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Surprisingly Facile Addition of Thiols to the Double Bonds of Bicyclopropylidene and Other Methylenecyclopropanes

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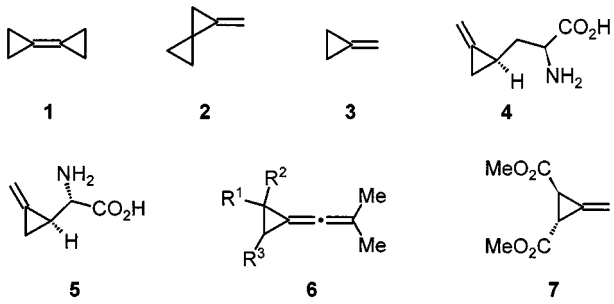
The addition of thiols **8a–h** onto the double bonds of bicyclopropylidene (**1**) and methylenespiropentane (**2**) proceeds quantitatively in benzene at 20 to 75 °C in the absence of catalysts or radical initiators to give products **9**, **10** with complete retention of both three-membered rings. Methylenespiropentane (**2**) yields exclusively the anti-Markovnikov adduct **10**. The unsubstituted methylenecyclopropane (**3**) gives 9% of the ring-opened compound **12** in addition to the anti-Markovnikov adduct **11**. The addition of thiols to *n*-heptylbicyclopropylidene (**13**), methylenecyclopropylacetic acid (**15**), and the amino acids **17**, **19** containing bicyclopropylidene or methylenespiropentane fragments, does not proceed stereoselectively, though in all cases the mercapto function adds to the double bond with retention of the cyclopropane ring to give interesting new amino acids containing bicyclopropyl and spiropentyl fragments, respectively. The probable mechanism of this thiol addition is discussed in the light of a test with the cyclizing intramolecular addition of 2-(2-methylenecyclopropyl)ethanethiol **27**.

Strain in an organic molecule often correlates with increased reactivity, at least for certain types of reactions[1]. Thus the chemistry of highly strained alkenes like the unusual tetrasubstituted alkene, bicyclopropylidene (**1**), as well as methylenespiropentane (**2**) and methylenecyclopropane (**3**) has proved to be fruitful both towards synthetic applications of such units[2][3], as well as understanding certain reaction principles[4]. Bicyclopropylidene (**1**) and methylenespiropentane (**2**) are both more highly strained cyclopropanated derivatives[2] of methylenecyclopropane (**3**), a molecule which occurs as a subunit in the particularly physiologically active natural amino acids α-(methylenecyclopropyl)glycine (**4**)[5] and hypoglycine A (**5**)[6]. As a consequence of its high lying HOMO[7] in addition to its high total strain energy[2], bicyclopropylidene is uniquely reactive towards a wide range of electrophiles and cyclophiles[2].

Unexpectedly, however, the relative rates of bromine addition to bicyclopropylidene (**1**), methylenespiropentane (**2**) as well as methylenecyclopropane (**3**) were found to be almost the same as those to analogously oligomethyl-substituted ethene derivatives[8], i.e. strain and reactivity of these compounds do not directly correlate, at least for the bromination which for **1** and **2** was mostly accompanied by ring-opening and ring-enlargement reactions to give complex mixtures of products. This is a consequence of cationic intermediates in the bromination of alkenes. As thiols normally add to C,C-multiple bonds via radical or carbanionic intermediates[9], we have tested the chemical behaviour of the peculiar alkenes **1**–**3** towards thiols.



In only a few cases so far reported in the literature does the addition of thiols onto a double bond not require radical initiators or acidic (basic for acceptor-activated olefins) catalysts, and all are highly strained allenes of the type **6**. While the radical addition of thiophenol (**8a**) onto these alkenylidenecyclopropanes **6** occurs without an initiator in benzene at 25 °C[10], the addition of **8a** onto Feist's methyl ester (**7**) has been reported to require heating at 100 °C for 15 h in the presence of di-*tert*-butyl peroxide[11]. The readily proceeding addition of **8a** to highly strained C–C single bonds like the central ones in [1.1.1]propellanes[12] or bi-

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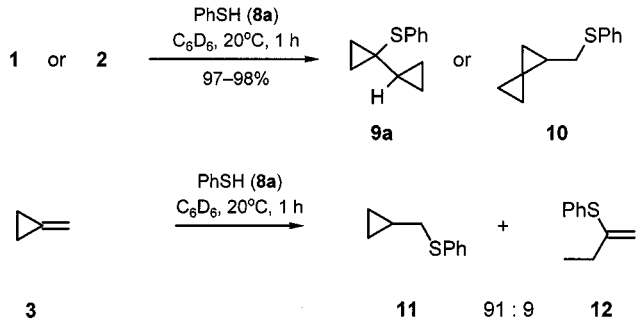
cyclobutanes[13] without added radical initiators are also believed to be radical reactions.

Surprisingly, the addition of **8a** onto the double bonds of the alkenes **1**−**3** in deuterobenzene occurs at room temperature in the dark and exothermally. The reactions of all three hydrocarbons were complete within 1 h, **1** and **2** gave the adducts **9a**, **10** quantitatively with complete retention of both three-membered rings, as detected by ^{1}H-NMR spectroscopy, and the spectrum indicated such a purity as if **9a**, **10** had been purified by column chromatography (Scheme 1).

Scheme 1



From methylenespiropentane (**2**), exclusively the anti-Markovnikov type adduct **10** was obtained. But for methylenecyclopropane (**3**), in addition to the anti-Markovnikov product **11**[14] (91%), 9% of the ring-opened vinyl sulfide **12** was formed, as detected by ^{1}H-NMR spectroscopy (Scheme 1). When run on a preparative (9 mmol) scale, these reactions proceed as cleanly with 77% isolated yield. These additions appear to be inhibited by palladium catalysts[15], e.g. the reaction of bicyclopropylidene (**1**) with thiophenol (**8a**) had reached only 15% conversion after 2 h at 20°C in the presence of 5 mol% of $Pd(OAc)_2 \cdot 2\ PPh_3$.

Apparently, these thiol additions are not initiated by protonation of the double bonds in **1**, **2**, **3**, since phenol, *p*-nitrophenol and acetic acid do not add under these conditions, and not even upon heating to 80°C for 3 h. Diphenyldisulfide did not react with bicyclopropylidene (**1**) as well. But, like in common cases[9a], strong acids do accelerate the addition of thiophenol onto the double bond of hydrocarbon **1**. The rate coefficients k_{BCP} for this reaction of **1** derived from kinetic measurements at 19°C under the conditions of a pseudo-first order rate law [five-fold excess of thiophenol (**8a**)] were equal to $2.85 \cdot 10^{-4}\ s^{-1}$ in the absence and $2.06 \cdot 10^{-3}\ s^{-1}$ in the presence of *p*-toluenesulfonic acid (5 mol%).

Aliphatic and functionally substituted thiols **8b**−**h** also undergo this clean and quantitative addition onto bicyclopropylidene (**1**), but 2 to 4 h heating is necessary to achieve complete conversion (Scheme 2). Isolated yields after column chromatography were 89−99%. Dithiols **8g**,**h** react with two equivalents of **1** to give bis(bicyclopropyl) derivatives **9g**, **h**.

But L-cysteine [**8i**, R = $CH_2CH(NH_2)COOH$] did not react with bicyclopropylidene (**1**), neither in benzene nor in methanol solution.

n-Heptylbicyclopropylidene (**13**) also reacted quantitatively and without ring opening with **8a** at 75°C, but unselectively to give an unseparable mixture of all four possible regio- and diastereoisomers **14** (ratio 6:5:3:1, Scheme 2). According to the ^{13}C-NMR spectrum of the mixture, the two major isomers bear the phenylthio and the heptyl group on the same three-membered ring.

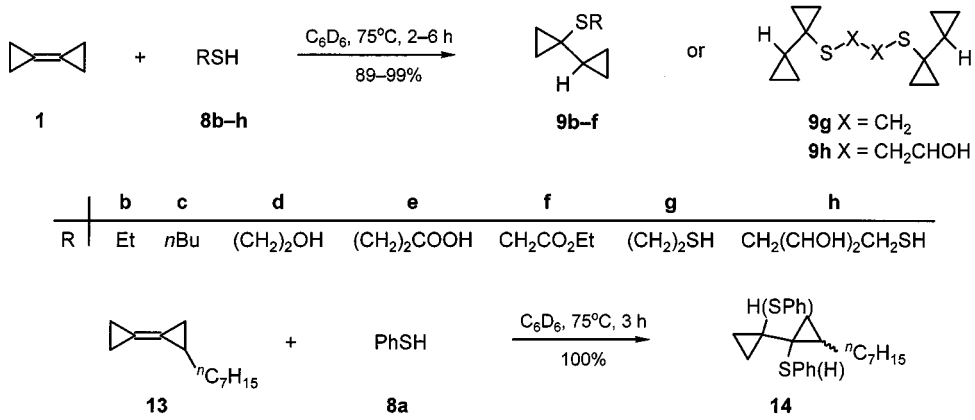
(Methylenecyclopropyl)acetic acid (**15**) which has been shown to be formed by enzymatic degradation of hypoglycine A (**5**) and is believed to play a crucial role in the biological action of **5**[6], also reacts with thiols **8a**, **d**, **i** giving mixtures of *cis*- and *trans*-isomers of the 2-substituted cyclopropylacetic acid derivatives **16a**, **b**, **c** (Scheme 3).

These additions to **15**, especially that of mercaptoethanol (**8d**), proceeded more slowly than those to **1**, **2**, and **3**, and the isolated yields are lower, but the main feature − addition onto the double bond with retention of the cyclopropane fragment − remains the same. Only in the reaction with thiophenol (**8a)** were traces of ring-opened products detected upon ^{1}H-NMR monitoring. In contrast to bicyclopropylidene (**1**), compound **15** really did undergo the reaction with L-cysteine (**8i**), but only when performed in water (75°C, 14 h) to give amino acid **16i** in 99% crude yield.

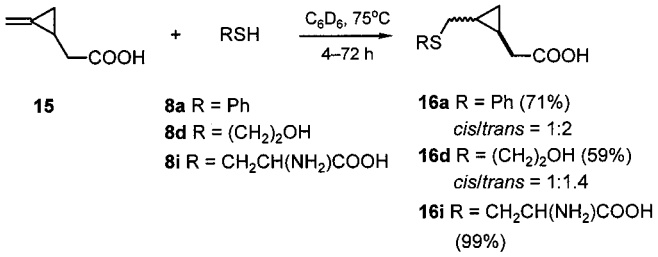
The spirocyclopropanated analogs of hypoglycine A (**5**), namely the amino acids **17** and **19**[16], reacted with mercaptoethanol (**8d**) in H_2O at 35°C to give complex mixtures of diastereomers **18** and **20**, respectively (Scheme 4). But in both cases the NMR spectra corroborate that the additions onto the double bonds occurred with complete retention of the three-membered rings.

As far as the mechanism of these additions is concerned, there appear to be some contradictions at the first glance. It is obvious only that the product **12** from methylenecyclopropane (**3**) and thiophenol (**8a**) is formed by a radical mechanism, i. e. via a (1-phenylthiocyclopropyl)methyl radical **21** which undergoes the well-established rapid ($k \approx 10^8\ s^{-1}$)[17] ring opening to the corresponding homoallyl radical **22** before it scavenges a hydrogen. In view of the relative kinetic stabilities of the cyclopropyl[18] and spiropentyl[19] radicals, it is not too surprising that the anti-Markovnikov products **11** and **10** from **3** and **2** are formed without ring opening. Feist′s ester **6** adds thiophenol (**8a**) in the anti-Markovnikov sense under typical radical-reaction conditions, i. e. initiated with di-*tert*-butyl peroxide[10], also with retention of the cyclopropane ring. But it is surprising that the 1-(1-phenylthiocyclopropyl)cyclopropyl radical (**23**) which would be the first intermediate in a radical addition of thiophenol (**8a**) to bicyclopropylidene (**1**) would not undergo rapid ring opening to the corresponding homoallyl radical **24**[20]. In different contexts it has been shown recently[21] that neither α-[21a] nor β-sulfur substitution[21b] do significantly influence the propensity for ring-opening of cyclopropylcarbinyl radicals.

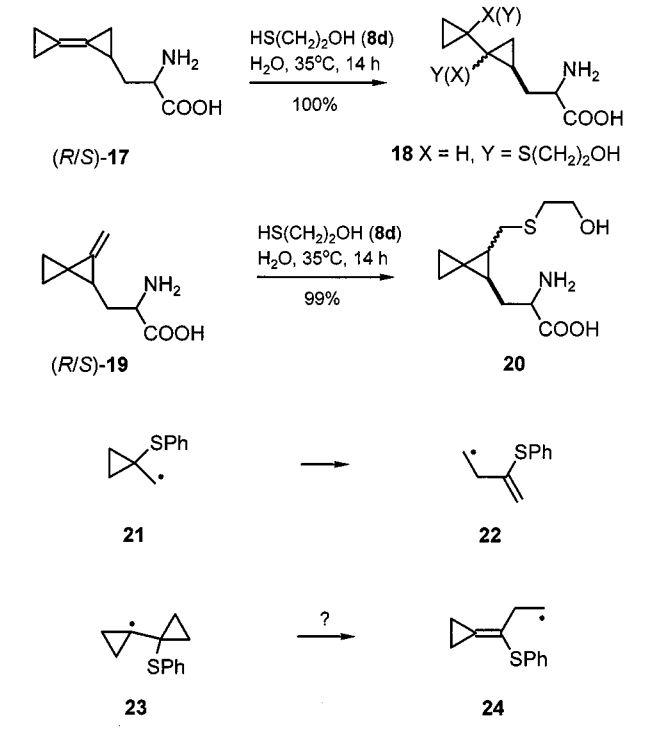
Scheme 2



Scheme 3

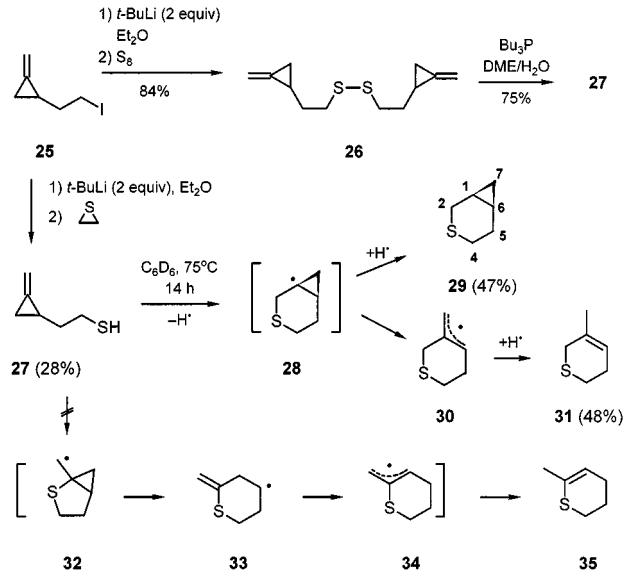


Scheme 4



In order to probe whether the mechanism of these thiol additions is a concerted [2σ + 2π] or a stepwise radical addition by applying the so-called "endocyclic restriction test"[22], the 2-(2-methylenecyclopropyl)ethanethiol (**27**) was prepared. Towards this, the 2-(2-iodoethyl)methylenecyclopropane (**25**)[23] was lithiated with *tert*-butyllithium, the resulting lithio derivative reacted with elemental sulfur to give the disulfide **26** which in turn was reduced with tributylphosphane/H_2O[24] to yield **27** (Scheme 5).

Scheme 5



The thiyl radical formed from **27** by homolytic S–H cleavage would be a hex-5-en-1-yl type and thus expected to undergo a 5-*exo*-*trig* cyclization[25] to give the bicyclic cyclopropylcarbinyl radical intermediate **32**, just as it has been observed for several 2′-substituted 3-(2-methylenecyclopropyl)prop-1-yl radicals[26].

However, upon heating the methylenecyclopropylethanethiol **27** in C_6D_6 at 75°C for 14 h, two products were observed in about equal amounts along with 5% of unreacted starting material **27**. These products were unequivocally identified as 3-thiabicyclo[4.1.0]heptane (**29**) and 3-methyl-5,6-dihydro-2*H*-thiopyran (**31**)[27] by their ^1H- and ^{13}C-NMR spectra. Both products are clearly derived from the same bicyclic cyclopropyl radical intermediate **28** which must have formed by a 6-*endo*-*trig* ring closure of the thiyl radical from **27** (Scheme 5). The ring opening of the cyclo-

propyl radical **28** to the allyl radical **30** must be facilitated by the bicyclic nature of **28**. In a control experiment, the thiabicycloheptane **29** did not rearrange to the dihydrothiopyran **31** in 24 h at 80°C. Apparently, 5-*exo-trig* ring closure of the initial thiyl radical from **27** to the bicyclic cyclopropylcarbinyl radical **32** does not occur, as the latter would at best have given the 2-methyl-5,6-dihydro-4*H*-thiopyran **35** which was not detected. In any event, although the 6-*endo-trig* ring closure of **27** is unusual, the formation of the ring-opened product **31** is a clear-cut evidence for a radical mechanism of this intramolecular thiol addition. Most probably, therefore, all of these thiol additions onto the double bonds of methylenecyclopropanes occur via radical intermediates. The apparent reason, then, for the 1-(1-phenylthiocyclopropyl)cyclopropyl **23** and analogous radicals from bicyclopropylidene (**1**) not to ring-open to **24** and its analogs is the increase in strain energy upon going to such a homoallyl radical which at the same time has a methylenecyclopropyl moiety. In fact, the ring opening of **23** to **24** would probably be reversible, as an analogous 3-*exo-trig* ring closure of a 1,1-bis(alkoxycarbonyl) substituted 3-cyclopropylidenepropyl radical to a 1-(2,2-dialkoxycarbonylcyclopropyl)cyclopropyl radical has previously been observed[28].

In conclusion, the addition of a thiol onto the double bond of a methylenecyclopropane derivative occurs with surprising facility, and, although by a radical mechanism, with retention of the cyclopropane ring in most cases. In contrast to the relative reactivities of the methylenecyclopropane moieties in hydrocarbons **1**−**3** towards bromine addition which follow a polar mechanism, the reactivities towards radical thiol additions appear to follow a strain-reactivity correlation. As methylenecyclopropane fragments are contained in certain biologically active natural products like the amino acids **4**, **5**, and as several enzymes contain thiol functional groups, it is justified to raise the question whether such thiol additions may play a role in the biological action of such compounds. To test this hypothesis, a solution of coenzyme A and methylenecyclopropylacetic acid (**15**) in D_2O was monitored by ^1H NMR. However, no reaction was detected after 72 h at 20°C and 72 h at 35°C. Only after 120 h at 70°C were new signals of cyclopropyl protons visible in the same region where thiol adducts of **15** would absorb, but the coenzyme A had completely decomposed.

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Experimental Section

^1H- and ^{13}C-NMR spectra: Measured at 250, 500 (^1H) and 62.9 MHz [^{13}C, additional DEPT (Distortionless Enhancement by Polarization Transfer)] on Bruker AM 250 and Varian INOVA-500 instruments in C_6D_6 soln, if not otherwise specified, CD_5H/C_6D_6 as internal reference. − FT-IR: Bruker IFS 66, measured as KBr pellets, oils as a film between NaCl plates. − MS (EI) and MS (HR-EI): Finnigan MAT 95 spectrometer (70 eV). MS (HR-EI): preselected ion peak matching at R >> 10000 to be within ±2 ppm of the exact masses. − CI-MS: with NH_3. − M. p.: Büchi 510 capillary melting point apparatus, uncorrected. − TLC: Macherey-Nagel precoated sheets, 0.25 mm Sil G/UV_{254}. − Column chromatography: Merck silica gel, grade 60, 230−400 mesh. − GC: Siemens Sichromat 1−4. − Preparative GC: Intersmat 130, 20% SE 30 on Chromosorb W-AW-DMCS, 1000 × 8.2 mm column.

Starting Materials: Anhydrous diethyl ether and THF were obtained by distillation from sodium benzophenone ketyl. Compounds **1**[29], **2**[30], **13**[31], **15**[32], and **25**[23] were prepared according to published procedures. All other chemicals were used as commercially available. Organic extracts were dried over $MgSO_4$.

General Procedure (GP1) for the Preparation of Sulfides **9a**−**h**, **10**, **11**, **16**, **18**, **20**, **29**, **31**: Under argon, an NMR tube was charged with the alkene (0.55 mmol or 1.05 mmol for **9g**, **h**), thiol (0.5 mmol) and anhydrous deuterobenzene or D_2O (H_2O) (for **16i** (**18**), **20**) (0.7 ml), hermetically closed and stored for 1 h at room temp. (for **9a**, **10**, **11**), at 35°C (14 h for **18**, **20**) or at 75°C (2 h for **9b**−**e**,**g**,**h**, 4 h for **16a**, 6 h for **9f**, 14 h for **16i**, **29**, **31** and 72 h for **16d**) in the dark. The conversion of starting materials was monitored by ^1H-NMR spectroscopy and secured to be complete before the work-up. After evaporation of the solvent, analytically pure samples were obtained by column chromatography (20 g of silica gel, 2 × 20 cm column) or recrystallization.

1-Cyclopropyl-1-(phenylthio)cyclopropane (**9a**): From bicyclopropylidene (**1**) (44 mg, 52 µl, 0.55 mmol) and thiophenol (**8a**) (55 mg, 52 µl, 0.5 mmol), 93 mg (98%) of the adduct **9a** was obtained after column chromatography: R_f = 0.33 (hexane). − IR: ν = 3079 cm^{-1}, 3004, 1584, 1479, 1439, 1418, 1089, 1025, 737, 691. − ^1H NMR: δ = 0.06−0.12 (m, 2 H, Cpr), 0.22−0.28 (m, 2 H, Cpr), 0.53−0.58 (m, 2 H, Cpr), 0.84−0.90 (m, 2 H, Cpr), 1.14−1.22 (m, 1 H, Cpr), 6.99−7.05 (m, 1 H, Ph), 7.10−7.16 (m, 2 H, Ph), 7.50−7.54 (m, 2 H, Ph). − ^{13}C NMR: δ = 4.40, 13.94 (2 CH_2), 128.92, 129.14 (2 CH), 17.38, 125.79 (CH), 27.01, 137.76 (C). − MS (EI), *m/z* (%): 190 (100) [M^+], 161 (13) [$M^+ - H - C_2H_4$], 157 (30) [$M^+ - SH$], 129 (42) [$M^+ - SH - C_2H_4$], 115 (20), 99 (20), 91 (68), 85 (58) [$SC_4H_5^+$]. − MS (HR-EI): 190.0816 ($C_{12}H_{14}S$, calcd. 190.0816). − $C_{12}H_{14}S$ (190.3): calcd. C 75.74, H 7.41; found C 75.63, H 7.61.

1-Cyclopropyl-1-(ethylthio)cyclopropane (**9b**): From bicyclopropylidene (**1**) (44 mg, 52 µl, 0.55 mmol) and ethanethiol (**8b**) (31 mg, 37 µl, 0.5 mmol), 67 mg (94%) of the adduct **9b** was obtained after column chromatography: R_f = 0.45 (hexane). − IR: ν = 3080 cm^{-1}, 3003, 2970, 2928, 2871, 1457, 1448, 1417, 1018, 885, 821. − ^1H NMR: δ = −0.05 to 0.08 (m, 2 H, Cpr), 0.21−0.31 (m, 2 H, Cpr), 0.35−0.46 (m, 2 H, Cpr), 0.79−0.85 (m, 2 H, Cpr), 1.02 (t, *J* = 7.6 Hz, 3 H, CH_3), 1.15−1.25 (m, 1 H, Cpr), 2.61 (q, *J* = 7.6 Hz, 2 H, SCH_2). − ^{13}C NMR: δ = 15.11 (CH_3), 3.66, 13.35 (2 CH_2), 25.63 (CH_2), 17.77 (CH), 26.09 (C). − MS (EI), *m/z* (%): 142 (13) [M^+], 141 (17) [$M^+ - H$], 127 (33) [$M^+ - CH_3$], 114 (39) [$M^+ - C_2H_4$], 113 (100) [$M^+ - C_2H_5$], 85 (38) [$M^+ - C_4H_9$], 81 (35) [$M^+ - SC_2H_5$], 79 (65) [$C_6H_7^+$], 73 (34). − MS (HR-EI): 142.0816 ($C_8H_{14}S$, calcd. 142.0816).

1-Butylthio-1-cyclopropylcyclopropane (**9c**): From bicyclopropylidene (**1**) (44 mg, 52 µl, 0.55 mmol) and butanethiol (**8c**) (45 mg, 54 µl, 0.5 mmol), 83 mg (97%) of the adduct **9c** was obtained after column chromatography: R_f = 0.41 (hexane). − IR: ν = 3080 cm^{-1}, 3004, 2958, 2930, 2872, 1465, 1416, 1017, 877, 820. − ^1H NMR: δ = −0.02 to 0.08 (m, 2 H, Cpr), 0.21−0.32 (m, 2 H, Cpr), 0.37−0.48 (m, 2 H, Cpr), 0.67−0.75 (m, 2 H, Cpr), 0.85 (t, *J* =

7.4 Hz, 3 H, CH_3), 1.15−1.23 (m, 1 H, Cpr), 1.23−1.45 (m, 2 H, CH_2), 1.45−1.61 (m, 2 H, CH_2), 2.64 (t, J = 7.4 Hz, 2 H, SCH_2). − ^{13}C NMR: δ = 13.90 (CH_3), 3.71, 13.50 (2 CH_2), 22.55, 31.48, 32.27 (CH_2), 17.81 (CH), 26.24 (C). − MS (EI), *m/z* (%): 260 (100) [M^+ + HSC_4H_9], 203 (31) [M^+ + SH], 170 (4) [M^+], 155 (4), 147 (8), 141 (14) [M^+ − H − C_2H_4], 127 (8), 114 (40) [M^+ − C_4H_8], 113 (39) [M^+ − C_4H_9], 85 (20) [$SC_4H_5^+$], 81 (10) [$C_6H_9^+$], 79 (15) [$C_6H_7^+$]. − $C_{10}H_{18}S$ (170.3): calcd. C 70.52, H 10.65; found C 70.78, H 10.61.

2-(1-Cyclopropylcyclopropylthio)ethanol (**9d**): From bicyclopropylidene (**1**) (44 mg, 52 µl, 0.55 mmol) and mercaptoethanol (**8d**) (39 mg, 35 µl, 0.5 mmol), 74 mg (93%) of the adduct **9d** was obtained after column chromatography: R_f = 0.29 (hexane/Et_2O, 1:1). − IR: ν = 3363 cm^{-1}, 3080, 3003, 2924, 2876, 1463, 1447, 1417, 1046, 1017, 876, 822. − ^{1}H NMR: δ = −0.04 to 0.01 (m, 2 H, Cpr), 0.24−0.30 (m, 2 H, Cpr), 0.37−0.42 (m, 2 H, Cpr), 0.65−0.71 (m, 2 H, Cpr), 1.13−1.20 (m, 1 H, Cpr), 2.80 (t, J = 6.5 Hz, 2 H, SCH_2), 3.70 (t, J = 6.5 Hz, 2 H, OCH_2). − ^{13}C NMR: δ = 3.83, 13.51 (2 CH_2), 34.93, 61.57 (CH_2), 17.82 (CH), 26.06 (C). − MS (EI), *m/z* (%): 158 (2) [M^+], 127 (100) [M^+ − CH_2OH], 114 (26) [M^+ − C_2H_4O], 113 (37) [M^+ − C_2H_4OH], 99 (11) [M^+ − SC_2H_3], 93 (22), 85 (73) [$SC_4H_5^+$], 81 (30) [$C_6H_9^+$], 79 (52) [$C_6H_7^+$]. − MS (HR-EI): 158.0765 ($C_8H_{14}OS$, calcd. 158.0765). − $C_8H_{14}OS$ (158.3): calcd. C 60.71, H 8.92; found C 60.76, H 8.79.

3-(1-Cyclopropylcyclopropylthio)propionic Acid (**9e**): From bicyclopropylidene (**1**) (44 mg, 52 µl, 0.55 mmol) and 3-mercaptopropionic acid (**8e**) (53 mg, 44 µl, 0.5 mmol), 83 mg (89%) of the adduct **9e** was obtained after column chromatography: R_f = 0.38 (hexane/Et_2O, 1:1). − IR: ν = 3380 cm^{-1}, 3080, 3004, 2263, 1711, 1417, 1336, 1263, 1195, 1020, 932, 886, 822. − ^{1}H NMR: δ = −0.06 to 0.04 (m, 2 H, Cpr), 0.23−0.26 (m, 2 H, Cpr), 0.35−0.38 (m, 2 H, Cpr), 0.64−0.66 (m, 2 H, Cpr), 1.12−1.19 (m, 1 H, Cpr), 2.50 (t, J = 7.5 Hz, 2 H, CH_2), 2.84 (t, J = 7.5 Hz, 2 H, SCH_2), 12.06 (s, 1 H, OH). − ^{13}C NMR: δ = 3.71, 13.24 (2 CH_2), 26.41, 35.13 (CH_2), 17.54 (CH), 26.05, 179.32 (C). − MS (EI), *m/z* (%): 186 (48) [M^+], 157 (23) [M^+ − H − C_2H_4], 141 (40) [M^+ − CO_2H], 127 (32) [M^+ − CO_2H − CH_2], 114 (42), 113 (90) [M^+ − CO_2H − C_2H_4], 85 (100) [$SC_4H_5^+$], 81 (50) [$C_6H_9^+$], 79 (80) [$C_6H_7^+$]. − MS (HR-EI): 186.0714 ($C_9H_{14}O_2S$, calcd. 186.0715). − $C_9H_{14}O_2S$ (186.3): calcd. C 58.03, H 7.58; found C 57.60, H 7.23.

Ethyl (1-Cyclopropylcyclopropylthio)acetate (**9f**): From bicyclopropylidene (**1**) (44 mg, 52 µl, 0.55 mmol) and ethyl mercaptoacetate (**8f**) (60 mg, 55 µl, 0.5 mmol), 95 mg (95%) of the adduct **9f** was obtained after column chromatography: R_f = 0.47 (hexane/Et_2O, 10:3). − IR: ν = 3081 cm^{-1}, 3002, 2937, 1734, 1464, 1447, 1416, 1366, 1269, 1131, 1031, 923, 877, 824. − ^{1}H NMR: δ = −0.03 to 0.03 (m, 2 H, Cpr), 0.23−0.30 (m, 2 H, Cpr), 0.39−0.44 (m, 2 H, Cpr), 0.68−0.73 (m, 2 H, Cpr), 1.02 (t, J = 7.1 Hz, 3 H, CH_3), 1.26−1.32 (m, 1 H, Cpr), 3.29 (s, 2 H, SCH_2), 3.97 (q, J = 7.1 Hz, 2 H, OCH_2). − ^{13}C NMR: δ = 14.13 (CH_3), 3.63, 13.24 (2 CH_2), 33.63, 60.88 (CH_2), 17.14 (CH), 26.75, 170.41 (C). − MS (EI), *m/z* (%): 200 (100) [M^+], 127 (88) [M^+ − $CO_2C_2H_5$], 113 (90) [M^+ − $CH_2CO_2C_2H_5$], 93 (22), 85 (60) [$SC_4H_5^+$], 81 (41) [$C_6H_9^+$], 79 (92) [$C_6H_7^+$]. − MS (HR-EI): 200.0871 ($C_{10}H_{16}O_2S$, calcd. 200.0871). − $C_{10}H_{16}O_2S$ (200.3): calcd. C 59.96, H 8.05; found C 59.69, H 8.06.

1,2-Bis(1-cyclopropylcyclopropylthio)ethane (**9g**): From bicyclopropylidene (**1**) (84 mg, 99 µl, 1.05 mmol) and ethanedithiol (**8g**) (47 mg, 42 µl, 0.5 mmol), 121 mg (95%) of the adduct **9g** was obtained after column chromatography: R_f = 0.46 (hexane/Et_2O, 20:1). − IR: ν = 3079 cm^{-1}, 3002, 2930, 2871, 1462, 1446, 1416, 1019, 876, 822. − ^{1}H NMR: δ = −0.11 to 0.03 (m, 4 H, Cpr), 0.21−0.33 (m, 4 H, Cpr), 0.35−0.44 (m, 4 H, Cpr), 0.63−0.72 (m, 4 H, Cpr), 1.10−1.25 (m, 2 H, Cpr), 3.0 (s, 4 H, SCH_2). − ^{13}C NMR: δ = 3.84, 13.51 (4 CH_2), 32.51 (2 CH_2), 17.88 (2 CH), 26.32 (2 C). − MS (EI), *m/z* (%): 254 (3) [M^+], 195 (10) [M^+ − SC_2H_3], 174 (13) [M^+ − C_6H_8], 145 (19), 141 (100) [M^+ − SC_6H_9], 113 (36) [$SC_6H_9^+$], 85 (39) [$SC_4H_5^+$], 81 (52) [$C_6H_9^+$], 79 (50) [$C_6H_7^+$]. − MS (HR-EI): 254.1162 ($C_{14}H_{22}S_2$, calcd. 254.1163). − $C_{14}H_{22}S_2$ (254.4): calcd. C 66.08, H 8.72; found C 65.91, H 8.48.

meso-1,4-Bis(1-cyclopropylcyclopropylthio)-2,3-butanediol (**9h**): From bicyclopropylidene (**1**) (84 mg, 99 µl, 1.05 mmol) and *meso*-1,4-dimercapto-2,3-butanediol (**8h**) (77 mg, 0.5 mmol), 156 mg (99%) of almost pure compound **9h** was obtained after evaporation of the solvent: m. p. 25°C (hexane). − ^{1}H NMR: δ = −0.03 to 0.07 (m, 4 H, Cpr), 0.24−0.35 (m, 4 H, Cpr), 0.36−0.48 (m, 4 H, Cpr), 0.64−0.78 (m, 4 H, Cpr), 1.16−1.32 (m, 2 H, Cpr), 2.87 (dd, J = 8.6, 13.4 Hz, 2 H, SCH_2), 3.10 (s, 2 H, 2 OH), 3.34 (dd, J = 3.3, 13.4 Hz, 2 H, SCH_2), 3.91 (dd, J = 3.3, 8.6 Hz, 2 H, 2 C*H*OH). − ^{13}C NMR: δ = 3.76, 4.21, 12.90, 14.10, 36.06 (2 CH_2), 17.76, 72.34 (2 CH), 26.32 (2 C). − MS (EI), *m/z* (%): 314 (8) [M^+], 286 (4) [M^+ − C_2H_4], 233 (18) [M^+ − C_6H_9], 200 (20) [M^+ − C_6H_9 − SH], 157 (100) [$C_6H_9SCH_2CHOH^+$], 113 (52) [$SC_6H_9^+$], 85 (50) [$SC_4H_5^+$], 81 (58) [$C_6H_9^+$], 79 (45) [$C_6H_7^+$]. − MS (HR-EI): 314.1374 ($C_{16}H_{26}O_2S_2$, calcd. 314.1374).

(Phenylthiomethyl)spiropentane (**10**): From methylenespiropentane (**2**) (44 mg, 0.55 mmol) and thiophenol (**8a**) (55 mg, 52 µl, 0.5 mmol), 92 mg (97%) of the adduct **10** was obtained after column chromatography: R_f = 0.29 (hexane). − IR: ν = 3060 cm^{-1}, 2997, 2915, 1585, 1480, 1438, 1420, 1238, 1090, 1025, 997, 855, 737, 690. − ^{1}H NMR ($CDCl_3$): δ = 0.69 (dd, J = 7.5, 3.3 Hz, 1 H, Cpr), 0.75−0.86 (m, 4 H, Cpr), 1.08 (dd, J = 7.5, 4.3 Hz, 1 H, Cpr), 1.38−1.48 (m, 1 H, Cpr), 2.92 (dd, J = 12.5, 7.0 Hz, 1 H, SCH_2), 3.03 (dd, J = 12.5, 7.0 Hz, 1 H, SCH_2), 7.15−7.22 (tt, J = 7.1, 1.5 Hz, 1 H, Ph), 7.25−7.32 (m, 2 H, Ph), 7.35−7.40 (dm, J = 7.0 Hz, 2 H, Ph). − ^{13}C NMR ($CDCl_3$): δ = 3.27, 6.17, 13.20, 38.08 (CH_2), 128.69, 129.28 (2 CH), 16.78, 125.72 (CH), 13.20, 136.98 (C). − MS (EI), *m/z* (%): 190 (28) [M^+], 175 (8), 161 (6) [M^+ − H − C_2H_4], 135 (16) [M^+ − C_4H_7], 123 (44), 110 (58) [M^+ − H − C_6H_7], 109 (22) [SPh^+], 81 (100) [M^+ − SPh], 79 (50) [$C_6H_7^+$]. − MS (HR-EI): 190.0816 ($C_{12}H_{14}S$, calcd. 190.0816). − $C_{12}H_{14}S$ (190.3): calcd. C 75.74, H 7.41; found C 75.61, H 7.23. In the repeated large-scale preparation, 1.676 g (97%) of sulfide **10** was obtained from olefin **2** (727 mg, 9.08 mmol) and **8a** (1 g, 0.932 ml, 9.08 mmol) after column chromatography (50 g of silica gel, 20 × 3 cm column).

(Phenylthiomethyl)cyclopropane (**11**)[14] *and 2-(Phenylthio)-1-butene* (**12**)[33]: After stirring a mixture of methylenecyclopropane (**3**) (ca. 30 mg, ca. 35 µl, 0.55 mmol) and thiophenol (**8a**) (55 mg, 52 µl, 0.5 mmol) at room temp. for 1 h according to GP1, a mixture of compounds **11** (91%) and **12** (9%) was obtained, as detected by ^{1}H NMR spectroscopy. − **11**: ^{1}H NMR: δ = 0.20−0.33 (m, 2 H, Cpr), 0.52−0.65 (m, 2 H, Cpr), 0.98−1.05 (m, 1 H, Cpr), 2.89 (d, J = 7.0 Hz, 2 H, SCH_2), 7.11−7.51 (m, 5 H, Ph). − ^{13}C NMR: δ = 5.52 (2 CH_2), 39.39 (CH_2), 128.97, 129.83 (2 CH), 10.54, 125.67 (CH), 136.96 (C). − **12**: ^{1}H NMR: δ = 1.13 (t, J = 7.4 Hz, 3 H, CH_3), 2.29 (qd, J = 7.4, 1.1 Hz, 2 H, CH_2), 4.95 (d, J = 1.1 Hz, 1 H, =CH_2), 5.21 (s, 1 H, =CH_2), signals of Ph group are covered. − ^{13}C NMR: δ = 13.17 (CH_3), 29.55, 111.83 (CH_2), 128.68, 132.93 (2 CH), 127.55 (CH), 136.96 (C), the signals of quaternary atoms could not be reliable interpreted. In the repeated large-scale preparation, 1.143 g (77%) of sulfide **11** was obtained from olefin **3** (ca. 0.49 g, ca. 0.58 ml, 9.1 mmol) and thiophenol (**8a**) (1 g, 0.932 ml, 9.08 mmol) after column chromatography (50 g of silica gel, 20 × 3 cm column).

cis- and trans-[2-(Phenylthiomethyl)cyclopropyl]acetic Acid (**16a**): From (methylenecyclopropyl)acetic acid (**15**) (56 mg, 0.5 mmol) and thiophenol (**8a**) (55 mg, 52 µl, 0.5 mmol), 79 mg (71%) of the adduct **16a** was obtained after column chromatography as a 1:2 mixture of *cis*- and *trans*-isomers: R_f = 0.33 (hexane/Et_2O, 1:1), m. p. 34−36°C (hexane). − *cis*-**16a**: ^1H NMR: δ = −0.20 (dd, *J* = 5.3, 5.3 Hz, 1 H, Cpr), 0.50−0.57 (m, 1 H, Cpr), 0.70−0.82 (m, 2 H, Cpr), 1.98 (dd, *J* = 7.5, 16.6 Hz, 1 H, CH_2), 2.22 (dd, *J* = 6.6, 16.6 Hz, 1 H, CH_2), 2.60 (d, *J* = 7.0 Hz, 2 H, SCH_2), 6.95−7.33 (m, 5 H, Ph), 11.71 (s, 1 H, OH). − ^{13}C NMR: δ = 11.98, 33.51, 38.17 (CH_2), 129.21, 129.63 (2 CH), 12.80, 15.0, 126.05 (CH), 137.10, 179.26 (C). − *trans*-**16a**: ^1H NMR: δ = 0.11−0.18 (m, 1 H, Cpr), 0.23−0.33 (m, 1 H, Cpr), 0.50−0.65 (m, 1 H, Cpr), 0.97 (pseudosept, *J* = 7.3, 1 H, Cpr), 1.81 (dd, *J* = 7.3, 16.3 Hz, 1 H, CH_2), 1.92 (dd, *J* = 7.0, 16.3 Hz, 1 H, CH_2), 2.46 (dd, *J* = 7.3, 13.0 Hz, 1 H, SCH_2), 2.67 (dd, *J* = 6.8, 13.0 Hz, 1 H, SCH_2), 6.95−7.33 (m, 5 H, Ph), 11.71 (s, 1 H, OH). − ^{13}C NMR: δ = 12.45, 34.27, 38.17 (CH_2), 129.14, 129.37 (2 CH), 15.21, 18.01, 125.93 (CH), 137.55, 179.02 (C). − MS (EI), *m/z* (%): 222 (100) [M^+], 181 (18), 163 (6) [$M^+ - CH_2CO_2H$], 135 (15), 123 (60) [$M^+ - C_5H_7O_2$], 113 (32) [M^+ − SPh], 110 (84) [$HSPh^+$], 109 (36) [SPh^+], 71 (53). − MS (HR-EI): 222.0714 ($C_{12}H_{14}O_2S$, calcd. 222.0715). − $C_{12}H_{14}O_2S$ (222.3): calcd. C 64.83, H 6.35; found C 64.56, H 6.06.

cis- and trans-[2-(2-Hydroxyethylthiomethyl)cyclopropyl]acetic Acid (**16d**): From (methylenecyclopropyl)acetic acid (**15**) (56 mg, 0.5 mmol) and mercaptoethanol (**8d**) (39 mg, 35 µl, 0.5 mmol), 56 mg (59%) of the adduct **16d** was obtained after column chromatography as a 1:1.4 mixture of *cis*- and *trans*-isomers: R_f = 0.34 (Et_2O). − *cis*-**16d**: ^1H NMR ($CDCl_3$): δ = 0.03 (dd, *J* = 5.3, 5.3 Hz, 1 H, Cpr), 0.81−0.98 (m, 2 H, Cpr), 1.15−1.18 (m, 1 H, Cpr), 2.19 (d, *J* = 6.8 Hz, 1 H, CH_2), 2.33 (d, *J* = 6.8 Hz, 1 H, CH_2), 2.48 (m, *J* = 16.5, 7.3, 7.2 Hz, 2 H, SCH_2), 2.71 (t, *J* = 6.1 Hz, 2 H, SCH_2), 3.67 (t, *J* = 6.1 Hz, 2 H, OCH_2), 7.0 (s, 1 H, OH), 10.1 (s, 1 H, COOH). − ^{13}C NMR ($CDCl_3$): δ = 11.73, 31.88, 33.29, 34.62, 60.46 (CH_2), 12.08, 15.12 (CH), 177.94 (C). − *trans*-**16d**: ^1H NMR ($CDCl_3$): δ = 0.44 (ddd, *J* = 1.7, 5.7, 7.4 Hz, 2 H, Cpr), 0.76−0.81 (m, 1 H, Cpr), 1.05 (pseudosept, *J* = 7.4, 1 H, Cpr), 2.21 (d, *J* = 6.8 Hz, 1 H, CH_2), 2.31 (d, *J* = 7.5 Hz, 1 H, CH_2), 2.46 (m, *J* = 16.3, 7.5, 7.3 Hz, 2 H, SCH_2), 2.71 (t, *J* = 6.1 Hz, 2 H, SCH_2), 3.66 (t, *J* = 6.1 Hz, 2 H, OCH_2), 7.0 (s, 1 H, OH), 10.1 (s, 1 H, COOH). − ^{13}C NMR ($CDCl_3$): δ = 12.13, 34.41, 35.84, 38.06, 60.46 (CH_2), 14.73, 18.46 (CH), 177.56 (C). − MS (EI), *m/z* (%): 190 (16) [M^+], 113 (52) [$M^+ - S(CH_2)_2OH$], 101 (31), 84 (25), 71 (20), 59 (41) [$CH_2CO_2H^+$], 43 (100). − MS (HR-EI): 190.0663 ($C_8H_{14}O_3S$, calcd. 190.0664). − $C_8H_{14}O_3S$ (190.3): calcd. C 50.50, H 7.42; found C 51.05, H 7.39.

S-{[2-(Carboxymethyl)cyclopropyl]methyl}-L-cysteine (**16i**): From (methylenecyclopropyl)acetic acid (**15**) (56 mg, 0.5 mmol) and L-cysteine (**8i**) (61 mg, 0.5 mmol), 116 mg (99%) of almost pure compound **16i** was obtained after evaporation of D_2O as a mixture of two main diastereomers: m. p. 154°C (dec.) (H_2O/acetone). − ^1H NMR (D_2O): δ = −0.09, 0.32, 0.71, and 0.95 (m, total 4 H, Cpr), 1.95−2.45 (m, total 4 H, CH_2 and SCH_2), 2.85−2.94 (m, 2 H, SCH_2), 3.71 (m, 1 H, CH). − ^{13}C NMR (D_2O, the chemical shift of the major diastereomer is marked as "m" in parentheses): δ = 11.82, 12.55(m), 32.62(m), 32.91, 34.07(m), 34.17, 36.48(m), 36.56 (CH_2), 12.71, 15.32, 15.41(m), 18.35(m), 54.37(m), 54.38 (CH), 173.63(m), 173.65, 179.28(m), 179.61 (C). − MS (CI), *m/z* (%): 251 (45) [$M^+ + NH_4$], 234 (83) [M^+ + H], 190 (6) [$M^+ + H - CO_2$], 181 (48) [$M^+ + NH_4 - CO_2 - C_2H_2$], 164 (100) [$M^+ + H - CO_2 - C_2H_2$], 147 (15), 130 (25), 116 (10). − $C_9H_{15}NO_4S$ (233.3): calcd. C 46.33, H 6.48; found C 46.96, H 6.48.

Reaction of β-Bicyclopropylidenyl-D,L-alanine (**17**) *with 2-Mercaptoethanol* (**8d**): From **17** (46 mg, 0.28 mmol) and mercaptoethanol (**8d**) (23.5 mg, 21 µl, 0.3 mmol), 68 mg (100%) of a complex mixture of adducts **18** as an oil was obtained after evaporation of H_2O. The spectral data of the mixture are rather complicated to be interpreted, but ^1H- as well as ^{13}C-NMR spectra (D_2O) reveal the typical groups of signals like compound **20** (see below). − MS (CI), *m/z* (%): 263 (12) [$M^+ + NH_4$], 246 (80) [M^+ + H], 202 (3) [$M^+ + H - CO_2$], 185 (8) [$M^+ - NH_2 - CO_2$], 180 (20), 172 (30), 163 (100) [$M^+ + NH_4 - CCH_2CH(NH_2)CO_2H$], 146 (81) [$M^+ + H - CCH_2CH(NH_2)CO_2H$].

β-[2-(2-Hydroxyethylthiomethyl)spiropentyl]-D,L-alanine (**20**) From *β*-(2-methylenespiropentyl)-D,L-alanine (**19**) (44 mg, 0.26 mmol) and mercaptoethanol (**8d**) (23.5 mg, 21 µl, 0.3 mmol), 63 mg (99%) of almost pure compound **20** was obtained after evaporation of H_2O, washing of the residue with acetone and drying in vacuo (24 h/0.1 Torr) as a mixture of diastereomers: m. p. 166−168°C (dec.). − ^1H NMR (D_2O): δ = −0.45 to 1.35 (m, 5 H, Cpr), 1.55−1.76 (m, 2 H, CH_2), 1.76−1.87 (m, 1 H, Cpr), 2.45−2.55 (m, 4 H, SCH_2), 3.40−3.56 (m, 3 H, CH and OCH_2). − ^{13}C NMR (D_2O, the signals of the individual diastereomers could not be reliable interpreted): δ = 1.44, 1.65, 3.71, 3.88, 4.04, 7.00 (CH_2, Cpr), 13.98, 18.26, 20.65, 20.85, 20.89, 24.44 (CH, Cpr), 22.24, 24.66, 29.91, 31.04, 31.12, 31.39, 33.84, 34.29, 35.08 (CH_2, SCH_2), 55.64, 55.71, 55.88 (CH), 59.98, 61.04 (OCH_2), 175.33, 175.41, 175.90 (C). − MS (CI), *m/z* (%): 263 (4) [$M^+ + NH_4$], 246 (32) [M^+ + H], 202 (8) [$M^+ + H - CO_2$], 187 (12), 185 (19) [$M^+ - NH_2 - CO_2$], 168 (19) [$M^+ - S(CH_2)_2OH$], 163 (100) [$M^+ + NH_4 - CCH_2CH(NH_2)CO_2H$], 146 (69) [$M^+ + H - CCH_2CH(NH_2)CO_2H$]. − $C_{11}H_{19}NO_3S$ (245.3): calcd. C 53.85, H 7.81; found C 53.78, H 7.63.

2-(2-Methylenecyclopropyl)ethanethiol (**27**): a) To a stirred solution of 2-(2-iodoethyl)methylenecyclopropane **25**[23] (4.202 g, 20.2 mmol) in anhydrous Et_2O (35 ml), *t*BuLi (24.5 ml of 1.65 N solution in pentane, 40.4 mmol) was added at −75°C over a period of 1 h. The mixture was stirred at the indicated temp. for an additional 1 h, and then sublimed sulfur powder (1.293 g, 2 equiv.) was added in one portion. The resulting suspension was allowed to warm to 20°C, quenched with 20.2 ml of 1 N HCl solution, extracted with Et_2O (2 × 30 ml), dried and concentrated under reduced pressure. Column chromatography (60 g of silica gel, 3 × 20 cm column, hexane) gave 1.91 g (84%) of *bis[2-(2-methylenecyclopropyl)ethyl]-disulfide* (**26**) as a mixture of two diastereomers (ratio 2:1), R_f = 0.47. − ^1H NMR ($CDCl_3$, major diastereomer): δ = 0.78−0.85 (m, 2 H, Cpr), 1.24−1.31 (m, 2 H, Cpr), 1.50−1.56 (m, 2 H, Cpr), 1.75−1.85 (m, 4 H, CH_2), 2.96 (t, *J* = 7.0 Hz, 4 H, SCH_2), 5.37 (br. s, 2 H, $=CH_2$), 5.44 (d, *J* = 1.3 Hz, 2 H, $=CH_2$). − ^{13}C NMR ($CDCl_3$, major diastereomer): δ = 9.52, 32.33, 38.32, 103.27 (2 CH_2), 14.60 (2 CH), 135.62 (2 C). − MS (EI), *m/z* (%): 145 (80) [$C_6H_9S_2^+$], 113 (100) [$C_6H_9S^+$], 86 (65) [$C_4H_5S^+$], 84 (95), 79 (80), 57 (78), 41 (60). − MS (CI), *m/z* (%): 261 (100) [$M^+ + NH_4 + NH_3$], 244 (45) [$M^+ + NH_4$], 227 (20) [M^+ + H], 145 (29) [$C_6H_9S_2^+$], 113 (55) [$C_6H_9S^+$].

Disulfide **26** (1.291 g, 5.7 mmol) was treated with *n*Bu_3P (2.31 g, 2.85 ml, 11.4 mmol) in a mixture of DME (25 ml) and H_2O (5 ml) at 0°C for 1 h, poured into ice-cold water (50 ml) and extracted with Et_2O (2 × 30 ml). The combined organic phases were washed with brine (2 × 30 ml), dried and concentrated under reduced pressure at 0°C. Rapid column chromatography (50 g of silica gel, 3 × 20 cm column, hexane/Et_2O, 4:1) gave 0.972 g (75%) of thiol **27** as a colorless oil, R_f = 0.70. − ^1H NMR: δ = 0.56−0.61 (m, 1 H, Cpr), 1.04−1.18 (m, 1 H, Cpr), 1.15 (s, 1 H, SH), 1.29−1.32

(m, 1 H, Cpr), 1.37−1.45 (m, 2 H, CH_2), 2.28 (t, J = 6.5 Hz, 2 H, SCH_2), 5.41−5.44 (m, 2 H, $=CH_2$). − ^{13}C NMR: δ = 9.13, 24.10, 37.42, 103.00 (CH_2), 14.55 (CH), 135.60 (C). − MS (EI), *m/z* (%): 114 (100) [M^+], 113 (38) [$M^+ - H$], 99 (35), 86 (20) [$M^+ - C_2H_4$], 81 (95) [$M^+ - SH$], 79 (60), 61 (80), 41 (55). − MS (HR-EI): 114.0503 ($C_6H_{10}S$, calcd. 114.0503).

b) The lithio compound prepared as described above from the same quantity of **25** was treated with thiirane (1.336 g, 1.32 ml, 22.2 mmol) at −75°C. The mixture was allowed to warm to room temp. and extracted with ice-cold solution of NaOH (1 g) in H_2O (40 ml). The water layer was acidified to pH 2 (3.9 ml of 12 N HCl solution was used) and extracted with Et_2O (2 × 30 ml). After drying and concentration of the combined ethereal extracts, the residue was condensed "bulb-to-bulb" (20°C/0.5 Torr) to give 634 mg (28%) of essentially pure **27**.

3-Thiabicyclo[4.1.0]heptane (**29**) *and 3,6-Dihydro-5-methyl-2H-thiopyran* (**31**): A sample of 2-(2-methylenecyclopropyl)ethanethiol (**27**) (300 mg, 2.6 mmol) was heated in C_6D_6 for 14 h with periodical GC and NMR monitoring. After disappearance of the olefinic proton signals, GC analysis proved the reaction mixture to consist of **29** (47%), **31** (48%), and 5% of unreacted **27** which were separated by preparative GC (70°C in column, 120°C injector and 150°C detector temperatures).

29: ^{1}H NMR (500 MHz): δ = 0.39 (dd, $J_{7',7}$ ca. 0, $J_{7',1}$ = 7.8, $J_{7',6}$ = 8.5 Hz, 7′-H), 0.40 (dd, $J_{7,7'}$ ca. 0, $J_{7,1}$ = 5.7, $J_{7,6}$ = 6.5 Hz, 7-H), 0.57 (ddddd, $J_{6,5}$ = 3.1, $J_{6,5'}$ = 7.9, $J_{6,7}$ = 6.5, $J_{6,7'}$ ca. $J_{6,1}$ = 8.5 Hz, 6-H), 0.70 (ttd, $J_{1,2}$ = 3.1, $J_{1,2'}$ ca. $J_{1,7}$ = 5.7, $J_{1,7'}$ = 7.8, $J_{1,6}$ = 8.5 Hz, 1-H), 1.51 (dddd, $J_{5,5'}$ = 14.0, $J_{5,4'}$ = 10.1, $J_{5,4}$ = 5.1, $J_{5,6}$ = 3.1 Hz, 5-H), 1.85 (ddt, $J_{5',5}$ = 14.0, $J_{5',4}$ ca. $J_{5',4'}$ = 5.1, $J_{5',6}$ = 7.9 Hz, 5′-H), 2.02 (dtd, $J_{4,4'}$ = 13.2, $^4J_{4,2}$ = 1.0, $J_{4,5}$ ca. $J_{4,5'}$ = 5.1 Hz, 4-H), 2.07 (ddd, $J_{4',4}$ = 13.2, $J_{4',5'}$ = 5.1, $J_{4',5}$ = 10.1 Hz, 4′-H), 2.47 (ddd, $J_{2,2'}$ = 13.5, $^4J_{2,4}$ = 1.0, $J_{2,1}$ = 3.1 Hz, 2-H), 2.83 (dd, $J_{2',2}$ = 13.5, $J_{2',1}$ = 5.7 Hz, 2′-H). The assignments of the ^{1}H-NMR signals were established by a COSY correlation experiment. − ^{13}C NMR: δ = 9.32, 23.90, 24.58, 26.81 (CH_2), 9.10, 9.39 (CH). − MS (EI), *m/z* (%): 114 (100) [M^+], 86 (88) [$M^+ - C_2H_4$], 73 (86) [$M^+ - C_3H_5$], 68 (76) [$M^+ - SCH_2$], 45 (78), 43 (58). − MS (HR-EI): 114.0503 ($C_6H_{10}S$, calcd. 114.0503).

31: ^{1}H NMR: δ = 1.57−1.66 (m, 2 H, CH_2), 1.72−1.88 (m, 2 H, CH_2), 1.85 (s, 3 H, CH_3), 2.52−2.56 (m, 2 H, SCH_2), 5.35−5.37 (m, 1 H =CH). − ^{13}C NMR: δ = 23.89 (CH_3), 22.20, 24.52, 27.17 (CH_2), 116.35 (CH), 128.54 (C). − MS (EI), *m/z* (%): 114 (100) [M^+], 113 (78) [$M^+ - H$], 99 (83) [$M^+ - CH_3$], 85 (92) [$M^+ - CH_3 - CH_2$], 79 (39), 71 (25), 59 (20), 45 (18). − MS (HR-EI): 114.0503 ($C_6H_{10}S$, calcd. 114.0503).

Kinetic Measurements: Under argon, an NMR tube was charged with bicyclopropylidene (**1**) (17.1 mg, 20 µl, 0.213 mmol), thiophenol (**8a**) (117.3 mg, 109 µl, 1.065 mmol) and anhydrous deuterobenzene (1 ml), hermetically closed, placed into the probe of an NMR instrument, and the reaction was monitored by recording the ^{1}H-NMR spectrum after measured intervals. In a second kinetic experiment, *p*-TsOH·H_2O (2 mg, 0.01 mmol, 4.9 mol%) was also added. The pseudo-first-order rate coefficients k_{BCP} derived from these measurements at 19°C were equal to $2.85 \cdot 10^{-4}$ s^{-1} in the absence and $2.06 \cdot 10^{-3}$ s^{-1} in the presence of *p*-toluenesulfonic acid with the correlation coefficients r = 0.951 and 0.998, respectively.

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