 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.09, 0.13 (each s, 9 H, $SiMe_3$), 1.79 (dd, ^3J = 4.4, ^3J = 9.2, 1 H, CH_2), 1.82 (dd, ^3J = 5.2, ^3J = 8.6, 1 H, CH_2), 2.08, 2.09 (each s, 3 H, SMe), 3.75 [dd, ^3J = 5.2, ^3J = 9.2, 1 H, CH$(SMe)_2$], 4.57 (ddt, ^4J = 1.0, ^3J = 4.4, ^3J = 8.6, 1 H, CHOSi), 5.38 (dd, ^4J = 1.0, ^2J = 3.0, 1 H, olef. CH_2), 5.82 (dd, ^4J = 1.2, ^2J = 3.0, 1 H, olef. CH_2) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 154.6 (olef. C), 124.5 (olef. CH_2), 74.2 (CHOSi), 51.1 [*C*H$(SMe)_2$], 43.9 (CH_2), 12.6, 12.2 (SMe), −0.3, −0.9 ($SiMe_3$) ppm. GC-MS: *m*/*z* = 322 (3) [M], 249 (3) [M − $SiMe_3$], 248 (11), 233 (5) [M − $OSiMe_3$], 202 (19), 147 (35), 113 (23), 107 (21), 74 (13), 73 (100) [$SiMe_3$], 59 (13).

1-[Dimethyl(phenyl)silyl]-4,4-bis(methylthio)cyclopent-1-ene (1c): This compound was prepared from **6e** (98 mg, 0.48 mmol) and protonated **5c** (104 mg, 0.58 mmol), purification by flash chromatography (PE/ethyl acetate, 5:1) and circular chromatography (chromatotron, eluent PE). Yield 92 mg (65%), light yellow oil. IR (film): $\tilde{\nu}$ = 1597 (C=C), 1427, 1252 ($SiMe_2$), 1198, 1113 (C−O), 1039, 846 ($SiMe_2$), 830, 799, 773, 731, 700 (Ph) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.38 (s, 6 H, $SiMe_2$), 2.08 (s, 6 H, SMe), 2.80 (m, 2 H, CH_2), 2.86 (m, 2 H, CH_2), 6.00 (t, J = 2.0 Hz, 1 H, olef. CH), 7.33−7.40 (m, 3 H, arom. CH), 7.48−7.57 (m, 2 H, arom. CH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.9, 137.7 (arom. C, olef. C), 139.3, 133.8, 129.0, 127.8 (arom. CH, olef. CH), 133.8 (arom. C), 63.6 [*C*($SMe)_2$], 51.3, 50.2 (CH_2), 13.4 (SMe), −3.2 ($SiMe_2$) ppm. $C_{15}H_{22}S_2Si$ (294.1): calcd. C 61.21, H 7.54, S 21.74; found C 60.92, H 7.84, S 20.65.

4,4-Bis(methylthio)-1-(triphenylsilyl)cyclopent-1-ene (1d): This compound was prepared from **6f** (82 mg, 0.25 mmol) and **5a** (34 mg, 0.3 mmol); flash chromatography (PE/ ethyl acetate, 5:1) and circular chromatography (chromatotron, eluent PE). Yield 63 mg (61%) light brown crystals (m.p. 110−111 °C). IR (film): $\tilde{\nu}$ = 1591 (C=C), 1428, 1111, 909, 737, 702 cm^{-1} (Ph). ^1H NMR (200 MHz, $CDCl_3$): δ = 2.08 (s, 6 H, SMe), 2.89, 2.96 (each m, 2 H, CH_2), 6.09 (dd, ^3J = 2.0, ^3J = 2.0, 1 H, olef. CH), 7.36−7.45 (m, 9 H, arom. CH), 7.50−7.58 (m, 6 H, arom. CH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 144.5 (olef. CH), 137.7 (olef. C), 136.0, 129.6, 127.9 (arom. CH), 133.8 (arom. C), 64.2 [*C*($SMe)_2$], 51.7, 50.2 (CH_2), 13.4 (SMe) ppm. $C_{25}H_{26}S_2Si$ (418.1): calcd. C 71.75, H 6.27, S 15.29; found C 71.89, H 6.30, S 14.73.

General Procedure for the Preparation of Allyloxiranes 15b from Alkenes 13: An acceptor-substituted α-lithioethene (1.0 equiv.) in THF (2 mL/mmol) was treated dropwise at −78 °C (−30 °C for the sulfur compound) with epichlorohydrin (1.0 equiv.), dissolved in THF (3 mL/mmol). The reaction mixture was allowed to warm to room temperature over 12 h. For workup, it was hydrolyzed with a mixture of diethyl ether/saturated NH_4Cl solution (1:1). The aqueous phase was separated, extracted twice with diethyl ether, and washed with brine. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo.

Reaction between Vinyl Sulfide 13a and Epichlorohydrin: Compound **13a** (1.362 g, 10.0 mmol) and epichlorohydrin (925 mg, 10.0 mmol) gave 648 mg (48%) recovered **13a** and **15a** after flash chromatography (eluent PE → PE/ethyl acetate, 40:1 → 10:1.

1-(Oxiranylmethyl)vinyl Phenyl Sulfide (15a): Yield 733 mg (38%), yellow oil. IR (film): $\tilde{\nu}$ = 1610 (C=C), 1583 (C=C), 1476, 1439, 835, 749, 692 cm^{-1} (Ph). ^1H NMR (200 MHz, $CDCl_3$): δ = 2.37 (ddd, ^4J = 0.8, ^3J = 6.0, ^2J = 15.6, 1 H, allylic CH_2), 2.50 (dd, ^3J = 2.8, ^2J = 4.8, 1 H, oxirane CH_2), 2.53 (dd, ^3J = 6.0, ^2J = 15.6, 1 H, allylic CH_2), 2.80 (dd, ^3J = 4.0, ^2J = 4.8, 1 H, oxirane CH_2), 3.14 (ddt, ^3J = 2.8, ^3J = 4.0, ^3J = 6.0, 1 H, oxirane CH), 5.03 (s, 1 H, olef. CH_2), 5.40 (broad s, 1 H, olef. CH_2), 7.28−7.48 (m, 5 H, arom. CH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.2 (olef. C), 133.1, 129.2, 128.0 (arom. CH), 132.5 (arom. C), 115.0 (olef. CH_2), 50.9 (oxirane CH), 47.0 (oxirane CH_2), 39.6 (allylic CH_2) ppm.

Reaction between Vinylsilane 13b and Epichlorohydrin: Compound **13b** (2.812 g, 7.7 mmol) and epichlorohydrin (712 mg, 7.7 mmol) gave 1.37 g (62%) of recovered **13b** and two additional fractions after flash chromatography (eluent PE → PE/ethyl acetate, 40:1 → 20:1 → 10:1 → 5:1).

First Fraction. [2-(Triphenylsilyl)allyl]oxirane (15b): Yield 230 mg (9%), colorless crystals (m.p. 75−76 °C). IR (film): $\tilde{\nu}$ = 1588 (C=C), 1484, 1428, 1260, 1188, 1110, 973, 944, 908, 850, 831, 740, 702 cm^{-1} (Ph). ^1H NMR (200 MHz, $CDCl_3$): δ = 2.19 (dd, ^3J = 2.8, ^2J = 5.0, 1 H, oxirane CH_2), 2.27 (ddt, ^4J = 1.2, ^3J = 5.8, ^2J = 16.0, 1 H, allylic CH_2), 2.47 (m, 1 H, allylic CH_2), 2.53 (m, 1 H, oxirane CH_2), 2.84 (tdd, ^3J = 2.8, ^3J = 4.0, ^3J = 5.8, 1 H, oxirane CH), 5.60 (dt, ^4J = 1.2, ^2J = 2.4, 1 H, olef. CH_2), 6.13 (dt, ^4J = 1.6, ^2J = 2.4, 1 H, olef. CH_2), 7.24−7.40 (m, 9 H, arom. CH), 7.46−7.53 (m, 6 H, arom. CH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 142.4 (olef. C), 136.2, 129.7, 127.9 (arom. CH), 133.4 (arom. C), 132.8 (olef. CH_2), 51.5 (oxirane CH), 47.2 (oxirane CH_2), 39.0 (CH_2) ppm. $C_{23}H_{22}OSi$ (342.14): calcd. C 80.67, H 6.48; found C 80.12, H 6.35.

Second Fraction. 1-Chloro-4-(triphenylsilyl)pent-4-en-2-ol (14b): Yield 465 mg (16%), colorless oil. IR (film): $\tilde{\nu}$ = 3569, 3561, 3433 (OH), 1589 (C=C), 1428, 1109, 743, 704 cm^{-1} (Ph). ^1H NMR (200 MHz, $CDCl_3$): δ = 1.98 (d, ^3J = 4.6, 1 H, OH), 2.48 (ddd, ^4J = 1.2, ^3J = 7.2, ^2J = 14.4, allylic CH_2), 2.58 (ddd, ^4J = 1.2, ^3J = 5.4, ^2J = 14.4, 1 H, allylic CH_2), 3.34 (dd, ^3J = 6.0, ^2J = 11.2, 1 H, CH_2Cl), 3.45 (dd, ^3J = 4.0, ^2J = 11.2, 1 H, CH_2Cl), 3.62 (m, 1 H, C*H*OH), 5.75 (d, ^2J = 2.6, 1 H, olef. CH_2), 6.16 (dt, ^4J = 1.2, ^2J = 2.6, 1 H, olef. CH_2), 7.34−7.49 (m, 9 H, arom.CH), 7.55−7.62 (m, 6 H, arom. CH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 142.5 (olef. C), 136.2, 129.8, 128.0 (arom.CH), 133.0 (arom. C), 134.2 (olef. CH_2), 69.7 (HCOH), 49.5 (CH_2Cl), 41.5 (allylic CH_2) ppm.

Conversion of Chlorohydrin 14b into Oxirane 15b: K_2CO_3 (80 mg, 0.58 mmol) was added to **14b** (178 mg, 0.47 mmol) in methanol (2.5 mL). The solution was stirred for several minutes and the reaction was monitored by TLC. If necessary, further K_2CO_3 was added. For workup, diethyl ether (45 mL/mmol) was added and the reaction mixture was filtered. The organic phase was washed with saturated NH_4Cl solution, water, and brine, dried ($MgSO_4$), and concentrated in vacuo. Flash chromatography (PE/ethyl acetate, 60:1) gave **15b** (123 mg, 76%) as colorless crystals (m.p. 75−76 °C).

3-(Methylthio)-5-(phenylthio)cyclohex-2-en-1-ol (21): Preparation from **5a** (216 mg, 1.2 mmol) and **15a** (192 mg 1.0 mmol); purification by flash chromatography (eluent PE → PE/ethyl acetate, 120:1 → 5:1). Yield 98 mg (39%) as a not quite pure solid. IR (film): $\tilde{\nu}$ = 3397 (OH), 1623, 1582 (C=C), 1477, 1438, 1068, 1025, 747, 692 cm^{-1} (Ph). ^1H NMR (200 MHz, $CDCl_3$): δ = 1.64 (ddd, ^3J = 8.4, ^3J = 11.2, ^2J = 12.8, 1 H, 6-H_{ax}), 2.23 (s, 3 H, SMe), 2.33 (m, 1 H, 6-H_{eq}), 2.37 (m, 2 H, 4-CH_2), 3.38 (dddd, ^3J = 2.8, ^3J = 5.6, ^3J = 9.2, ^3J = 11.2, 1 H, 5-H_{ax}), 4.35 (ddd, ^3J = 2.4, ^3J = 6.0, ^3J = 8.4, 1 H, 1-H_{ax}), 5.34 (broad s, 1 H, olef. CH), 7.25−7.47 (m, 5 H, arom. CH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 136.0, 132.2 (olef. C, arom. C), 132.9, 129.0, 127.6 (arom. CH), 119.7 (olef. CH), 67.6 (HCOH), 41.4 (H*C*SPh), 38.5, 36.2 (CH_2), 14.0 (SMe) ppm.

Reaction between Thioacetal 5a and Allyloxirane 15b: Protonated **5a** (78 mg, 0.43 mmol) and **15b** (103 mg, 0.3 mmol) gave two fractions after flash chromatography (eluents PE → PE/ethyl acetate, 150:1 → 5:1).

First Fraction. 3,3-Bis(methylthio)-1-(trimethylsiloxy)-5-(triphenylsilyl)cyclohexane (19b): Yield 55 mg (35%). IR (film): $\tilde{\nu}$ = 1589 (C=C), 1428, 1250 ($SiMe_3$), 1110 (C−O), 1065, 908, 841 ($SiMe_3$), 741, 702 cm^{-1} (Ph). ^1H NMR (200 MHz, $CDCl_3$): δ = 0.08 (s, 9 H, $SiMe_3$), 1.47−1.80 (m, 4 H, 2 CH_2), 1.94, 2.02 (each s, 3 H, SMe), 2.18−2.44 (m, 2 H, CH_2), 2.35 (tt, J = 2.6, J = 13.2, 1 H, HCSi), 4.05 (tt, J = 4.4, J = 10.8, 1 H, HCOSi), 7.32−7.61 (m, 15 H, arom. CH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 135.9, 129.6, 128.0 (arom. CH), 133.3 (arom. C), 67.9 (HCOSi), 60.7 [*C*($SMe)_2$],

45.7, 36.5, 36.4 (CH_2), 17.9 (HCSi), 11.3, 11.1 (SMe), 1.0 ($SiMe_3$) ppm.

Second Fraction: Solid, inseparable mixture of **20b** (30%) and **22** (10%). Determination of both structures was based on NOE and also inverse H,H-COSY and C,H-COSY NMR measurements.

3,3-Bis(methylthio)-5-(triphenylsilyl)cyclohexanol (20b): IR (film): $\tilde{\nu}$ = 3416 (OH), 1589 (C=C), 1428, 1109 (C−O), 1038, 847, 738, 702 cm^{-1} (Ph). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.79 (s, 1 H, OH), 1.29 (td, J = 11.0, J = 12.8, 1 H, 6-H_{ax}), 1.56 (dd, J = 9.0, J = 13.2, 1 H, 2-H_{ax}), 1.84 (s, 3 H, SMe), 1.85 (t, J = 12.8 Hz, 1 H, 4-H_{ax}), 1.85 (s, 3 H, SMe), 2.31 (tt, J = 6.6, J = 2.4, 1 H, 6-H_{eq}), 2.35 (m, 2 H, 2-H_{eq}, 4-H_{eq}), 2.56 (tt, J = 2.4, J = 12.8, 1 H, 5-H_{ax}), 4.03 (m, 1 H, C*H*OH), 7.15−7.70 (m, 15 H, arom.CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.4, 136.3, 128.3, 128.2, 128.0, 127.7 (arom. CH), 129.8 (arom. C), 67.7 (HCOH), 61.2 [*C*$(SMe)_2$], 46.2 (2-CH_2), 37.3, 37.2 (4,6-CH_2), 18.6 (5-CHSi), 11.2, 10.9 (SMe) ppm.

3-(Methylthio)-5-(triphenylsilyl)cyclohex-3-en-1-ol (22): IR (film): $\tilde{\nu}$ = 3416 (OH), 1589 (C=C), 1428, 1109 (C−O), 1038, 847, 738, 702 cm^{-1} (Ph). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.72 (q, ^2J = ^3J = ^3J = 11.2, 1 H, 6-H), 2.11 (m, 1 H, 6-H), 2.17 (m, 1 H, 2-H), 2.46 (ddd, J = 2.6, J = 4.8, J = 16.0, 1 H, 2-H), 2.56 (m, 1 H, 5-H), 3.74 (m, 1 H, 1-H), 5.62 (t, ^3J = ^4J = 2.6, 1 H, 4-CH), 7.15−7.70 (m, 15 H, arom. CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.4, 136.3, 128.3, 128.2, 128.0, 127.7 (arom. CH), 129.8 (arom. C), 129.8 (olef. C), 119.4 (olef. CH), 68.8 (HCOH), 39.4 (2-CH_2), 33.7 (6-CH_2), 25.7 (CHSi), 14.1 (SMe) ppm.

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