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A New and Convenient Synthetic Method for Cyclopropyl Phenyl Sulfides

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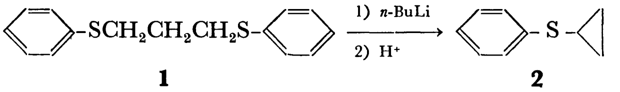
The reactions of a variety of 1,3-bis(phenylthio)propanes with butyllithium have been shown to produce cyclopropyl phenyl sulfides in good to high yields. A new and convenient *in situ* preparation of 1-lithiocyclopropyl phenyl sulfide can be readily carried out by treating 1,3-bis(phenylthio)propane with 2 equiv. of butyllithium at 0 °C in THF. The reaction with electrophiles proceeds in good yield. *O*-Aryl and *O*-alkyl *S*-cyclopropyl dithiocarbonates also can be prepared in good yields. 1,2-Bis(phenylthio)ethane was converted to phenyl vinyl sulfide on treatment with butyllithium, while 1,4-bis(phenylthio)butane was recovered unchanged by a similar treatment.

In 1973 Trost has reported that 1-lithiocyclopropyl phenyl sulfide, prepared by deprotonation of cyclopropyl phenyl sulfide is a useful reagent in the preparation of cyclobutanones and cyclobutenes.[1,2] Later, Miller and Cohen showed the transformations of 1-lithiocyclopropyl phenyl sulfide into useful synthetic intermediates such as γ-keto sulfides,[3] vinyl sulfides,[4] and 1-methoxycyclopropyl phenyl sulfide.[5] Cyclopropyl phenyl sulfide can be prepared by cyclization of 3-chloropropyl phenyl sulfide in liquid ammonia.[1a,6] Recently, Cohen has found the efficient method for conversion of 1,1,3-tris(phenylthio)propane into 1,1-bis(phenylthio)cyclopropane, which upon reductive lithiation with lithium naphthalenide affords lithiocyclopropane.[7a] In 1980 we reported preliminary results of one-step synthetic method for 1-lithiocyclopropyl phenyl sulfide utilizing readily available 1,3-bis(phenylthio)propane as the starting material.[8]

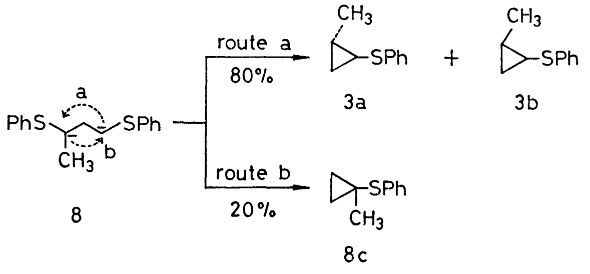
In this paper we investigated the scope and limitations of the new cyclization reaction as a viable route to various types of cyclopropyl phenyl sulfides.

Results and Discussion

Synthesis of Cyclopropyl Phenyl Sulfides. When 1 equiv. of butyllithium was added to THF solution of 1,3-bis(phenylthio)propane (**1**),[8,9] cyclopropyl phenyl sulfide (**2**)[1a] was obtained in 77% yield after quenching with aqueous ammonium chloride solution. The use of butyllithium in THF at −78 °C—0 °C for 3 h was found to be a convenient method for the synthesis of **2**. Additives such as hexamethylphosphoric triamide (HMPA) or *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA) were found to have a negligible effect on yield of **2**. The possibility that various types of substituted 1,3-bis(phenylthio)propanes may be converted to the corresponding cyclopropanes by this method was further investigated. A variety of the alkyl-substituted 1,3-bis(phenylthio)propanes used in this study were prepared by the reported procedures.[1a,10–13] The cyclization of sulfides was efficiently carried out in addition of 1 equiv. of butyllithium at −78 °C—0 °C in THF in the presence of HMPA. Results are summarized in Table 1. The structures and stereochemistry of the substituted cyclopropyl phenyl sulfides were accomplished through the utilization of comparative spectroscopic data,[1] GLPC analyses, and authentic sample prepared from 1-lithiocyclopropyl phenyl sulfide. For example, GLPC analysis of cyclopropanes derived from sufide **3** showed a 9:1 mixture of **3a** and **3b** which was confirmed by comparison with the reported data.[1a] 1,3-Bis(phenylthio)butane (**8**) afforded three peaks, A, B, and C, in the ratio of 3:5:2. Peak A (retention time of 3.4 min) was shown to be 1-methylcyclopropyl phenyl sulfide (**8c**) by GLPC comparison with the authentic sample prepared from 1-lithiocyclopropyl phenyl sulfide and iodomethane.[1a,7c] Peak B (retention time of 4.3 min) and peak C (retention time of 5.7 min) were identified as trans-isomer (**3a**) and cis-isomer (**3b**) of 2-methylcyclopropyl phenyl sulfide by comparing the result from the reaction of sulfide **3**. These results clearly reflect the difference in acidity between C-1 hydrogen and C-3 hydrogen of sulfide **8** (Scheme 1).

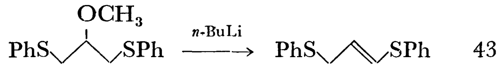


1 **2**



Scheme 1.

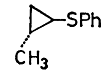
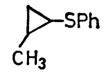
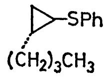
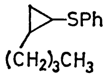
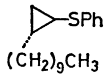
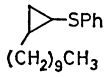
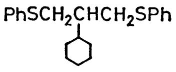
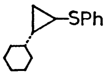
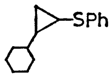
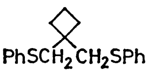
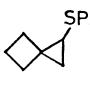
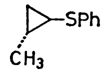
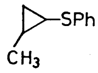
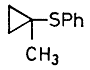
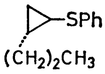
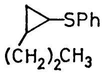
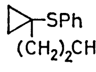
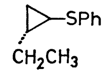
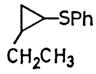
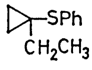
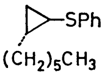
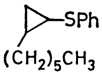
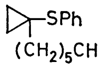
Reaction of 2-methoxy-1,3-bis(phenylthio)propane (**12**) with 1 equiv. of butyllithium in THF gave only the elimination product **13**;[14] no cyclopropane could be detected. An interesting change was observed with 2-hydroxy analogue **14**. Thus, reaction of 1,3-bis(phenylthio)-2-propanol (**14**) with 2 equiv. of butyllithium gave cyclopropanol **16** in good yield, most probably through a dianion intermediate **15**. The protection of OH group was readily carried out by adding 1-chloromethoxy-2-methoxyethane[15] or chlorotrimethylsilane into the reaction mixture (Scheme 2).



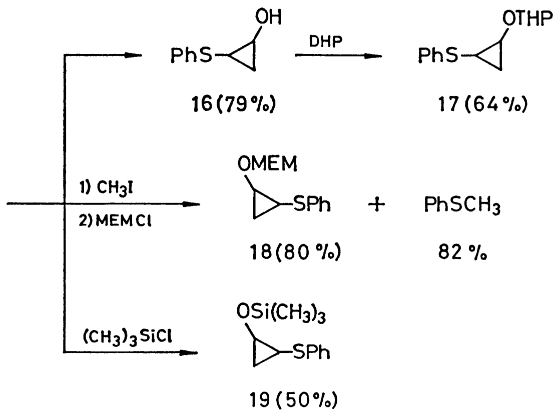
12 **13**

The mechanism of this facile ring closure has not been studied in detail, but it may be pictured in terms of an initial formation of the sulfur-stabilized carbanion

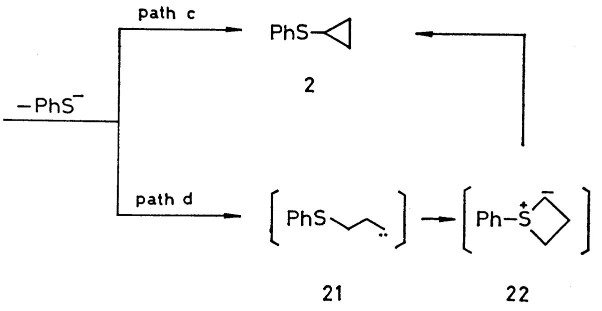
Table 1. Preparation of cyclopropyl sulfides from 1,3-bis(phenylthio)propanes

1,3-Bis(phenylthio)propanes		Products	Ratio	Yield/%
$PhSCH_2\underset{\substack{\mid\\CH_3}}{C}HCH_2SPh$	(3)	 (3a)  (3b)	9:1[a)]	88
$PhSCH_2\underset{\substack{\mid\\(CH_2)_3CH_3}}{C}HCH_2SPh$	(4)	 (4a)  (4b)	4:1[a)]	79
$PhSCH_2\underset{\substack{\mid\\(CH_2)_9CH_3}}{C}HCH_2SPh$	(5)	 (5a)  (5b)	7:1[a)]	74
	(6)	 (6a)  (6b)	>19:<1[a)]	76
	(7)	 (7a)		61
$PhSCH_2CH_2\underset{\substack{\mid\\CH_3}}{C}HSPh$	(8)	 (3a)  (3b)  (8c)	5:2:3[b)]	65
$PhSCH_2CH_2\underset{\substack{\mid\\(CH_2)_2CH_3}}{C}HSPh$	(9)	 (9a)  (9b)  (9c)	2:4:5[b)]	73
$PhSCH_2CH_2\underset{\substack{\mid\\CH_2CH_3}}{C}HSPh$	(10)	 (10a)  (10b)  (10c)	2:2:1[b)]	74
$PhSCH_2CH_2\underset{\substack{\mid\\(CH_2)_5CH_3}}{C}HSPh$	(11)	 (11a)  (11b)  (11c)	1:2:2[b)]	73

a) The trans/cis ratios of cyclopropyl sulfides were determined by ^{1}H-NMR and GLPC analyses. b) GLPC analyses showed three peaks. The first peak was presumed to be 1-alkylcyclopropyl phenyl sulfide by comparison of the data obtained from ^{1}H-NMR and GLPC.



Scheme 2.

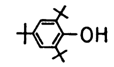
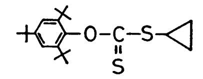
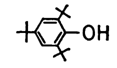
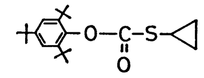
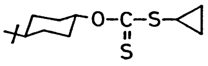
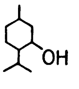
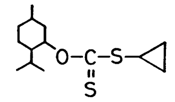
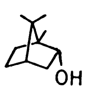
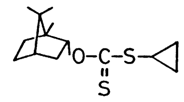


Scheme 3.

20 followed by an intramolecular nucleophilic displacement of benzenethiolate anion (path c, Scheme 3).[7e)] Recently, Cohen proposed a similar cyclization in the reaction of 1,1,3-tris(phenylthio)propane with methyllithium in the presence of TMEDA in THF.[7a)] An alternative mechanism to that proposed would involve a carbene intermediate **21** which rearranges to a ylide **22** to give **2** (path d).[16)] This pathway (d) is considered unlikely, however, since the reaction of 1,3-bis(phenylthio)propane (**1**) with butyllithium in the presence of excess of cyclohexane gave none of the addition product derived from the carbene **21**. Cyclopropyl phenyl sulfide (**2**) was formed as the only isolable product (59%).

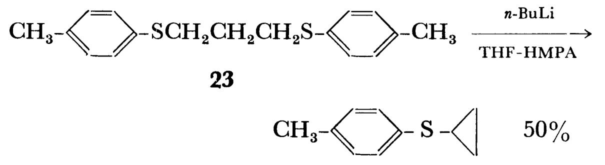
In investigating the scope and limitations of this

TABLE 2. PREPARATION OF *S*-(3-CHLOROPROPYL) AND *S*-CYCLOPROPYL THIOCARBONATES

ROH (**34**)	CXS	Yield of **35**/%	Product **36**	Yield of **36**/%
	CS_2	75 (**35a**)		(**36a**) 77
	COS	85 (**35b**)		(**36b**) 94
	CS_2	80 (**35c**)		(**36c**) 86
	CS_2	76 (**35d**)		(**36d**) 80[a]
	CS_2	66 (**35e**)		(**36e**) 82[b]

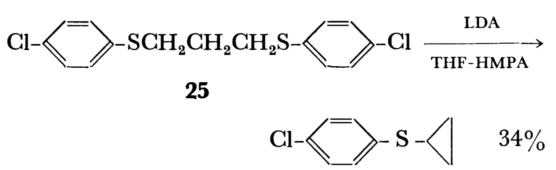
a) $[\alpha]^{25}_{D}$ −59.4° (*c* 1.47, $CHCl_3$). b) $[\alpha]^{23}_{D}$ −17.6° (*c* 1.61, $CHCl_3$).

new cyclization, it was found that when the sulfides contain *p*-methyl or *p*-chloro substituent on benzene ring, the yields of cyclopropanes were decreased under the same reaction conditions cited above, possibly due to insolubility of these sulfides **23** and **25** in THF at a lower temperature. The use of 1.5—2.5 equiv. of HMPA as a co-solvent gave satisfactory results.



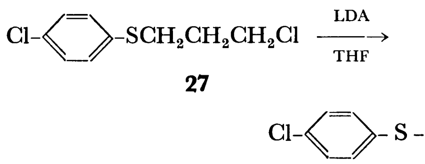
23

24 50% (20% without HMPA)



25

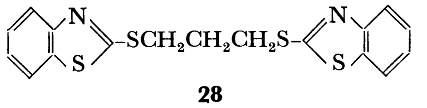
26 34% (trace without HMPA)



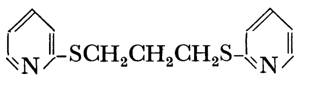
27

26 46%

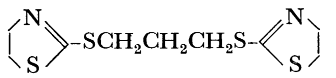
Attempts to cyclize the sulfides **28**—**30** using lithium diisopropylamide (LDA) or butyllithium in the presence of HMPA, however, were not successful due to the decomposition of sulfides under these reaction conditions.



28



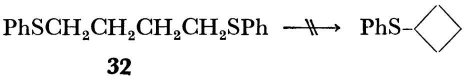
29



30

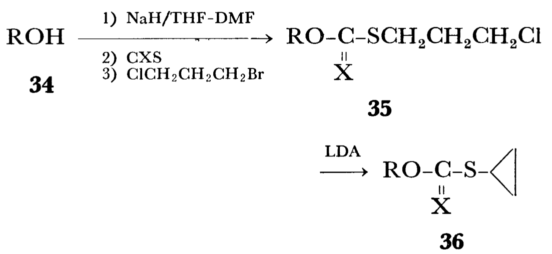
We briefly investigated the reaction of 1,2-bis(phenylthio)ethane (**31**)[17] or 1,4-bis(phenylthio)butane (**32**) with butyllithium in THF. Treatment of **31** in a mixture solvent of THF and HMPA afforded phenyl vinyl sulfide (**33**)[18] in 52% yield. However, the similar reaction of **31** in THF gave little of **33**; the Michael type addition of butyllithium to **33** took place. Treatment of **32** with butyllithium under various reaction conditions led to the recovery of the starting material **32**.

$$\underset{\mathbf{31}}{\mathrm{PhSCH_2CH_2SPh}} \xrightarrow[\text{THF-HMPA}]{n\text{-BuLi}} \underset{\mathbf{33}}{\mathrm{PhSCH{=}CH_2}}$$



32

Next, we have developed a new method for the preparation of *S*-cyclopropyl thiocarbonate and dithiocarbonates. As outlined in Scheme 4, *S*-(3-chloropropyl) dithiocarbonates **35** were prepared from the corresponding alcohols and phenols **34**.[6,19] Treatment



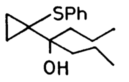
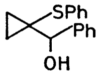
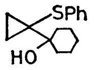
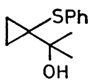
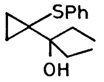
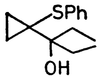
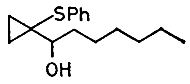
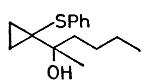
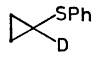
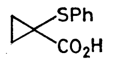
$$\underset{\mathbf{34}}{\mathrm{ROH}} \xrightarrow[\substack{2)\ \mathrm{CXS}\\ 3)\ \mathrm{ClCH_2CH_2CH_2Br}}]{1)\ \mathrm{NaH/THF\text{-}DMF}} \underset{\mathbf{35}}{\mathrm{RO\text{-}\underset{\underset{X}{\|}}{C}\text{-}SCH_2CH_2CH_2Cl}}$$

35

36

Scheme 4.

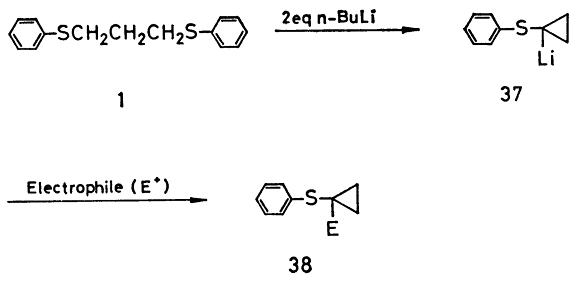
TABLE 3. REACTIONS OF 1,3-BIS(PHENYLTHIO)PROPANE (**1**) AND ELECTROPHILES IN THE PRESENCE OF BUTYLLITHIUM

Electrophile[a]	Additive	Product (**38**)		Yield/%
4-Heptanone	—		(**38a**)	71
Benzaldehyde	—		(**38b**)	67
Cyclohexanone	—		(**38c**)	60
Acetone	—		(**38d**)	34
3-Pentanone	—		(**38e**)	69
3-Pentanone	CuI (10 mmol)		(**38e**)	85
Heptanal	CuI (10 mmol)		(**38f**)	59
2-Hexanone	CuI (10 mmol)		(**38g**)	65
D_2O	—		(**38h**)	65
CO_2	—		(**38i**)	55

a) The reaction was carried out by using 1,3-bis-(phenylthio)propane (**1**) (10 mmol) and butyllithium (22 mmol) in THF.

of **35** in THF with 1.1 equiv. of LDA resulted in smooth cyclization to give *S*-cyclopropyl derivatives **36** in good to high yields as summarized in Table 2. The optically active *S*-cyclopropyl dithiocarbonates **36d** and **36e** could also be obtained by this procedure.

Direct Generation of 1-*Lithiocyclopropyl Phenyl Sulfide.* The finding that cyclopropyl phenyl sulfide (**2**) was formed on treatment of 1,3-bis(phenylthio)propane (**1**) with 1 equiv. of butyllithium suggested that it might be possible to trap 1-lithiocyclopropyl phenyl sulfide (**37**) with electrophiles in the reaction of **1** with 2 equiv. of butyllithium. Thus, treatment of sulfide **1** with 2 equiv. of butyllithium at 0 °C in THF gave a pale yellow solution of lithium reagent **37** after 3 h. Addition of 1 equiv. of 4-heptanone at −78 °C and allowing the reaction mixture to warm to room temperature resulted in the formation of the adduct **38a** in 51% yield. The yield of adduct was increased when 0.5 equiv. of 4-heptanone was added to the reaction mixture (71% yield). Results of one-pot reaction with a variety of electrophiles are summarized in Table 3. It was found that yields were improved when CuI was added to the reaction mixture to scavenge the thiolate anion as a copper(I) thiolate.



Experimental

General. All reactions involving organometallic species were run in flame-dried glasswares under an atmosphere of nitrogen or argon. ^{1}H-NMR spectra were determined in the indicated solvent on a JEOL Model PS-100 or a Hitachi Model R-24B spectrometer. Chemical shifts are expressed in parts per million downfield from internal tetramethylsilane. Infrared spectra were recorded on a Hitachi Model 215 spectrophotometer. GLPC analyses were performed on a Varian Aerograph Model 920 gas chromatograph using a 0.15 cm × 120 cm glass column (20% Silicone DC-550 on Celite 545). Mass spectra were recorded on a Hitachi Model M-52 mass spectrometer. Silica-gel columns for chromatography utilized Wakogel-200. Optical rotations were measured in 1-dm path length cell of 10 ml capacity using a JASCO Model DIP-181 polarimeter. Boiling points and melting points are uncorrected. All solvents and reagents were used as purchased unless otherwise specified. Aldehydes and ketones were purified by distillation. Tetrahydrofuran (THF) was dried by distillation from calcium hydride and subsequent distillation from lithium aluminium hydride under a nitrogen atmosphere, or distilled from sodium benzophenone ketyl under a nitrogen atmosphere. Diisopropylamine and *N,N,N′,N′*-tetramethylethylenediamine were distilled from calcium hydride and stored over 4 Å molecular sieves. Hexamethylphosphoric triamide (HMPA) was distilled at 0.2—0.3 mmHg (1 mmHg≈133.322 Pa) from calcium hydride and stored over 13 Å molecular sieves. Hexane and *N,N*-dimethyformamide were distilled from calcium hydride and stored over 4 Å molecular sieves. Elemental analyses were performed by the Microanalytical Laboratory, operated by the Institute for Chemical Research, Kyoto University.

1,3-Bis(phenylthio)propane (1). According to the method[8] previously described, sulfide **1** was prepared in 93% yield: bp 160—161 °C/0.2—0.3 mmHg; ^{1}H-NMR (CCl_4) δ 7.10 (m, 10H, C_6H_5S), 2.90 (t, J=7.5 Hz, 4H, CH_2S), 1.84 (q, J=7.5 Hz, 2H, CH_2).

Cyclopropyl Phenyl Sulfide (2). To a stirred solution of 2.60 g (10 mmol) of 1,3-bis(phenylthio)propane (**1**) in 20 ml of THF at −78 °C was added butyllithium (7.7 ml of a 1.5 M (1 M=1 mol dm^{-3}) solution in hexane, 12 mmol). After it was stirred for 5 min, the cold bath was removed and the reaction mixture was stirred for 3 h in the ice bath. The reaction was quenched with saturated ammonium chloride solution (10 ml) and extracted four times with ether. The ether layers were combined, dried over anhydrous sodium sulfate, and evaporated to give a mixture of **2** and benzenethiol. Distillation under reduced pressure gave pure cyclopropyl phenyl sulfide (**2**):[1a,6] 1.15 g (77%); bp 89—90 °C/4.7 mmHg; IR (thin film) 3080, 3020, 1580, 1480, 1440, 1095, 1025 cm^{-1}; ^{1}H-NMR (CCl_4) δ 6.90—7.40 (m, 5H, SC_6H_5), 1.90—2.20 (m, 1H, CH), 0.80—1.00 (m, 2H), 0.50—0.80 (m, 2H). Found: C, 71.90; H, 6.83%. Calcd for $C_9H_{10}S$: C, 71.95; H, 6.71%. MS (20 eV) *m/e* 150 (M^+, 100).

Preparation of 1-(Phenylthio)-2-[(phenylthio)methyl]hexane (4): Diethyl 1,1-pentanedicarboxylate was prepared from diethyl malonate according to the literature.[10] Reduction of diethyl 1,1-pentanedicarboxylate (43.2 g, 0.2 mol) with lithium aluminium hydride (14.5 g, 0.38 mol) in dry ether under reflux gave 20.5 g (78%) of 2-(hydroxymethyl)-1-hexanol: bp 140—141 °C/18 mmHg. 1-Chloro-2-(chloromethyl)hexane was prepared from 2-(hydroxymethyl)-1-hexanol in 85% yield by the method of Trost:[1a] ^{1}H-NMR (CCl_4) δ 3.60 (m, 4H), 2.00 (m, 1H), 1.40 (m, 6H), 0.92 (m, 3H). To a stirred and cooled (ice-bath) solution prepared from Na (4.6 g, 0.2 mol) and methanol (150 ml) was added dropwise 22.1 g (0.2 mol) of benzenethiol. A solution of 12 g (0.07 mol) of 1-chloro-2-(chloromethyl)hexane in 10 ml of methanol was added dropwise. After being stirred at 0—5 °C for 1 h, the mixture was stirred at room temperature for 1 h, and then refluxed for 6 h. After evaporation of the solvent, the residue was diluted with ether, dried over anhydrous sodium sulfate, and concentrated. Distillation under reduced pressure gave 17.5 g (79%) of 1-(phenylthio)-2-[(phenylthio)methyl]hexane (**4**): bp 185—186 °C/0.8 mmHg; ^{1}H-NMR (CCl_4) δ 7.15 (m, 10H), 2.90 (m, 4H), 1.82 (m, 1H), 0.7—1.7 (m, 9H).

1-(Phenylthio)-2-[(phenylthio)methyl]dodecane (5): ^{1}H-NMR (CCl_4) δ 7.15 (m, 10H), 2.95 (m, 4H), 1.85 (m, 1H), 0.80—1.60 (m, 21H).

2-Cyclohexyl-1,3-bis(phenylthio)propane (6): ^{1}H-NMR (CCl_4) δ 7.10 (m, 10H), 2.95 (m, 4H), 0.60—2.00 (m, 12H).

1,3-Bis(phenylthio)butane (8): To a stirred and cooled (ice-bath) solution of 2.13 g (0.0926 mol) of Na in 300 ml of ethanol was added benzenethiol (10.2 g, 92.6 mmol) in 30 ml of ethanol. After an additional 30 min at 0 °C, a catalytic amount of sodium iodide was added, the cold bath was removed and the reaction mixture was refluxed for 10 h. Usual workup and distillation under reduced pressure gave pure sulfide **8** (8.42 g, 66%): bp 165—170 °C/0.6 mmHg; ^{1}H-NMR (CCl_4) δ 7.15 (m, 10H, C_6H_5S), 3.30 (q, J=7.1 Hz, 1H, CH), 3.00 (t, J=7.1 Hz, CH_2S), 1.80 (m, 2H, CH_2), 1.25 (d, J=7.1 Hz, 3H, CH_3).

Preparation of 1-(Phenylthio)-3-pentanol: According to Corey's procedure,[13] to a solution of 22 mmol of 1,4-diazabicyclo[2.2.2]octane (purified by sublimation) and 22 mmol of methyl phenyl sulfide in 40 ml of THF at 0 °C was added over 7 min 24 mmol of butyllithium. After stirring was continued at room temperature for 45 min, 20 mmol of 1,2-epoxybutane in 2 ml of THF was added dropwise at 0 °C. The reaction mixture was stirred for 45 h at room temperature and quenched with 20 ml of aqueous ammonium chloride solution. Usual workup gave 1-(phenylthio)-3-pentanol in 86% yield: bp 140—142 °C/3 mmHg; IR (thin film) 3370 (OH), 3050, 1575, 1480, 1435, 1020 cm^{-1}. ^{1}H-NMR (CCl_4) δ 6.90—7.30 (m, 5H, C_6H_5S), 3.40—3.70 (m, 1H, CH), 2.80—3.10 (m, 2H, SCH_2), 2.50—2.80 (m, 1H, OH), 1.20—1.80 (m, 4H), 0.88 (t, J=7 Hz, 3H, CH_3); MS (20 eV) *m/e* 196 (M^+, 85), 86 (100). Found: C, 67.26; H, 8.38%. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22%.

In a similar way, 1-(phenylthio)-3-nonanol was obtained in 76% yield as white crystals after recrystallization from hexane: mp 45.0—45.7 °C; ^{1}H-NMR (CCl_4) δ 7.00—7.40 (m, 5H, C_6H_5S), 3.50—3.80 (m, 1H, CH), 2.90—3.10 (m, 2H, SCH_2), 1.98 (s, 1H, OH), 1.60—1.90 (m, 2H, CH_2), 1.24 (m, 10H), 0.86 (t, 3H, CH_3); MS (20 eV) *m/e* 252 (M^+, 45), 72 (100). Found: C, 71.17; H, 9.88%. Calcd for $C_{15}H_{24}OS$: C, 71.38; H, 9.58%.

1,3-Bis(phenylthio)pentane (**10**) was prepared from 1-(phenylthio)-3-pentanol: bp 184—187 °C/1.6 mmHg; ^{1}H-NMR (CCl_4) δ 7.00—7.40 (m, 10H, C_6H_5S), 2.90—3.20 (m, 3H), 1.40—1.90 (m, 4H, CH_2), 0.96 (t, J=7 Hz, 3H, CH_3); MS (20 eV) *m/e* 288 (M^+, 98), 123 (100).

1,3-Bis(phenylthio)nonane (**11**) was prepared from 1-(phenylthio)-3-nonanol: oil; ^{1}H-NMR (CCl_4) δ 7.00—7.40 (m, 10H, C_6H_5S), 2.90—3.30 (m, 3H), 1.10—2.00 (m, 12H), 0.85 (t, J=7 Hz, 3H, CH_3). MS (20 eV) *m/e* 344 (M^+, 100).

Reaction of 2-Methyl-1,3-bis(phenylthio)propane (3): To a solution of 10 mmol of sulfide **3** and 25 mmol of HMPA in 20 ml of THF at −78 °C was added over 10 min 12 mmol of butyllithium, and stirring was continued for 10 min. The cooling bath was removed, and the reaction mixture was stirred at 0 °C for 3 h. After quenching with 10 ml of saturated ammonium chloride solution, the mixture was acidified with 10% hydrochloric acid (50 ml) and extracted three times with ether. The combined extracts were washed twice with brine, dried over anhydrous sodium sulfate, and concentrated. Distillation under reduced pressure gave a mixture of cyclopropyl sulfides **3a** and **3b** of 9:1 ratio in 88% yield: bp 71—72 °C/0.8 mmHg; ^{1}H-NMR (CCl_4) δ 7.00—7.70 (m, 5H, C_6H_5S), 2.10—2.40 (m, 0.1H, SCH), 1.80—2.00 (m, 0.9H, SCH), 1.20—1.30 (m, 3H, CH_3), 0.20—1.20 (m, 3H); IR (thin film) 3060, 2950, 1580, 1480, 1440, 1090, 1025 cm^{-1}; MS (20 eV) *m/e* 164 (M^+, 100). Found: C, 73.50; H, 7.58%. Calcd for $C_{10}H_{12}S$: C, 73.12; H, 7.37%.

Reaction of 1-(Phenylthio)-2-[(phenylthio)methyl]hexane (4): Reaction of 10 mmol of sulfide **4** with 12 mmol of butyllithium in 20 ml of THF containing 20 mmol of HMPA gave a mixture of cyclopropyl sulfides **4a** and **4b**: bp 112—114 °C/1.7 mmHg; ^{1}H-NMR (CCl_4) δ 6.80—7.30 (m, 5H, C_6H_5S), 2.00—2.30 (m, 0.2H, CHS), 1.70—1.90 (m, 0.8H, SCH), 0.20—1.70 (m, 12H); IR (thin film) 3080, 2925, 1580, 1480, 1440, 1095, 1030 cm^{-1}; MS (20 eV) trans-isomer **4a** *m/e* 206 (M^+, 77), 55 (100); cis-isomer **4b** *m/e* 206 (M^+, 69), 142 (100). Found: C, 75.42; H, 9.02%. Calcd for $C_{13}H_{18}S$: C, 75.73; H, 8.74%.

Reaction of 1-(Phenylthio)-2-[(phenylthio)methyl]dodecane (5): Reaction of 10 mmol of sulfide **5** with 12 mmol of butyllithium in 20 ml of THF containing 20 mmol of HMPA gave a mixture of cyclopropyl sulfides **5a** and **5b**: bp 171—173 °C/1.6 mmHg; ^{1}H-NMR (CCl_4) δ 6.90—7.30 (m, 5H, C_6H_5S), 2.10—2.40 (m, 0.13H, SCH), 1.70—1.90 (m, 0.87H, SCH), 0.60—1.60 (m, 24H); IR (thin film) 3060, 2920, 1580, 1475, 1435, 1090, 1020 cm^{-1}; MS (20 eV) trans-isomer **5a** *m/e* 290 (M^+, 82), 82 (100); cis-isomer **5b** *m/e* 290 (M^+, 63), 82 (100). Found: C, 78.63; H, 10.51%. Calcd for $C_{19}H_{30}S$: C, 78.62; H, 10.27%.

Reaction of 2-Cyclohexyl-1,3-bis(phenylthio)propane (6): Reaction of 10 mmol of sulfide **6** with 12 mmol of butyllithium in 20 ml of THF containing 20 mmol of HMPA gave a mixture of cyclopropyl sulfides **6a** and **6b**: bp 136—136.5 °C/1.1 mmHg; ^{1}H-NMR (CCl_4) δ 6.90—7.40 (m, 5H, C_6H_5S), 0.50—2.00 (m, 15H); IR (thin film) 3070, 2920, 1580, 1480, 1450, 1440, 1090, 1025 cm^{-1}; MS (20 eV) trans-isomer *m/e* 232 (M^+, 81), 136 (100). Found: C, 77.81; H, 8.69%. Calcd for $C_{15}H_{20}S$: C, 77.59; H, 8.62%.

Reaction of 1,1-Bis[(phenylthio)methyl]cyclobutane (7): Reaction of 9.8 mmol of sulfide **7** with 12 mmol of butyllithium in 20 ml of THF containing 20 mmol of HMPA gave a 61% of 1-(phenylthio)spiro[2.3]hexane (**7a**): bp 83—84 °C/0.3 mmHg; IR (thin film) 3060, 2970, 1480, 1435, 1090, 1025 cm^{-1}; ^{1}H-NMR (CCl_4) δ 6.80—7.40 (m, 5H), 1.80—

2.50 (m, 6H), 0.78—1.80 (m, 2H), 0.50—0.78 (t, J=6 Hz, 1H). MS (20 eV) *m/e* 190 (M$^+$, 100). Found: C, 75.88; H, 7.67%. Calcd for $C_{12}H_{14}S$: C, 75.79; H, 7.37%.

*Reaction of 1,3-Bis(phenylthio)butane (**8**)*: Reaction of sulfide **8** with 12 mmol of butyllithium in 20 ml of THF gave a mixture of cyclopropyl sulfides **3a**, **3b**, and **8c** (5:4:1) in 21% yield. A similar reaction of 10 mmol of sulfide **8** with 12 mmol of butyllithium in 20 ml of THF containing 25 mmol of HMPA gave a mixture of sulfides **3a**, **3b**, and **8c** (5:2:3) in 65% yield: bp 72—75 °C/2.2 mmHg; ^{1}H-NMR (CCl_4) δ 7.00—7.50 (m, 5H, C_6H_5S), 0.20—2.40 (m, 7H); IR (thin film) 3100, 1590, 1485, 1445, 1105, 1030 cm^{-1}; MS (20 eV) 1-methylcyclopropyl phenyl sulfide (**8c**): *m/e* 164 (M$^+$, 27), 131 (100); trans-isomer **3a**: *m/e* 164 (M$^+$, 100); cis-isomer **3b**: *m/e* 164 (M$^+$, 94), 110 (100). Found: C, 73.43; H, 7.60%. Calcd for $C_{10}H_{12}S$: C, 73.12; H, 7.37%.

*Reaction of 1,3-Bis(phenylthio)hexane (**9**)*: Reaction of 10 mmol of sulfide **9** with 12 mmol of butyllithium in 20 ml of THF containing 20 mmol of HMPA gave a mixture of cyclopropyl sulfides **9a**, **9b**, and **9c**: bp 96—102.5 °C/2.8 mmHg; ^{1}H-NMR (CCl_4) δ 6.90—7.30 (m, 5H, C_6H_5S), 0.20—2.40 (m, 11H); IR (thin film) 3060, 2950, 1580, 1475, 1435, 1090, 1020 cm^{-1}; MS (20 eV) 1-propylcyclopropyl phenyl sulfide (**9c**): MS (20 eV) *m/e* 192 (M$^+$, 63), 159 (100); 2-propylcyclopropyl phenyl sulfides (**9a** and **9b**) *m/e* 192 (M$^+$, 94), 149 (100). Found: C, 75.09; H, 8.42%. Calcd for $C_{12}H_{16}S$: C, 75.00; H, 8.33%.

*Reaction of 1,3-Bis(phenylthio)pentane (**10**)*: Reaction of 10 mmol of sulfide **10** with 12 mmol of butyllithium in 20 ml of THF containing 25 mmol of HMPA gave a mixture of cyclopropyl sulfides **10a**, **10b**, and **10c** in 74% yield: bp 100—106 °C/3.9 mmHg; ^{1}H-NMR (CCl_4) δ 6.90—7.40 (m, 5H, C_6H_5S), 0.30—2.40 (m, 9H); IR (thin film) 3070, 2960, 1580, 1480, 1435, 1090, 1025 cm^{-1}. Found: C, 74.23; H, 7.93%. Calcd for $C_{11}H_{14}S$: C, 74.10; H, 7.91%.

*Reaction of 1,3-Bis(phenylthio)nonane (**11**)*: Reaction of 10 mmol of sulfide **11** with 12 mmol of butyllithium in 20 ml of THF containing 25 mmol of HMPA gave a mixture of cyclopropyl sulfides, **11a**, **11b**, and **11c**: bp 123—127 °C/0.9 mmHg; ^{1}H-NMR (CCl_4) δ 6.90—7.40 (m, 5H, C_6H_5S), 0.30—2.40 (m, 17H); IR (thin film) 3060, 2920, 1580, 1470, 1435, 1090, 1020 cm^{-1}. Found: C, 77.10; H, 9.60%. Calcd for $C_{15}H_{22}S$: C, 76.86; H, 9.46%.

*Preparation of 2-Methoxy-1,3-bis(phenylthio)propane (**12**)*: According to Corey's procedure,[14] sulfide **12** was prepared from 1,3-bis(phenylthio)-2-propanol (**14**) (*vide infra*) and iodomethane in 91% yield: bp 180—182 °C/0.7 mmHg; ^{1}H-NMR (CCl_4) δ 6.90—7.40 (m, 10H, C_6H_5S), 3.20—3.50 (m, 1H, CH), 3.24 (s, 3H, OCH_3), 3.60 (d, J=6 Hz, 4H, CH_2); MS (20 eV) *m/e* 290 (M$^+$, 39), 135 (100).

*Reaction of Sulfide **12** with Butyllithium*: Reaction of 10 mmol of sulfide **12** with 12 mmol of butyllithium in THF containing 25 mmol of HMPA gave a mixture of 1,3-bis(phenylthio)propene (**13**) and sulfide **12**. Silica gel chromatography after distillation gave 1.12 g (43%) of **13** and 1.03 g (35%) of the starting material **12**. 1,3-Bis(phenylthio)propene (**13**): bp 192—198 °C/3.2 mmHg; ^{1}H-NMR (CCl_4) δ 6.90—7.40 (m, 10H, C_6H_5S), 5.60—6.20 (m, 2H, CH=CH), 3.40—3.70 (m, 2H, CH_2); MS (20 eV) *m/e* 258 (M$^+$, 14), 149 (100). This compound had properties (NMR, MS, TLC) with those of an authentic sample prepared by tosylation of 1,3-bis(phenylthio)-2-propanol (**14**), followed by elimination with LDA in THF.

*Preparation of 1,3-Bis(ohenylthio)-2-propanol (**14**)*: According to Corey's procedure,[14] to a solution of 0.6 mol of sodium benzenethiolate in methanol was added 0.3 mol (27.8 g) of 1-chloro-2,3-epoxypropane at room temperature. After stirring was continued for 1 h, the mixture was heated at 50—60 °C for 1 h. Usual workup gave 77.3 g (93%) of **14**: bp 187—188 °C/0.3 mmHg; ^{1}H-NMR (CCl_4) δ 7.00—7.40 (m, 10H, C_6H_5S), 3.60—3.90 (m, 1H, CH), 2.80—3.20 (m, 5H, OH and CH_2); IR (thin film) 3420 (OH) cm^{-1}; MS (20 eV) *m/e* 276 (M$^+$, 23), 110 (100).

*Synthesis of 2-(Phenylthio)cyclopropanol (**16**)*: To a solution of 40 mmol (11.06 g) of 1,3-bis(phenylthio)-2-propanol (**14**) in 80 ml of THF at −78 °C was added over 36 min 88 mmol of butyllithium, and stirring was continued for 10 min at −78 °C and for 3 h at 0 °C. The mixture was quenched with 10 ml of aqueous ammonium chloride and was extracted with ether three times. The combined extracts were washed once with brine, dried over anhydrous sodium sulfate, and concentrated to give a crude product. Distillation under reduced pressure gave 5.23 g (79%) of **16**: bp 114—119 °C/0.8—0.9 mmHg; ^{1}H-NMR (CCl_4) δ 7.10—7.50 (m, 5H, C_6H_5S), 4.25 (brs, 1H, OH), 3.40—3.70 (m, 1H, CH), 2.10—2.30 (m, 1H, CHS), 0.60—1.30 (m, 2H, CH_2); IR (thin film) 3330 (OH), 3000, 1580, 1480, 1435, 1325, 1200, 1090, 1025 cm^{-1}. Found: C, 65.24; H, 5.99%. Calcd for $C_9H_{10}OS$: C, 65.02; H, 6.06%.

*2-[2-(Phenylthio)cyclopropyloxy]tetrahydropyran (**17**)*: A mixture of 5.9 mmol (0.98 g) of cyclopropanol **16**, 7.1 mmol (0.60 g) of 3,4-dihydro-2*H*-pyran and a catalytic amount of *p*-toluenesulfonic acid monohydrate in dry dichloromethane was stirred at 0 °C for 18 h. Workup and column chromatography on silica gel gave 0.94 g (64%) of **17**: bp 135—141 °C/0.8—0.9 mmHg; ^{1}H-NMR (CCl_4) δ 6.90—7.40 (m, 5H, C_6H_5S), 4.40—4.70 (m, 1H, OCH), 3.30—4.00 (m, 3H), 2.00—2.50 (m, 1H, SCH), 0.70—2.00 (m, 8H).

*1-[(2-Methoxyethoxy)methoxy]-2-(phenylthio)cyclopropane (**18**)*: To a stirred solution of 40 mmol (11.04 g) of **14** in 120 ml of THF at −78 °C was added over 30 min 88 mmol of butyllithium. After completion of the addition, the reaction mixture was stirred at −78 °C for 10 min and at 0 °C for 3 h. The solution was then cooled to −78 °C, and treated with 60 mmol (8.50 g) of iodomethane and stirred at this temperature for 30 min and at 0 °C for 1 h. After the addition of 1-chloromethoxy-2-methoxyethane (5.48 g, 44 mmol), the reaction mixture was stirred at 0 °C for 15 h. Aqueous workup and distillation gave 4.08 g (82%) of methyl phenyl sulfide and 8.12 g (80%) of **18**: bp 146—151 °C/1.0—1.2 mmHg; ^{1}H-NMR (CCl_4) δ 6.90—7.40 (m, 5H, C_6H_5S), 4.62 (s, 2H, OCH_2), 3.30—3.90 (m, 4H, CH_2), 3.28 (s, 3H, CH_3O), 2.20—2.50 (m, 1H, CHO), 0.70—1.60 (m, 3H); MS (20 eV) *m/e* 254 (M$^+$, 4) 59 (100).

*1,3-Bis(4-methylphenylthio)propane (**23**)*: According to the procedure for the preparation of **1**, sulfide **23** was prepared by adding a solution of 0.101 mol (20.3 g) of 1,3-dibromopropane in 50 ml of ethanol to a solution of sodium 4-methylbenzenethiolate (0.201 mol) in ethanol (200 ml). The crude sulfide was purified by distillation to yield 27.14 g (94%) of **23**: bp 167—168 °C/0.2—0.5 mmHg; ^{1}H-NMR (CCl_4) δ 7.12 (d, J=9.2 Hz, 4H), 6.93 (d, J=9.2 Hz, 4H), 2.88 (t, J=7.7 Hz, 4H, CH_2S), 1.80 (q, J=7.7 Hz, 2H, CH_2).

In a similar way, 1,3-bis(4-chlorophenylthio)propane (**25**) was prepared in 80% yield: mp 40—41 °C (ethanol–acetone); ^{1}H-NMR (CCl_4) δ 7.61 (s, 8H), 2.94 (t, 4H, CH_2S), 1.87 (q, J=6.6 Hz, 2H).

*1-Chloro-3-(4-chlorophenylthio)propane (**27**)*: Reaction of 0.05 mol of sodium 4-chlorobenzenethiolate with 0.06 mol of 1-bromo-3-chloropropane in ethanol gave **27** in 90% yield: bp 109—112 °C/0.3—0.4 mmHg; ^{1}H-NMR (CCl_4) δ 7.20 (m, 4H), 3.60 (t, J=7.5 Hz, 2H, CH_2Cl), 3.00 (t, J=7.5 Hz, 2H, CH_2S), 2.00 (q, J=7.5 Hz, 2H, CH_2).

Reaction of 19.2 mmol of sulfide **23** with 23 mmol of butyllithium in 50 ml of THF containing 28.7 mmol of HMPA at −78 °C for 30 min and at 0 °C for 3 h gave cyclopropyl 4-methylphenyl sulfide (**24**) in 50% yield: bp 84—86 °C/1.5 mmHg (lit,[6] bp 87 °C/2.3 mmHg); ^{1}H-NMR (CCl_4) δ 6.90—7.20 (m, 4H, C_6H_5S), 2.27 (s, 3H, CH_3), 1.90—2.20 (m, 1H, CH), 0.50—1.10 (m, 4H); IR (thin film) 3080, 3010, 1490, 1280, 1090, 1025 cm^{-1}. Found: C, 73.29; H, 7.64%. Calcd for $C_{10}H_{12}S$: C, 73.12; H, 7.37%.

Reaction of 10 mmol of sulfide **25** with 11 mmol of LDA in 20 ml of THF containing 24.7 mmol of HMPA at −78—0 °C for 3 h gave 4-chlorophenyl cyclopropyl sulfide (**26**) in 34%: bp 79—81 °C/0.4 mmHg; ^{1}H-NMR (CCl_4) δ 7.16 (s, 4H, C_6H_5S), 2.08 (m, 1H), 1.00 (m, 2H), 0.65 (m, 2H); IR (thin film) 3080, 3000, 1470, 1090, 1010, 810 cm^{-1}. Found: C, 58.79; H, 5.00%. Calcd for C_9H_9ClS: C, 58.53; H, 4.91%.

Reaction of 30 mmol of sulfide **27** with 31 mmol of LDA in THF at −78 °C to room temperature gave the same sulfide **26** in 46% yield.

*1,2-Bis(phenylthio)ethane (**31**)*: Mp 68—69 °C (lit,[17] mp 69 °C); ^{1}H-NMR (CCl_4) δ 7.20 (m, 10H, C_6H_5S), 3.00 (s, 4H, CH_2).

Reaction of 10 mmol of sulfide **31** with 22 mmol of butyllithium in 20 ml of THF containing 25 mmol of HMPA at −78 °C for 3 h gave phenyl vinyl sulfide (**33**) in 52% yield: bp 80 °C/16 mmHg; ^{1}H-NMR was agreement with the literature.[18]

Preparation of O-*(2,4,6-Tri-*t*-butylphenyl)* S-*(3-Chloropropyl) dithiocarbonate (**35a**)*: To a stirred suspension of 1.83 g of sodium hydride (50% mineral oil; washed with hexane three times) in 40 ml of THF was added 2,4,6-tri-*t*-butylphenol (10 g, 0.0381 mol) with ice-bath cooling. After the addition, the bath was removed and the reaction mixture was stirred for 1 h. Carbon disulfide (4.64 g, 0.061 mol) was then added and the stirring was continued for 1 h. The above reaction mixture was added to the solution of 6.00 g (0.381 mol) of 1-bromo-3-chloropropane in 20 ml of dry DMF at 0 °C. After the mixture was stirred for 4 h at room temperature, aqueous workup and recrystallization from methanol gave 11.9 g (75%) of **35a**: mp 47—49 °C. ^{1}H-NMR (CCl_4) δ 7.25 (s, 2H), 3.65 (t, J=7 Hz, 2H), 3.40 (t, J=7 Hz, 2H), 2.30 (m, 2H), 1.40 (s, 27H).

Analogous procedures were followed for the preparation of **35b**, **35c**, **35d**, and **35e**.

O-*(2,4,6-Tri-*t*-butylphenyl)* S-*(3-Chloropropyl) Thiocarbonate (**35b**)*: Mp 75—77 °C (MeOH); ^{1}H-NMR (CCl_4) δ 7.24 (s, 2H), 3.60 (t, J=6.9 Hz, 2H), 3.04 (t, J=6.9 Hz, 2H), 2.12 (m, 2H), 1.36 (m, 27H, CH_3).

O-*(4-*t*-Butylcyclohexyl)* S-*(3-Chloropropyl) Dithiocarbonate (**35c**)*: A viscous oil; ^{1}H-NMR (CCl_4) δ 5.34 (m, 1H), 3.60 (t, J=6.9 Hz, 2H, CH_2), 3.25 (t, J=6.9 Hz, 2H, CH_2), 2.05—2.40 (m, 4H), 0.80—2.05 (m, 16H).

O-L-*Menthyl* S-*(3-Chloropropyl) Dithiocarbonate (**35d**)*: A viscous oil; ^{1}H-NMR (CCl_4) δ 5.83 (m, 1H), 3.55 (t, J=6.9 Hz, 2H, CH_2), 3.20 (t, J=6.9 Hz, 2H, CH_2), 2.00—2.40 (m, 3H), 1.60—2.00 (m, 17H).

O-L-*Bornyl* S-*(3-Chloropropyl) Dithiocarbonate (**35e**)*: Bp 163—165 °C/2—3 mmHg. ^{1}H-NMR ($CDCl_3$) δ 5.45 (m, 1H), 3.60 (t, J=7 Hz, 2H, CH_2Cl), 3.25 (t, J=7 Hz, CH_2S), 2.60—0.80 (m, 18H).

Synthesis of O-*(2,4,6-Tri-*t*-butylphenyl)* S-*Cyclopropyl Dithiocarbonate (**36a**)*: To a stirred solution of 30 mmol (4.2 ml) of diisopropylamine in 40 ml of THF was added at −78 °C over 20 min 30 mmol of butyllithium. The solution was stirred at this temperature for 20 min, and treated dropwise with 28.7 mmol of **35a** in 20 ml of THF. After 3 h, the reaction mixture was allowed to warm to room temperature with stirring (4 h) and then quenched with 10 ml of aqueous ammonium chloride solution. The mixture was poured onto 50 ml of 10% hydrochloric acid and extracted with ether (4×50 ml). The ethereal extracts were washed with saturated sodium chloride solution, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give pale yellow solid **36a**. The sample for analysis was prepared by repeated recrystallizations from methanol twice to give pale yellow crystals **36a** in 77% yield (8.40 g): mp 68—69 °C; ^{1}H-NMR (CCl_4) δ 7.20 (s, 2H), 2.40 (m, 1H), 1.35 (s, 27H, CH_3), 1.16 (m, 2H), 0.76 (m, 2H). Found: C, 69.62; H, 9.09%. Calcd for $C_{22}H_{34}OS_2$: C, 69.79; H, 9.05%.

Similar procedures to the above were used for cyclization.

O-*(2,4,6-Tri-*t*-butylphenyl)* S-*Cyclopropyl Thiocarbonate (**36b**)*: Mp 77—78 °C (MeOH); ^{1}H-NMR (CCl_4) δ 7.28 (s, 2H), 2.20 (m, 1H), 1.36 (m, 27H, CH_3), 1.04 (m, 2H), 0.68 (m, 2H). Found: C, 72.65; H, 9.57%. Calcd for $C_{22}H_{34}O_2S$: C, 72.88; H, 9.45%.

O-*(4-*t*-Butylcyclohexyl)* S-*Cyclopropyl Dithiocarbonate (**36c**)*: Mp 35—35.5 °C (EtOH); ^{1}H-NMR (CCl_4) δ 5.30 (m, 1H), 0.80—2.40 (m, 21H), 0.71 (m, 2H). Found: C, 61.65; H, 9.01%. Calcd for $C_{14}H_{24}OS_2$: C, 61.72; H, 8.88%.

O-L-*Menthyl* S-*Cyclopropyl Dithiocarbonate (**36d**)*: Mp 26—27 °C (EtOH); bp 117—120 °C/0.2 mmHg; ^{1}H-NMR (CCl_4) δ 5.40 (m, 1H), 2.30 (m, 2H), 0.50—2.10 (m, 21H); $[\alpha]_D^{25}$ −59.4° (c 1.47, $CHCl_3$). Found: C, 61.42; H, 9.08%. Calcd for $C_{14}H_{24}OS_2$: C, 61.72; H, 8.88%.

O-L-*Bornyl* S-*Cyclopropyl Dithiocarbonate (**36e**)*: Bp 119—125 °C/0.2 mmHg; ^{1}H-NMR ($CDCl_3$) δ 5.40 (m, 1H), 0.50—2.60 (m, 21H); $[\alpha]_D^{23}$ −17.6° (c 1.61, $CHCl_3$). Found: C, 62.51; H, 8.51%. Calcd for $C_{14}H_{22}OS_2$: C, 62.17; H, 8.20%.

General Procedure for Addition of 1-Lithiocyclopropyl Phenyl Sulfide (37) to Carbonyl Compounds. To a stirred solution of 1,3-bis(phenylthio)propane (**1**) (2.6 g, 10 mmol) in 20 ml of THF was added butyllithium (21 mmol) at −78 °C. After 5 min, the bath was removed and the mixture was stirred for 3 h at 0 °C. The resulting pale yellow solution was cooled to −78 °C, and the mixture of a carbonyl compound (10 mmol) in 3 ml of THF was added dropwise. After an additional 30 min at −78 °C, the solution was slowly warmed to room temperature. Saturated ammonium chloride solution (10 ml) was then added, and the reaction mixture was poured into 300 ml of water. The organic layer was removed, and the aqueous layer was extracted with ether (3×50 ml). The organics were combined, dried over anhydrous sodium sulfate and evaporated to give a crude adduct **38**. After chromatography on silica gel, eluted with hexane–benzene, a pure adduct **38** was obtained.

Physical Properties of Adduct. *4-[1-(Phenylthio)cyclopropyl]-4-heptanol (**38a**)*: Bp 140 °C/0.9 mmHg; IR (thin film) 3530 (OH), 2970, 1585, 1480, 1440, 1025 cm^{-1}; ^{1}H-NMR (CCl_4) δ 7.10—7.50 (m, 5H, C_6H_5S), 0.70—1.80 (m, 19H); MS (20 eV) m/e 264 (M$^+$, 20), 117 (100). Found: C, 73.10; H, 9.49%. Calcd for $C_{16}H_{24}OS$: C, 72.68; H, 9.15%.

*α-[1-(Phenylthio)cyclopropyl]benzyl Alcohol (**38b**)*: IR (thin film) 3410 (OH), 2920, 1575, 1475, 1020 cm^{-1}; ^{1}H-NMR (CCl_4) δ 7.00—7.40 (m, 10H, C_6H_5), 4.63 (brs, 1H, CH), 2.64 (brs, 1H, OH), 0.80—1.21 (m, 4H); MS (20 eV) m/e 256 (M$^+$, 41), 150 (100). Found: C, 75.18; H, 6.50%. Calcd for $C_{16}H_{16}OS$: C, 74.96; H, 6.29%.

*1-[1-(Phenylthio)cyclopropyl]cyclohexanol (**38c**)*: IR (thin film) 3480 (OH), 2920, 1575, 1475, 1430, 1025 cm^{-1}; ^{1}H-NMR (CCl_4) δ 6.90—7.50 (m, 5H, C_6H_5S), 1.30—1.90 (m, 11H), 0.70—1.20 (m, 4H); MS (20 eV) m/e 248 (M$^+$, 20), 117 (100). Found: C, 72.62; H, 8.33%. Calcd for $C_{15}H_{20}OS$: C, 72.54; H, 8.12%.

2-[1-(Phenylthio)cyclopropyl]-2-propanol (**38d**): Bp 100 °C/0.9 mmHg; ^{1}H-NMR (CCl_4) δ 6.90—7.40 (m, 5H, C_6H_5S), 2.18 (brs, 1H, OH), 1.23 (s, 6H, CH_3), 0.80—1.20 (m, 4H); MS (20 eV) *m/e* 208 (M$^+$, 17), 59 (100). Found: C, 69.45; H, 8.05%. Calcd for $C_{12}H_{16}OS$: C, 69.19; H, 7.74%.

3-[1-(Phenylthio)cyclopropyl]-3-pentanol (**38e**): Bp 121 °C/0.6 mmHg; IR (thin film) 3490 (OH), 2960, 1580, 1475, 1430, 1025 cm^{-1}; ^{1}H-NMR (CCl_4) δ 7.10—7.60 (m, 5H, C_6H_5S), 1.40—1.90 (m, 4H), 0.70—1.40 (m, 11H); MS (20 eV) *m/e* 236 (M$^+$, 24), 117 (100). Found: C, 71.18; H, 8.82%. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.53%.

1-[1-(Phenthio)cyclopropyl]-1-heptanol (**38f**): Bp 151—152 °C/0.8 mmHg; IR (thin film) 3410 (OH), 2920, 1580, 1475, 1435, 1020 cm^{-1}; ^{1}H-NMR (CCl_4) δ 7.00—7.50 (m, 5H, C_6H_5S), 3.10—3.30 (m, 1H), 1.90—2.20 (m, 1H, OH), 0.70—1.80 (m, 17H); MS (20 eV) *m/e* 264 (M$^+$, 31), 117 (100). Found: C, 72.87; H, 9.30%. Calcd for $C_{16}H_{24}OS$: C, 72.68; H, 9.15%.

2-[1-(Phenylthio)cyclopropyl]-2-hexanol (**38g**): Bp 129 °C/0.6—0.7 mmHg; IR (thin film) 3495 (OH) cm^{-1}; ^{1}H-NMR (CCl_4) δ 6.90—7.40 (m, 5H, C_6H_5S), 0.70—1.80 (m, 17H); MS (20 eV) *m/e* 250 (M$^+$, 22), 117 (100). Found: C, 72.09; H, 9.19%. Calcd for $C_{15}H_{22}OS$: C, 71.95; H, 8.86%.

1-(Phenylthio)cyclopropanecarboxylic Acid (**38i**): ^{1}H-NMR (CCl_4) δ 9.80 (brs, 1H, COOH), 7.00—7.50 (m, 5H, C_6H_5S), 1.20—1.90 (m, 4H).[7c]

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