ligand in 20 mL of $C_2H_4Cl_2$ at room temperature. Addition of excess 80% ROOH to the solution at 0 °C resulted in a deep-brown solution which was concentrated at 20 °C in vacuo. Addition of excess pentane resulted in the precipitation of the expected complexes in a pure form. These complexes are stable in the solid state if kept in a refrigerator. They are soluble in most organic solvents except alkanes.

VO(OO-*t*-Bu)(OPhsal) (IIa). Yield 80%. Anal. Calcd for $VC_{17}H_{18}NO_5$: C, 55.59; H, 4.90; N, 3.81; O, 21.8; active oxygen, 4.36. Found: C, 55.38; H, 4.78; N, 3.86; O, 21.70; active oxygen (by iodometry), 4.38.

VO(OO-*t*-Bu)(CH_3OPhsal) (IIb). Yield 78%. Anal. Calcd for $VC_{18}H_{20}NO_5$: C, 56.69; H, 5.25; N, 3.67; O, 21.0; active oxygen, 4.2. Found: C, 56.43; H, 5.19; N, 3.80; O, 20.78; active oxygen, 4.3.

VO(OO-*t*-Bu)(ClOPhsal) (IIc). Yield 80%. Anal. Calcd for $VC_{17}H_{17}NO_5Cl$: C, 50.81; H, 4.23; N, 3.49; O, 19.92; Cl, 8.84; active oxygen, 3.99. Found: C, 50.56; H, 4.15; N, 3.56; O, 19.74; Cl, 8.67; active oxygen, 4.0.

VO(OO-*t*-Bu)(NO_2OPhsal) (IId). Yield 85%. Anal. Calcd for $VC_{17}H_{17}N_2O_7$: C, 4..51; H, 4.13; N, 6.8; O, 27.18; active oxygen, 3.88. Found: C, 49.2; H, 4.05; N, 6.62; O, 26.97; active oxygen, 3.9.

VO(OO-*t*-Bu)(ClOPhsalCl) (IIe). Yield 70%. Anal. Calcd for $VC_{17}H_{16}NO_5Cl_2$: C, 46.79; H, 3.67; N, 3.21; O, 17.32; Cl, 16.28; active oxygen, 3.67. Found: C, 43.3; H, 3.37; N, 3.58; O, 17.06; Cl, 16.05; active oxygen, 3.75.

VO(OOCMe$_2$Ph)(OPhsal) (IIf). Yield 68%. Anal. Calcd for $VC_{22}H_{20}NO_5$: C, 61.54; H, 4.66; N, 3.26; O, 18.64; active oxygen, 3.73. Found: C, 61.18; H, 4.54; N, 3.45; O, 18.31; active oxygen, 3.85.

Preparation of [VO(OPhsal)]$_2$ (IVa). Cyclohexene (5 mL) dissolved in 20 mL $C_2H_4Cl_2$ was added to a solution of 367 mg of IIa (1 mmol) in 10 mL of $C_2H_4Cl_2$ at 30 °C. The epoxidation took place for 3 h. At the end of the reaction, addition of excess pentane resulted in the precipitation of IVa. Yield 75%. Anal. Calcd for $V_2C_{26}H_{18}N_2O_6$: C, 56.1; H, 3.24; N, 5.03; O, 17.27. Found: C, 55.7; H, 3.21; N, 4.9; O, 17.1. The same complex was prepared from the reaction of $VOCl_2$ with 1 equiv of OPhsalH_2 in EtOH according to the method of Ginsberg.[15]

Oxidation Procedure and Product Analysis. The olefins were stoichiometrically oxidized by complexes II in a thermostated Schlenck apparatus connected to a vacuum N_2 line. In a typical experiment, the olefin (5 mmol) was added in N_2 to the solution of complex II (0.1 mmol) in $C_2H_4Cl_2$ (3 mL), and the mixture was stirred at the required temperature (30 °C). The reaction was followed by GC quantive analysis of aliquot samples quenched by addition of excess triphenylphosphine to destroy the remaining peroxide. Various internal standards were used: *o*-dichlorobenzene for cyclohexene, norbornene, styrene, and 1-octene (column = FFAP 10% on Chromosorb GCQ 3 m); *n*-propylacetate for 2-butenes, 2-methylpentene, tetramethylethylene (column = Carbowax 20M on Chromosorb WAWDMCS).

Kinetics. All the runs for liquid olefins were carried out under ambient pressure with dry N_2 in a 10-mL Schlenck glass flask. The reaction was started by addition of olefin to the dry $C_2H_4Cl_2$ solution of II. All reaction rates are determined at early reaction times (<50% conversion) and are reproducible to within 10%. When the initial concentration of olefin was changed, e.g., for the experiments described in Figures 4 and 5, the corresponding amount of paraffin was added to keep the total amount of hydrocarbon constant, thus avoiding a change in the solvent effect.

The catalytic epoxidation was carried out as follows. To a solution of vanadium complex (0.1 mmol) in $C_2H_4Cl_2$ (3 mL), 20 equiv of cyclohexene and 20 equiv of pure *t*-BuOOH dissolved in $C_2H_4Cl_2$ were added. The reaction was followed by GC analysis of aliquot sample and iodometric titration of the *t*-BuOOH consumed.

Supplementary Material Available: Epoxide formation vs. time in the oxidation of cyclohexene by IIa (Figure 1) and plot of the initial rate of epoxidation of cyclohexene by IIa vs. concentration (Figure 3) (2 pages). Ordering information is given on any current masthead page.

Carbenoid Anion Behavior of Dilithio Derivatives of Thioacetal Alcohols. Stereochemistry and Mechanism of Ring Closures by Oxyanion-Facilitated CH Bond Insertion

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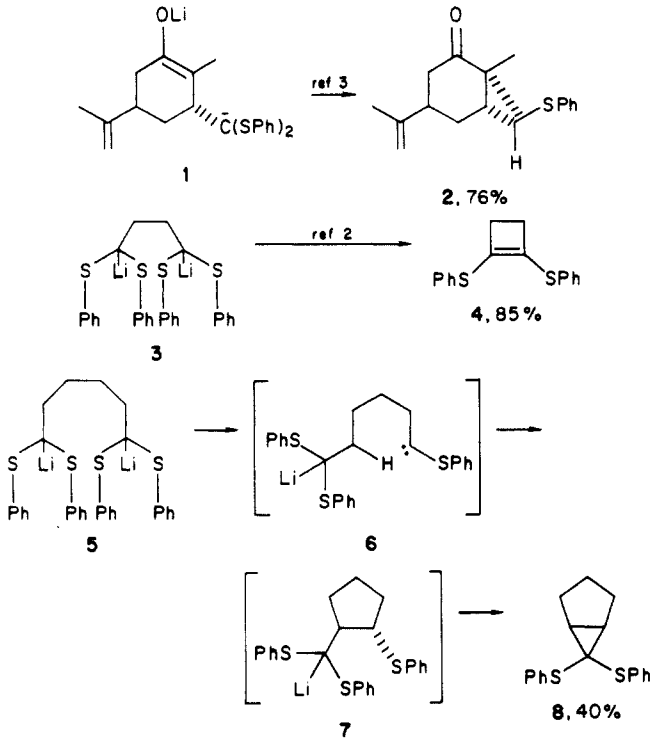
Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260. *Received October 15, 1985*

Abstract: Like other lithio derivatives of thioacetals bearing a second anionic site, dilithio derivatives of 3,3-, 5,5-, and 6,6-bis(phenylthio) alcohols decompose at or below ambient temperature to yield products ascribable to carbenoid intermediates. The 5,5-derivatives decompose far faster than the other types, and they yield mainly 2-(phenylthio)cyclopentanols and none of the unsaturated alcohols and glycols, arising from 1,2-hydrogen transfer and carbenoid dimerization, respectively, which are the major products from the other two types of reactants. The five-membered ring formation observed in the 5,5-systems results from insertion of a carbenoid carbon atom into the activated carbinol CH bond of the oxyanion, and a stereochemical study reveals that this process is not concerted. The evidence suggests that this ring closure is a result of displacement of a thiophenoxide ion from the lithiothioacetal by a hydride ion which is transferred from the carbinyl carbon atom in a transition state involving coordination of the lithium atom of the carbenoid with the oxyanion.

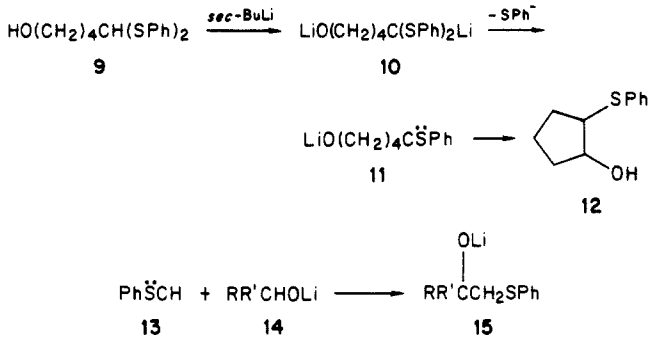
Recently, we proposed the following principle which has led to the discovery of several new reaction types: Normally stable lithio salts of diphenyl thioacetals, when they are contained in molecules possessing another anionic site, decompose to products which can be ascribed to carbene-like species, and the behavior of the latter may be controlled by the nature and position of the other anionic site.[1] Among several examples[2-4] of this phenomenon which have been discovered in this laboratory are the conversion of the dilithio derivatives **1** and **3** to **2** and **4**, respectively. A particularly intriguing example is the conversion of **5** mainly to **8** and to only a small quantity of the six-membered analogue of **4**;[1] it was proposed that one of the thioacetal anionic groups decomposes to or behaves like a carbene (see **6**) which inserts into the weak[5] CH bond adjacent to the other negatively charged carbon atom to yield the intermediate lithiothioacetal **7**.

(1) Cohen, T.; Ritter, R. H.; Ouellette, D. *J. Am. Chem. Soc.* **1982**, *104*, 7142.
(2) Cohen, T.; Ouellette, D.; Senaratne, K. P. A.; Yu, L.-C. *Tetrahedron Lett.* **1981**, *22*, 3377.
(3) Cohen, T.; Yu, L.-C. *J. Am. Chem. Soc.* **1983**, *105*, 2811.
(4) Cohen, T.; Yu, L.-C. *J. Org. Chem.* **1984**, *49*, 605.

0002-7863/86/1508-3718$01.50/0



In a previous publication,[1] we very briefly mentioned a potentially more synthetically significant application of the same mechanistic concept, namely the conversion of the dilithio derivative **10** of 5,5-bis(phenylthio)-1-pentanol (**9**), to a mixture of *cis*- and *trans*-2-(phenylthio)cyclopentanol (**12**) by warming to

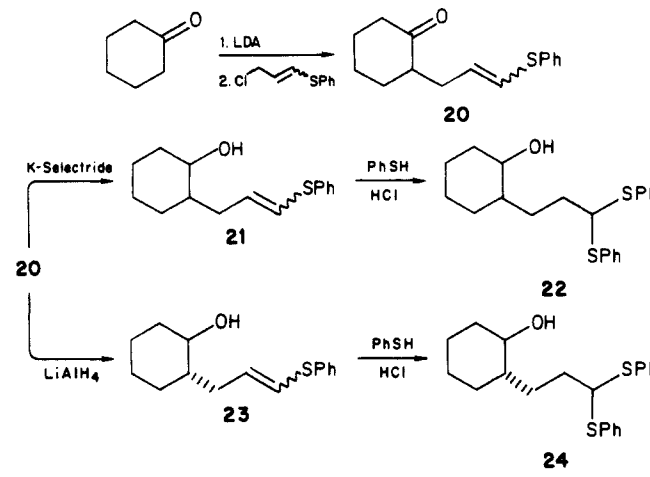


0 °C; the formation of **10** was inferred from trapping experiments with D_2O. An excellent precedent for the insertion of the carbenoid carbon atom of **11** into the weak[5] carbinyl CH bond is the finding by Harada and Oku[6] that putative carbene **13**, generated by treatment of (chloromethyl)phenyl sulfide with base, inserts into the carbinyl CH bonds of various sodium alkoxides. In this paper, we provide significant information concerning this (**10** → **12**) and closely related ring closures; we propose an unusual mechanism for the insertion step which raises questions about the concerted process suggested by Harada and Oku[6] for the intermolecular analogue, and we present the results of studies on two homologous systems.[7]

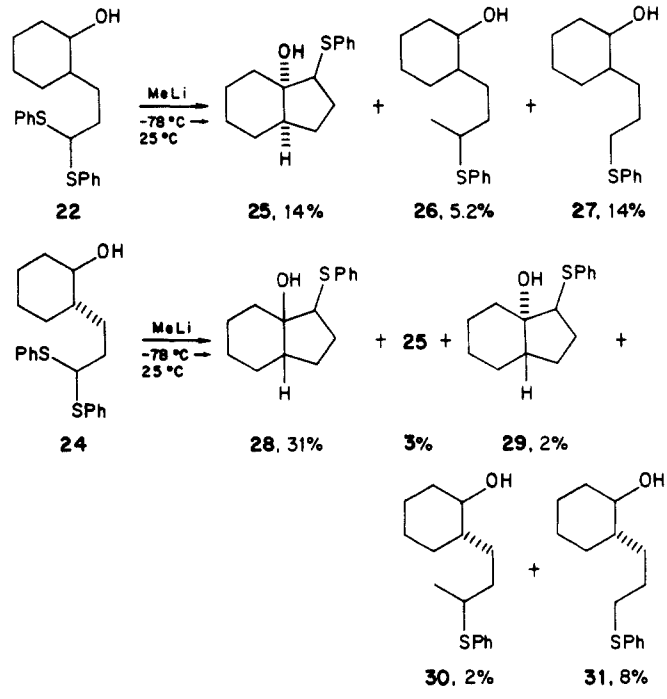
Results

Decomposition of Dimetallo Derivatives of 5,5-Bis(phenylthio)pentanols. We have found that the ring closure of **9** gives

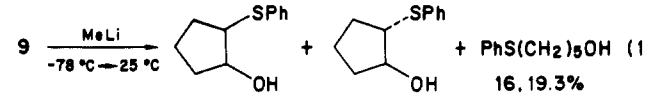
Scheme I

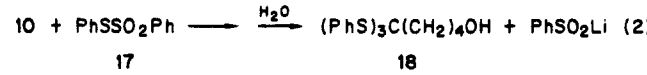


Scheme II



higher yields when methyllithium is used as the base instead of *sec*-butyllithium which was employed in the previous[1] study. As indicated in eq 1, a nearly 2:1 ratio of *cis*-(**12c**):*trans*-2-(phenylthio)cyclopentanol (**12t**) is produced and a significant yield of 5-(phenylthio)-1-pentanol (**16**) was also isolated. The dipotassio derivative of 5,5-bis(phenylthio)-1-pentanol (**9**) could be generated by sulfenylating the corresponding dilithio derivative **10** with phenyl benzenethiosulfonate (**17**)[8] (eq 2) and treating the resulting





5,5,5-tris(phenylthio)pentan-1-ol (**18**) with potassium hydride followed by potassium naphthalenide (KN);[9] as indicated in eq

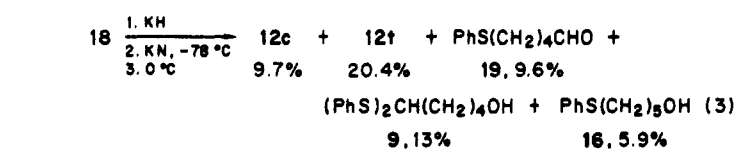
(5) Evans, D. A.; Baillargon, D. J. *Tetrahedron Lett.* **1978**, 3319. Steigerwald, M. L.; Goddard, W. A.; Evans, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 1994 and references cited therein.

(6) Harada, T.; Oku, A. *J. Am. Chem. Soc.* **1981**, *103*, 5965.

(7) Much of this work, including the main mechanistic conclusion, was presented at the ACS Symposium on Carbene Chemistry: Cohen, T.; Ritter, R. H.; Yu, L.-C. *Abstracts of Papers*, 186th National Meeting of the American Chemical Society, Washington, DC, American Chemical Society: Washington, DC, 1983; ORGN 159.

(8) Trost, B. M.; Massiot, G. S. *J. Am. Chem. Soc.* **1977**, *99*, 4405.

3, the decomposition of the dipotassio derivative provided ca. a

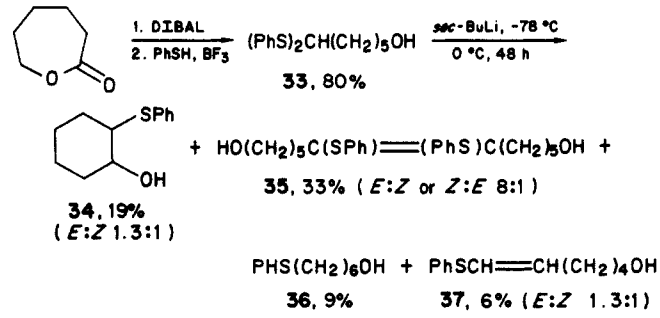


1:2 mixture of cis and trans isomers of **12**, as compared to the 2:1 mixture ratio obtained by decomposition of the dilithio derivative, and several noncyclic products are formed as well. In order to provide evidence concerning the concerted or nonconcerted nature of the insertion process, the cis **22** and trans **24** cyclohexanol analogues of **9** were treated under the ring closure conditions. In a concerted process, the *cis*-**22** and *trans*-**24** isomers would be expected to provide trans and cis fused hydrindanols, respectively. As indicated in Scheme I, **22** and **24** were prepared by alkylation of the enolate of cyclohexanone with the readily available 3-chloro-1-(phenylthio)propene,[10] reduction of the resulting product **20** with K-Selectride or lithium aluminum hydride to provide the *cis*[11]-**21** or *trans*[12]-**23** alcohols, respectively, and the HCl-induced addition of thiophenol[13] to the resulting vinyl sulfides.[14] The stereochemical assignments were easily made on the basis of NMR spectroscopy as outlined in the Experimental Section.

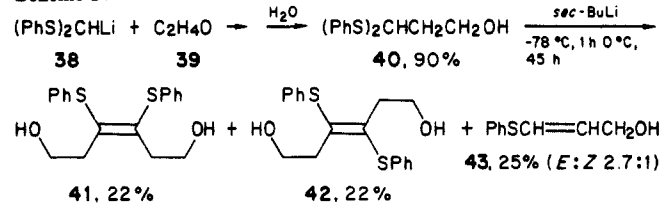
The products of reaction of the *cis*-**22** and *trans*-**24** isomers with excess methyllithium at −78 °C followed by warming to ambient temperature are shown in Scheme II. The structures assigned to **26**, **27**, **30**, and **31** are consistent with their exact masses as determined by mass spectrometry and with their ^{1}H NMR spectra, which in the cases of **26** and **27** displayed characteristic undifferentiated equatorial carbinol CH peaks at lower fields than the corresponding axial carbinol CH peaks of **30** and **31**; in the case of **31**, this peak (δ 3.20) was a typical triplet of doublets with axial–axial coupling constants of 9.3 Hz and an axial–equatorial coupling constant of 4.4 Hz, whereas the peak of the analogous proton of **30** (δ 3.16–3.27) overlapped that of the proton on the sulfur-bearing carbon atom. When the protons on the sulfur-bearing carbon atoms of **26** and **30** were irradiated at δ 3.2, the methyl doublet collapsed to a singlet.

The general structures of the hydrindanols **25**, **28**, and **29** were surmised from their exact masses, the absence of vinyl peaks in their ^{1}H NMR spectra, and the identities of the *cis*- and *trans*-hydrindanols, obtained by Raney nickel desulfurization, with authentic samples;[15] the latter comparison also established the stereochemistry of the ring fusion in these three products. Proof of the structures and stereochemical arrangements of **25** and **29** was obtained by an independent synthesis of a 78:22 mixture of the two by treating a 78:22 mixture of the epoxides **32t** and **33c**,

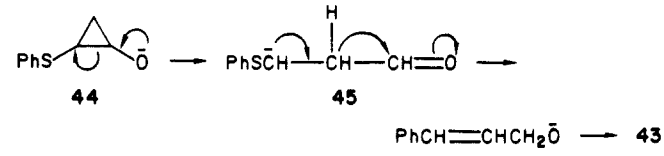
Scheme III



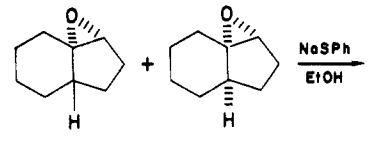
Scheme IV

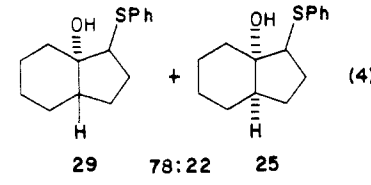


Scheme V



prepared by the method of Crandall,[15b] with sodium thiophenoxide (eq 4). The assignment of **28** as an epimer of **25** about the





(4)

carbon-bearing sulfur atom is based on its desulfurization to the same hydrindanol obtained from **25**, the near identities of the chemical shifts of the NMR peaks due to the protons at the bridgehead and on the sulfur-bearing carbon atoms for **25** and **28**, and the fact that the proton on the sulfur-bearing carbon atom of **28** appears as a clean doublet of doublets with similar coupling constants (J = 9.4, 8.6 Hz) to the two neighboring protons; the latter fact rules out all other positions on the carbon framework for the phenylthio group.

Control experiments established that neither **22** nor **24** epimerized to the other in the presence of 1 equiv of methyllithium. The possibility that **25** from ring closure of **22** was produced from isomerization of **29**, the product expected from a concerted insertion, or that **28**, the main ring closed product from **24**, was produced by isomerization of **25** or **29** under the reaction conditions was ruled out by the finding that the composition of the 78:22 mixture of **29** and **25** obtained as in eq 4 did not significantly change when submitted to the action of methyllithium.

Decomposition of the Dilithio Derivative of 6,6-Bis(phenylthio)-1-hexanol (33). Substrate **33** was readily prepared[16] as shown in Scheme III, which also indicates the course of decomposition of its dilithio derivative. This decomposition was far slower than that of the five-carbon chain analogue **10**.

(9) For the use of radical anions in the reductive metallation of phenylthio compounds, see: Cohen, T.; Sherbine, J. P.; Matz, J. R.; Hutchins, R. R.; McHenry, B. M.; Willey, P. R. *J. Am. Chem. Soc.* **1984**, *106*, 3245. For the replacement of phenylthio groups with potassium, see: Hoffmann, R. W.; Kemper, B. *Tetrahedron Lett.* **1981**, *22*, 5263. Cohen, T.; Yu, L.-C. *J. Org. Chem.* **1985**, *50*, 3266.

(10) Mura, A. J., Jr.; Bennett, D. A.; Cohen, T. *Tetrahedron Lett.* **1975**, 4433.

(11) The cis product is expected on the basis of the propensity of this reagent to deliver a hydrogen atom from the least hindered side. Brown, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 4100. Brown, H. C.; Krishnamurthy, S. J. *J. Am. Chem. Soc.* **1972**, *94*, 7159.

(12) Consistent with literature precedents, **23** and **21** were produced in a ratio of 2.6:1; for example, see: Dauben, W. G.; Fonken, G. J.; Noyce, D. S. *J. Am. Chem. Soc.* **1956**, *78*, 2579.

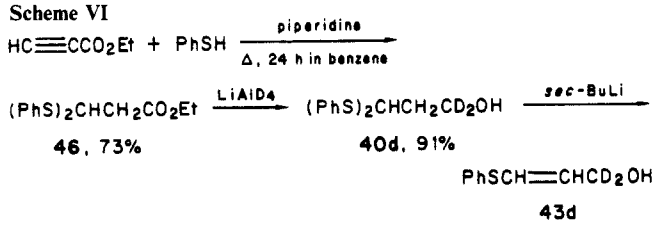
(13) Mura, A. J., Jr.; Majetich, P. A.; Grieco, P. A.; Cohen, T. *Tetrahedron Lett.* **1975**, 4437.

(14) The major product of treatment of the *cis*-cyclohexanol mixture **21** with excess HCl and 1.5 equiv of thiophenol for 20 h was the octahydrochromene resulting from intramolecular attack of the hydroxyl group on the cation produced by protonation of the vinyl sulfide group, but, as expected, (see, for example, Scheme III) further treatment of this material led to the monocyclic thioacetal in good yield. An analogous product was formed from **23** along with a much larger amount of **24** after a 5-h treatment with HCl in neat thiophenol (40 equiv).

(15) (a) Crandall, J. K.; Magha, H. S. *J. Org. Chem.* **1982**, *47*, 5368. (b) Crandall, J. K.; Magha, H. S.; Henderson, M. A.; Widner, R. K.; Tharp, G. A. *Ibid.* **1982**, *47*, 5372.

(16) We thank M.-T. Lin[17a] for the preparation of **33**.

Scheme VI



Decomposition of the Dilithio Derivative of 3,3-Bis(phenylthio)-1-propanol (40). Since the most common intramolecular reaction of carbenes, aside from the usual insertion into an adjacent CH bond (1,2-hydrogen migration),[18] is insertion into a more distant CH bond to form a cyclopropane ring,[19] it was expected that any carbene anion generated from the dianion of **40** would greatly favor insertion into the *activated* carbinyl CH bond. As shown in Scheme IV, the substrate **40**, which was readily prepared by treatment of bis(phenylthio)methyllithium (**38**) with ethylene oxide (**39**), yields a dilithio derivative which decomposes far more sluggishly than that of **10**, its longer chain analogue. None of the expected 2-(phenylthio)cyclopropanol was found. The only products isolated, aside from a small amount of reactant, were the isomeric "carbene dimers", **41** and **42**, presumably formed by reaction of some electrophilic intermediate with its precursor dianion, and the product **43** of insertion into the *adjacent* CH bond. Nevertheless, the possibility existed that the conjugate base **44**[20] of the cyclopropanol was indeed produced but that it decomposes as shown in Scheme V to form **43** or that a similar rearrangement occurs during workup of the cyclopropanol. However, the results of the labeling experiment outlined in Scheme VI show this hypothesis to be untenable since both deuterium atoms were located at C1, whereas Scheme V predicts an equal distribution between C1 and C3.

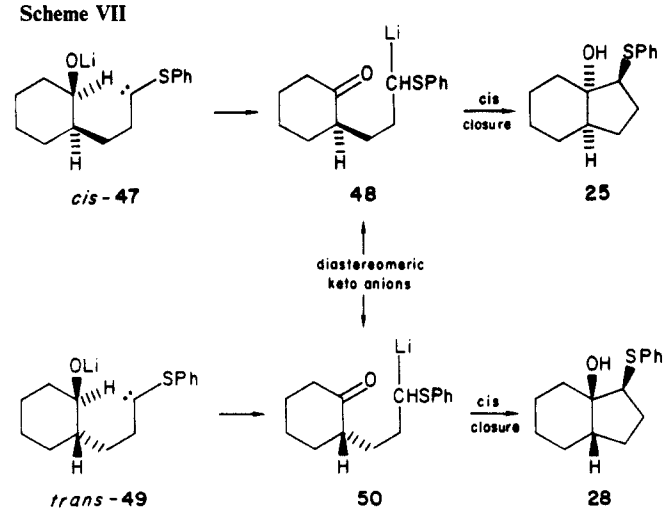
Discussion

It is clear that **25**, the ring closure product of the dilithio derivative of **22**, cannot be formed by a concerted insertion with retention of configuration. If one makes the very reasonable assumption that the ring closures of the dilithio derivatives of **22** and **24** occur by essentially the same mechanism, then both major ring closure products, **25** and **28**, are formed via an intermediate. Since these two alcohols are diastereomerically related, we can also conclude that the intermediates are diastereomers. This finding contrasts sharply with the retention of configuration that is observed when carbenes insert into a CH bond leading to a five-membered ring;[21] any explanation of our results must rationalize this contrast.

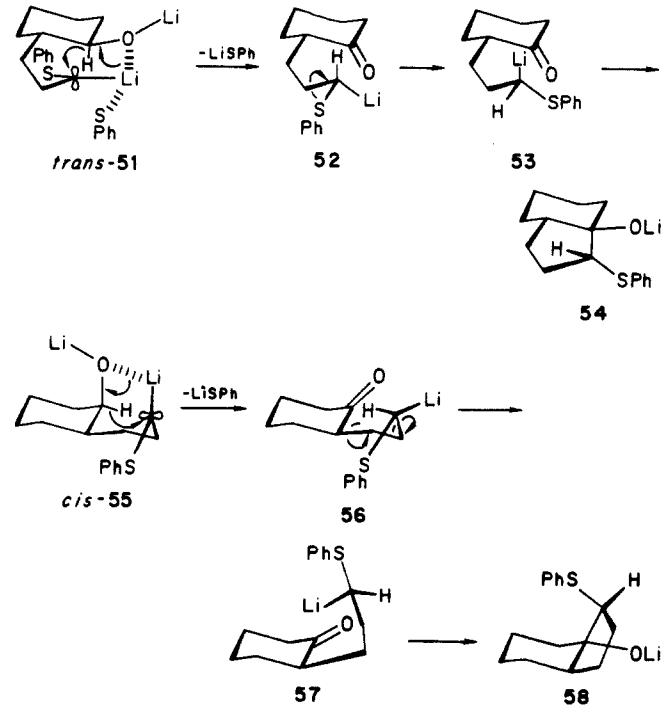
In view of the undoubted singlet nature of the lithio derivatives of thioacetals and of the expectation[22] that any carbenes produced from them would also be singlets, it appears very likely that the intermediate is produced by hydride ion, rather than hydrogen atom, transfer from the oxyanion to the carbenoid carbon atom. On the basis of a hydride ion transfer, it is not surprising that the diastereomeric alcohols **22** and **24** yield as the major ring-closed products diastereomeric cis fused hydrindanols. Scheme VII shows the structures (**47** and **49**) of one enantiomer of each of the carbenes expected from **22** and **24**; for purposes of simplicity and clarity, the carbenoids in this scheme are represented as free carbenes even though it is recognized that the lithium and thiophenoxide ions are probably at least loosely associated with the carbenoid carbon atom. If the very reasonable assumption is made that, whatever the exact mechanism of hydride transfer, it would be the same for the diastereomeric carbenes or carbenoids **47** and **49**, then it is clear that the proximate products of the transfer process will be diastereomeric keto anions (shown in Scheme VII as **48** and **50**). Ring closures of such species would be expected to be very rapid and to give mainly the cis fused bicyclic products.[15a] Since the latter are diastereomeric, it is clear that loss of stereochemistry at the anionic sites of the intermediate keto anions (**48** and **50**) is slower than ring closure.

Molecular models indicate that the hydride transfer transition states leading to the products which are formed have the C–Li bonds of the carbenoids pointing toward the oxyanions. It is not difficult to understand this fact, since, as indicated in Scheme VIII, such transition states, which are here approximated by **55** and **51**, allow coordination between the lithium attached to the carbenoid carbon atom and the oxyanion, and they appear to be nearly strain-free. (Justification will be provided below for the approximate placement of the lithium and nucleofugal thiophenoxide groups about the carbenoid carbon atoms in Scheme VIII; the presence of the latter has no influence on the gross stereochemical picture.) In the case of the trans starting material, the carbanion formed upon hydride transfer must undergo a bond rotation, as

Scheme VII

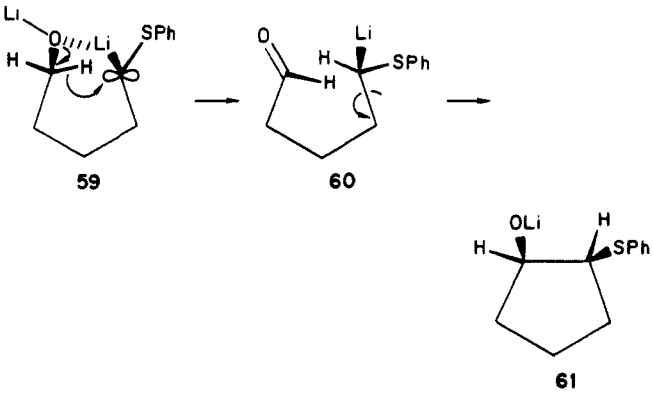


Scheme VIII



(17) Lin, M.-T., Ph.D. Thesis, University of Pittsburgh, 1984 (a) p 120; (b) p 68; (c) p 99.
(18) Schaeffer, H. F., III. *Acc. Chem. Res.* **1979**, *12*, 288.
(19) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1971; p 236. Wulfman, D. S.; Poling, B. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. 1, p 31.
(20) Tanaka, K.; Uneme, H.; Matsui, S.; Tanikaga, R.; Kaji, A. *Chem. Lett.* **1981**, 287.
(21) For examples, see: Gilbert, J. C.; Giamalva, D. H.; Baze, M. E. *J. Org. Chem.* **1985**, *50*, 2557; Taber, D. F.; Petty, E. H.; Raman, K. *J. Am. Chem. Soc.* **1985**, *107*, 196.
(22) Unpublished STO-3G calculations by K. N. Houk and P. Mueller indicate that the singlet state of HCSH is 14 kcal/mol lower in energy than the triplet state. We thank Professor Houk for this information.

Scheme IX

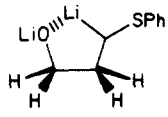


shown in **52**, before the carbon–lithium bond can approach the carbonyl group with the proper trajectory. The same kind of bond rotation must occur in the carbanion, **56**, formed from the cis starting material, but, in addition, the bond connecting the side chain to the ring must rotate as shown in order that the carbanion can approach the carbonyl group from the most favored angle which results in a cis ring fusion.[15a]. Indeed, it is this latter bond rotation, that would only be observed in an intramolecular insertion because of the unfavorable transition state for formation of a trans fused ring, which allows us to observe that this insertion is not a concerted process. This may account for the failure of Harada and Oku[6] to detect an intermediate in the intermolecular attack of a putative (phenylthio)carbene on the sodium salt of an oxyanion since in that case hydride transfer would be expected to be rapidly followed by recombination before rotation; however, it is not inconceivable that a different mechanism is operative in the case of the sodium salt.[23]

As shown in Scheme IX (the nucleofugal thiophenoxide group is omitted from this scheme for purposes of clarity), the same mechanistic picture predicts that the dilithio derivative of the noncyclic **9** would yield **61**, the precursor of the cis cyclopentanol **12c**, provided that ring closure of the anion aldehyde intermediate **60** occurs more rapidly than either inversion at the chiral carbon atom or rotation about the bond connecting the carbonyl group to the chain. Since **12c** is indeed the major ring-closed product, this concept may be of some generality. The corresponding dipotassio derivative yields mainly the trans cyclopentanol possibly because the transition state is less influenced by the type of chelation shown in **59** or because of a greater rate of inversion in the potassium analogue of **60** in which the metal–carbon bond would be more ionic.

In sharp contrast to the decomposition behavior of the dilithio derivatives of 5-hydroxythioacetals **9**, **22**, and **24**, which yield none of the usual 1,2-hydrogen transfer or "carbene dimer" products, that of the 6-hydroxythioacetal **33** provides mainly the latter type of product and only 19% of the ring-closed product resulting from participation of the oxyanionic site. Even more striking is the complete lack of cyclic alcohol production in the decomposition of the dianion derived from the 3-hydroxythioacetal **40**; only the 1,2-hydrogen transfer and "carbene dimer" products are formed. It is probably also significant that the decompositions of the dilithio derivatives of the 5-hydroxythioacetals were far faster than those of their longer and shorter chain analogues.

These results can be readily rationalized by considering the less favorable nature of transition states involving hydride transfer to a carbenoid center in the cases of the dilithio derivatives of **33** and **40**. Such transfer is possible in that derivative of **33**, but 1,6-hydride transfers are far rarer and presumably less favorable than 1,5-hydride transfers.[24] The failure of the dilithio derivative of **40** to generate a cyclopropanol by hydride transfer followed by ring closure of the resulting aldehyde anion or by carbenoid insertion[25] can probably be explained by assuming that the lithium atom attached to the carbenoid carbon atom is coordinated with the oxyanion (see **62**; the leaving thiophenoxide has been omitted for clarity); this arrangement forces both carbinol CH bonds to point away from the carbenoid carbon atom.



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It is evident that the relative ease of decomposition of the dianions (carbenoid anions) is related to the availability of a low-energy transition state in which a hydride ion can be transferred to the carbenoid carbon atom. In a subsequent publication, we shall reveal a striking example of a particularly facile carbenoid type decomposition of a lithio derivative of a thioacetal contained in a molecule possessing a nucleophilic site that is positioned such that it can readily attack the carbenoid carbon atom; this decomposition occurs at −45 °C.[26]

This correlation implies that the electrophilic intermediate in these reactions is not formed in the rate-determining step of the decomposition of the dianion, but that the quenching of this species is the rate-determing step. It is thus no longer a mystery why metallo derivatives of thioacetals often behave as carbenoids when they are contained in molecules possessing a second anionic site; the decomposition of the metallo derivative is actually induced by reaction with this site.

Halogen-substituted carbenoids often exhibit similar behavior.[27] Elegant experiments by Walborsky[28] have demonstrated that the attack of nucleophiles on such species are actually displacements of the halide ion occurring with inversion of configuration, reactions that he has termed metal-assisted ionizations. In view of the calculations of Schleyer and Houk[29] which indicate that sulfur-substituted organoalkali compounds are quite similar in structure to such halocarbenoids, it is not greatly surprising that metallo derivatives of thioacetals can also behave as carbenoids, particularly in the presence of a built-in nucleophile; in the absence of the latter type of function the sulfur-substituted organometallics are more stable than their halo-substituted analogues due to the poorer leaving ability of thiophenoxide compared to halide. Indeed, it has been known for some time that tris(phenylthio)methyllithium, a special case of a lithio derivative of a thioacetal, behaves as a carbenoid at temperatures approaching ambient.[30]

The depictions (**51** and **55**) of the transition states for five-membered ring formation are more detailed than is justified by the stereochemical results alone. The approximate placement of the leaving thiophenoxide group can be surmised from the facts that metallo derivatives of thioacetals undergo decomposition which is greatly facilitated by neighboring nucleophiles, that their behavior is apparently analogous to that of halocarbenoids, the destruction of which by nucleophilic attack is now reasonably well understood,[28] and that their theoretically deduced structures show the metal ion to be bridging the sulfur atom and the carbenoid carbon atom.[29] It can be reasonably assumed that we are dealing here with a metal ion assisted ionization and either that a hydride ion actually displaces the thiophenoxide group directly, in analogy

(23) More recent findings of Oku and co-workers in which a hydride transfer mechanism is postulated for a related insertion is discussed below.

(24) Fry, J. L.; Karabatsos, G. J. *Carbonium Ions*; Olah, G. A., Schleyer, P. R., Eds.; Wiley-Interscience: New York, 1970; Vol. II, Chapter 14.

(25) An example is known in which a carbene, which cannot readily undergo 1,2-hydrogen transfer because it is a part of a cyclopropane ring, inserts into a carbinol CH bond of an oxyanion. Nilsen, N. O.; Skattebøl, L.; Sydnes, L. K. *Acta Chem. Scand., Ser. B*: **1982**, 587.

(26) Unpublished results of M. Bhupathy.

(27) Reviews: Köbrich, G.; et al. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 41. Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 473. Stang, P. J. *Chem. Rev.* **1978**, *78*, 383. Taylor, K. G. *Tetrahedron* **1982**, *38*, 2751. Siegel, H. *Top. Curr. Chem.* **1982**, *106*, 55.

(28) Walborsky, H. M.; Duraisamy, M. *Tetrahedron Lett.* **1985**, *26*, 2743. Duraisamy, M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 5035.

(29) Schleyer, P. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467.

(30) Nitche, M.; Seebach, D.; Beck, A. K. *Chem. Ber.* **1978**, *111*, 3644. Wildschut, G. A.; Bos, H. J. T.; Brandsma, L.; Arens, J. F. *Monatsh. Chem.* **1967**, *98*, 1043. Beak, P.; Worley, J. W. *J. Am. Chem. Soc.* **1972**, *94*, 597.

to a classical S_N2 reaction, or that the thiophenoxide ionizes reversibly and the resulting metallocarbocation is attacked by the hydride ion in the rate-determining step.

Whereas Oku and collaborators concluded that the insertion of the putative (phenylthio)carbene into the sodium salt of 4-(*tert*-butyl)cyclohexanol is a concerted process[6] and that the insertion of dichlorocarbene into the lithium salt of benzyl alcohol is also concerted (however, it was mentioned in a footnote that a hydride ion transfer in this case is possible provided that the combination of the anion and aldehyde occurs within a solvent cage),[31] a very recent contribution from that laboratory concludes that the insertion product formed when 1-chloro-2-methylpropene is treated with butyllithium in the presence of salts of menthol is generated via a hydride ion transfer, and, indeed, they found that the intermediate menthone is captured with various organolithium compounds.[32] Furthermore, these workers concluded that the reaction proceeds through a carbenoid rather than a free carbene, since the latter, when generated in a different fashion, exhibits quite different behavior. It is quite satisfying that their conclusions with respect to the insertion reactions of halocarbenoids into the carbinol CH bonds of oxyanions, although derived independently and from different evidence, are quite consistent with our own mechanistic conclusions concerning the insertion of sulfur-substituted carbenoids into similar bonds.

Experimental Section

High-pressure liquid chromatography (HPLC) was performed with a Waters Model ALC/GPC 301 with delivery system Model 6000 equipped with a Waters UK6 injector. Preparative scale HPLC was performed at 2000 psi with four 0.75 × 30 cm columns packed with 10 μm Licosorb. Analysis was done on a 5-m silica gel or octadecylsilyl reverse phase column.

Cyclization of the Dilithio Derivative of 5,5-Bis(phenylthio)-1-pentanol (9). Methyllithium (0.73 mL, 1.76 M in diethyl ether, 1.3 mmol) was added to a solution of **9**[1] (129 mg, 0.425 mmol) in 42.5 mL of THF at −78 °C under argon, and the resulting solution was stirred for 1 h at −78 °C and at ambient temperature for 24 h, during which time the intensely yellow colored solution became nearly colorless. Aqueous workup and purification of the residue from evaporation of the ether extract by column chromatography (10 g of silica gel, sequentially eluted with 5%, 10% and 20% ethyl acetate in hexanes) gave, in order of elution, (1) 24.2 mg (29.4%) of *cis*-2-(phenylthio)cyclopentanol (**12c**),[1] (2) 13.6 mg (16.5%) of *trans*-2-(phenylthio)cyclopentanol (**12t**)[1], and (3) 16.1 mg (19.3%) of 5-(phenylthio)-1-pentanol (**16**).

5,5,5-Tris(phenylthio)-1-pentanol (18). *sec*-Butyllithium (8.0 mL, 0.90 M in hexanes, 7.2 mmol) was added to a solution of 5,5-bis(phenylthio)-1-pentanol[1] (**9**, 1.0 g, 3.4 mmol) in 40 mL of THF at −78 °C under argon, and the solution was stirred for 1 h at −78 °C; the addition of phenyl benzenethiosulfonate (0.91 g, 3.6 mmol) caused the yellow solution to turn to a cloudy white color within 10 min. The mixture was slowly warmed to room temperature over 2 h, and the reaction was quenched by the addition of 10 mL of a 10% aqueous NH_4Cl solution. Purification of the residue from ether extraction by RP-MPLC (310 × 25 mm Lobar RP-8 column, eluted with 30% water in methanol, followed by methanol) gave 0.16 g (15%) of 5,5-bis(phenylthio)-1-pentanol (**9**) as the more mobile component, followed by 1.1 g (75%) of the desired product **18** as a viscous yellow oil which slowly crystallized on standing; mp 62–64 °C.

Decomposition of the Dipotassium Derivative of 5,5-Bis(phenylthio)-pentan-1-ol (9). 5,5,5-Tris(phenylthio)pentan-1-ol (**18**, 0.215 g, 0.522 mmol) was added to a suspension of oil-free KH (0.125 g, 3.12 mmol), obtained by washing a dispersion of KH in oil with pentane (3 × 15 mL) and drying under a stream of argon, and the resulting solution was stirred under a stagnant atmosphere of argon until no hydrogen evolution was detected (ca. 1.5 h). The THF solution of the potassium alkoxide was transferred to an addition funnel and slowly added to a solution of potassium naphthalenide (2.60 mL, 0.463 M, 1.20 mmol) at −78 °C under argon, prepared by stirring potassium (0.217 g, 5.55 mmol) and naphthalene (0.715 g, 5.55 mmol) in 12 mL of THF overnight under argon. The resulting solution was stirred for 1 h at −78 °C and then at 0 °C for 24 h. The reaction was quenched by the addition of 5 mL of 10% aqueous NH_4Cl. The usual workup and purification by column chromatography (20 g of silica gel, eluted with 5%, 10%, and 20% ethyl acetate in hexanes) gave (1) 0.0209 g of a 1.02:1.00:0.09 mixture of *cis*-2-(phenylthio)cyclopentanol (**12c**), 5-(phenylthio)pentanal (**19**), and what seemed to be 5,5-bis(phenylthio)pentanal, inseparable by silica gel chromatography, (2) 0.0207 g (20.4%) of *trans*-2-(phenylthio)cyclopentanol (**12t**), and (3) 0.0226 g of a 2.21:1.00 mixture of 5,5-bis(phenylthio)-1-pentanol (**9**, 13.0%) and 5-(phenylthio)-1-pentanol (**16**, 5.9%).

A pure sample of 5-(phenylthio)pentanal (**19**) was obtained by RP-MPLC (240 × 10 mm Lobar RP-8 column eluted with 35% water in methanol) to remove the 5,5-bis(phenylthio)pentanal. The fractions containing the 5-(phenylthio)pentanal and *cis*-2-(phenylthio)cyclopentanol were dissolved in ether and washed (3 × 10 mL) with 10% $NaHSO_3$ solution. The combined bisulfite washings were neutralized with $NaHCO_3$ to pH 9. The bisulfite layer was then extracted with ether (3 × 10 mL), and the combined ether extracts were dried ($MgSO_4$), filtered, and concentrated to give a pure sample of 5-(phenylthio)pentanal (**19**).

(*E* and *Z*)-2-(3-(Phenylthio)prop-2-en-1-yl)cyclohexanone (20). A stirring solution of diisopropylamine (0.90 mL, 6.4 mmol) in 15 mL of THF was cooled to −78 °C under argon prior to the addition of *n*-butyllithium (5.6 mL, 1.15 M in hexanes, 6.4 mmol). Stirring was continued for 1 h at −78 °C followed by 1 h at 0 °C, after which time cyclohexanone (0.65 mL, 6.3 mmol) was added. After the mixture had stirred for 1 h at 0 °C, 3-chloro-1-(phenylthio)prop-1-ene[10] (1.2 g, 6.5 mmol, ca. a 1:1 mixture of *E* and *Z* isomers) in 1.0 mL of THF was added followed by anhydrous LiI (75 mg, 0.56 mmol). The resulting solution was stirred for 1 h at 0 °C, warmed to ambient temperature, stirred for an additional 19 h, and finally poured into 30 mL of 10% aqueous NH_4Cl solution. The usual workup followed sequentially by column chromatography (silica gel, eluted with 7% ethyl acetate in hexanes), and MP-RPLC (25 × 310 mm Lobar C-8 column, eluted with 20% water in methanol, followed by methanol) gave 0.57 g (40%) of **20** as a 1:1 mixture of *E* and *Z* isomers.

***cis*-2-(3-(Phenylthio)prop-2(*E* and *Z*)-en-1-yl)cyclohexanol (21).** To a solution of (*E* and *Z*)-2-(3-(phenylthio)prop-2-en-1-yl)cyclohexanone (**20**, 0.215 g, 0.874 mmol) in 2.0 mL of THF at −78 °C under argon was added an excess of K-Selectride (4.5 mL, 0.5 M in THF, 2.25 mmol). The resulting solution was allowed to slowly warm to ambient temperature over the next 3 h at which time TLC analysis showed that no starting material remained. To the reaction mixture was carefully added 2.0 mL of 25% aqueous NaOH followed by 2.0 mL of a 30% hydrogen peroxide solution. The resulting solution was stirred for 30 min, diluted with ether, and washed with 5% aqueous $Na_2S_2O_3$ solution (1 × 10 mL) followed by brine (1 × 10 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to give 0.213 g (98.3%) of **21** as a yellow oil.

***trans*-2-(3,3-Bis(phenylthio)prop-1-yl)cyclohexanol (24).** To a stirred suspension of lithium aluminum hydride (0.439 g, 11.6 mmol) in 8.0 mL of THF at −23 °C under argon was slowly added a solution of (*E* and *Z*)-2-(3-(phenylthio)prop-2-en-1-yl)cyclohexanone (**20**, 0.232 g, 0.943 mmol) in 2.0 mL of THF. The resulting solution was stirred at −23 °C for 1 h and warmed to ambient temperature over the next 2 h. The reaction was quenched by successive, dropwise addition of 0.45 mL of water and 0.45 mL of 15% aqueous NaOH solution followed by 1.20 mL of water to produce a white granular precipitate. The solution was then diluted with ether, filtered, dried ($MgSO_4$), and concentrated to give 0.300 g of a yellow oil whose 300-MHz NMR spectrum indicated a 2.6:1 mixture of *trans*:*cis*-2-(3-(phenylthio)prop-2(*E* and *Z*)-en-1-yl)cyclohexanol (**21** and **23**).

Dry HCl gas was passed for 5.5 h through a stirring solution of the mixture of *cis*- and *trans*-2-(3-(phenylthio)prop-2(*E* and *Z*)-en-1-yl)-cyclohexanols (0.300 g, 1.21 mmol) and 5.0 mL of thiophenol. The HCl supply was removed, and stirring was continued for an additional 14 h. The resulting solution was diluted with ether and washed with 10% aqueous NaOH solution (2 × 20 mL) and water (1 × 20 mL). Concentration of the dried ($MgSO_4$) organic layer gave 0.443 g of a crude product mixture. Purification by column chromatography (25 g of silica gel, eluted with 10% ethyl acetate in hexanes) followed by additional purification of the mixed fractions by MPLC (15 × 250 mm silica gel column, eluted with 10% ethyl acetate in hexanes) gave, in order of elution, (1) 0.1136 g of an impure yellow oil which contained some diphenyl disulfide and a nearly 1:1 mixture of anomers of *trans*-2-(phenylthio)-3,4,4a,5,6,7,8,8a-octahydro-2*H*-chromene, as determined by comparison with an authentic sample,[17b,c] (2) 0.0768 g (22.7%) of *cis*-2-(3,3-bis(phenylthio)prop-1-yl)cyclohexanol (**22**), whose 300-MHz ^1H NMR spectrum was identical with that of the compound prepared as described below, and (3) 0.1016 g (56.1%) of **24** as a nearly colorless oil: IR (film) 3650–3100 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.03–2.18 (m, 14 H, CH_2, OH, and OCHC*H*), 3.20 (td, *J* = 9.6, 4.4 Hz, 1 H, CHO), 4.40 (t, *J* = 6.4 Hz, 1 H, C*H*(SPh)$_2$), 7.24–7.49 (m, 10 H, Ph); MS, (15 eV) *m/e* (rel intensity) 358 (M^+) (0.85), 249 (41), 248 (18), 247 (8.5), 232 (22), 149 (13), 139 (100), 136 (69), 123 (19), 122 (39),

(31) Harada, T.; Akiba, E.; Oku, A. *J. Am. Chem. Soc.* **1983**, *105*, 2771.
(32) Harada, T.; Nozaki, Y.; Yamaura, Y.; Oku, A. *J. Am. Chem. Soc.* **1985**, *107*, 2189.

121 (11), 110 (20), 81 (22); high-resolution mass spectrum calcd for $C_{21}H_{26}OS_2$ 358.1425, found 358.1420.

***cis*-2-(3,3-Bis(phenylthio)prop-1-yl)cyclohexanol (22).** Dry HCl gas was passed through a stirring solution of *cis*-2-(3-(phenylthio)prop-2(*E* and *Z*)-en-1-yl)cyclohexanol (**21**, 0.16 g, 0.66 mmol) and thiophenol (0.10 mL, 0.98 mmol) in 5.0 mL of benzene at 0 °C for 20 min. The resulting solution was stirred in a stoppered flask for 20 h at ambient temperature, diluted with ether, and washed with 10% aqueous NaOH solution (2 × 10 mL) and water (1 × 10 mL). Workup gave 0.17 g of crude product which was purified by column chromatography (25 g of silica gel, eluted with 10% ethyl acetate in hexanes) to give 0.10 g of an impure yellow oil which contained a 1:1 mixture of anomers of *cis*-2-(phenylthio)-3,4,4a,5,6,7,8,8a-octahydro-2*H*-chromene, as judged by comparison of the 300-MHz NMR spectrum of the authentic material,[17c] as the more mobile component. The slower moving component consisted of 48 mg (20%) of **22** isolated as a yellow oil: IR (film) 3650–3150 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.00–1.91 (m, 14 H, CH_2, *H*OCH*CH*), 3.79 (br s, 1 H, CHO), 4.39 (t, J = 6.5 Hz, 1 H, C*H*(SPh)$_2$), 7.24–7.54 (m, 10 H, Ph); MS, (15 eV) m/e (rel intensity) 358 (M^+) (1.4), 249 (19), 248 (6.5), 231 (8.8), 149 (15), 139 (100), 120 (12), 110 (4.2); high-resolution mass spectrum calcd for $C_{21}H_{26}OS_2$ 358.1425, found 358.1420.

Dry HCl gas was passed through a stirring solution of the chromene mixture (0.104 g, 0.420 mmol) in 4.0 mL of thiophenol at ambient temperature for 10 h. The resulting solution was diluted with ether and washed with 10% aqueous NaOH solution (3 × 25 mL), followed by water (1 × 25 mL). Concentration of the dried ($MgSO_4$) organic layer gave 0.142 g of the crude product which was purified by column chromatography (14 g of silica gel, eluted with 10% ethyl acetate in hexanes) to give 0.108 g (71.6%) of **22**. The combined yield was 80%.

Cyclization of the Dilithio Derivative of *trans*-2-(3,3-Bis(phenylthio)prop-1-yl)cyclohexanol (24). Methyllithium (0.60 mL, 1.68 M in diethyl ether, 1.0 mmol) was added to a solution of **24** (74.5 mg, 0.208 mmol) in 21 mL of THF at −78 °C under argon. The resulting solution was stirred for 1 h at −78 °C and 0 °C for 2 h, and it was warmed to ambient temperature. After 19 h at room temperature, during which time a yellow colored solution, characteristic of thioacetal anions, never appeared, 10 mL of water was added. The resulting solution was concentrated by removal of the THF in vacuo and extracted (3 × 15 mL) with ether. The combined ether extracts were dried ($MgSO_4$, K_2CO_3), filtered, and concentrated to give 69.3 mg of a yellow oil. Purification by preparative scale HPLC (10 μm LiChrosorb Si 60, eluted with 15% ethyl acetate in hexanes) gave, in order of elution, **28** (16.1 mg, 31.2%), **25** (1.4 mg, 2.7%), **29** (1.0 mg, 1.9%), **30** (1.1 mg, 2.0%), and **31** (4.0 mg, 7.9%). Each of the bicyclic products was heated in ethanol with commercial Raney nickel whereupon **25** and **28** gave *cis*-hexahydro-3a*H*-inden-3a-ol, and **29** gave the trans isomer, as shown by GLC coinjection experiments with authentic samples.[15] Furthermore, **25** and **29** were shown to have identical 300-MHz ^1H NMR spectra with authentic samples (see below). **28**: IR (film) 3620–3200 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.07–2.12 (m, 12 H, cyclohexyl CH and CH_2 and PhSCHCH*HCH*$_2$), 2.27–2.40 (m, 1 H, cyclopentyl β-H syn to PhS), 2.43 (br s, 1 H, OH), 3.70 (dd, J = 9.4, 8.6 Hz, 1 H, PhSC*H*), 7.15–7.49 (m, 5 H, Ph); MS, (15 eV) m/e (rel intensity) 248 (M^+) (63), 139 (100), 138 (19), 121 (5.8), 110 (19), 109 (5.2), 97 (4.5), 69 (4.5); high-resolution mass spectrum calcd for $C_{15}H_{20}OS$ 248.1235, found 248.1234. **25**: IR (film) 3610–3175 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.19–1.81, 1.96–2.13 (m, 13 H, cyclohexyl CH_2 and CH, OH, and PhSCHCH*HCH*$_2$), 2.21–2.38 (m, 1 H, cyclopentyl β-H syn to PhS), 3.50 (t, J = 9.7 Hz, 1 H, PhSC*H*), 7.14–7.51 (m, 5 H, Ph); MS, (15 eV) m/e (rel intensity) 248 (M^+) (59), 139 (100), 138 (19), 121 (6.7), 110 (19), 109 (5.4), 97 (4.9), 69 (4.3); high-resolution mass spectrum calcd for $C_{15}H_{20}OS$ 248.1235, found 248.1234. **29**: IR (film) 3625–3200 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.12–2.09 (m, 13 H, cyclohexyl CH_2 and CH, OH, and PhSCHCH*HCH*$_2$), 2.38–2.51 (m, 1 H, cyclopentyl β-H syn to PhS), 3.61 (dd, J = 8.3, 2.6 Hz, 1 H, C*H*SPh), 7.12–7.42 (m, 5 H, Ph); MS, (15 eV) m/e (rel intensity) 248 (M^+) (55), 139 (100), 138 (20), 121 (8), 110 (22), 109 (8.0), 97 (7.0), 96 (7.0), 82 (6.3), 59 (16); high-resolution mass spectrum calcd for $C_{15}H_{20}OS$ 248.1235, found 248.1234.

Cyclization of the Dilithio Derivative of *cis*-2-(3,3-Bis(phenylthio)-prop-1-yl)cyclohexanol (22). This reaction was performed as for the trans isomer. HPLC purification gave, in order of elution, **25** (6.3 mg, 14%), identical with that previously isolated, **26** (2.4 mg, 5.2%), and **27** (6.0 mg, 14%) as the only characterizable products.

***trans*-3-(Phenylthio)-3a-hydroxy-(*trans*- and *cis*)-2,3,3a,4,5,6,7,7a-octahydro-1*H*-indene (29 and 25).** A 78:22 mixture of epoxides **32t** and **32c**[15] (55 mg, 0.40 mmol) was added to a solution of sodium thiophenoxide, prepared from sodium (94 mg, 4.1 mmol) and thiophenol (0.42 mL, 4.1 mmol), in 10 mL of absolute ethanol. The resulting solution was stirred for 3 h at ambient temperature and then heated at reflux for 12 h. After the mixture had cooled to ambient temperature, the ethanol was removed in vacuo, and the residual material was diluted with water and extracted with ether (3 × 25 mL). The combined ether extracts were washed with 10% aqueous NaOH solution (2 × 10 mL) and water (1 × 10 mL). Concentration of the dried ($MgSO_4$, K_2CO_3) ether extract gave 120 mg of the crude product mixture which was purified by column chromatography (10 g of silica gel, eluted with 20% ether in hexanes) to give 68 mg (68%) of a yellow oil whose 300-MHz NMR (spectrum) and subsequent desulfurization with Raney nickel, vide infra, indicated that a 78:22 mixture of hydrindanols **29** and **25** was formed: IR (film) 3625–3150 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz); cis isomer **25** δ 1.11–2.10 (m, 13 H, CH_2 and OH), 2.19–2.34 (m, 1 H, bridgehead methine H), 3.46–3.53 (m, 1 H, C*H*SPh), 7.09–7.56 (m, 5 H, Ph); trans isomer **29** δ 1.11–2.10 (m, 13 H, CH_2 and OH), 2.36–2.50 (m, 1 H, bridgehead methine H), 3.61 (dd, J = 8.3, 2.6 Hz, 1 H, C*H*SPh), 7.09–7.56 (m, 5 H, Ph); MS, (15 eV) m/e (rel intensity) 248 (M^+) (59), 139 (100), 121 (11), 110 (22); high-resolution mass spectrum calcd for $C_{15}H_{20}OS$ 248.1234, found 248.1235.

To a small aliquot (2.8 mg, 0.011 mmol) of the 78:22 mixture of **29** and **25** was added ca. 1 mL of a suspension of Raney nickel in ethanol. The resulting solution was heated at 80 °C under argon for 1.5 h, cooled to ambient temperature, and filtered. Analysis of the filtrate by gas chromatography (6 ft 10% Carbowax 20 M on 80/100 Supelcoport, 100–200 °C at 8 °C/min) including coinjection experiments with authentic samples of *cis*-hexahydro-3a*H*-inden-3a-ol[15] and of a 75:25 mixture of *trans*- and *cis*-hexahydro-3a*H*-inden-3a-ols, produced by reduction of the mixture of epoxides **32t** and **32c**, showed that the ratio of trans:cis ring junction isomers produced was 74:26.

Determination of the Stability of the Cyclohexanols 22 and 24 to the Ring Closure Conditions. Since alcohols sometimes epimerize under basic conditions (albeit usually at temperatures far above ambient temperature) via oxidation to a trace of ketone and disproportionation of the latter and the alcoholate anion, both **22** and **24** were subjected to the action of a slight deficiency of methyllithium at −78 °C, and the solutions were warmed to 25 °C; in order to ensure that sufficient air was present during the control tests, 0.50 mL of dry air was injected into the solutions, and they were allowed to stir for 25 h and then worked up. HPLC analysis indicated that neither alcohol underwent epimerization.

Determination of the Stability of the Ring-Closed Products 25 and 29 to the Ring-Closure Conditions. Treatment of the 78:22 mixture of **29** and **25**, obtained from the reaction of the epoxide mixture **32** and sodium thiophenoxide, with excess methyllithium under argon at −78 °C followed by 24 h at ambient temperature gave a yellow oil, the ^1H NMR spectrum of which indicated that it was a 79:21 mixture of **29** and **25**.

6,6-Bis(phenylthio)hexan-1-ol (33).[1,16] To a solution of δ-caprolactone (1.15 g, 10.1 mmol) in 10 mL of toluene at −78 °C under argon was added 10.5 mL of diisobutylaluminum hydride solution (1.49 g, 10.5 mmol). The reaction mixture was stirred at −78 °C for 1 h before thiophenol (2.67 g, 24.3 mmol) and boron trifluoride etherate (2.88 g, 20.3 mmol) were added. The cold bath was then removed, and the reaction mixture was warmed to room temperature and stirred overnight. The reaction was quenched with water and extracted with ether. The ether layer was extracted with successive portions of aqueous 5% NaOH solution until a portion of the extract was shown to be free of thiophenol by failing to yield a precipitate of diphenyl disulfide when mixed with bleach solution. The crude product was purified by bulb-to-bulb distillation, bp 165–173 °C/0.05 mmHg, providing 2.57 g (80%) of **33** as a colorless oil.

Decomposition of the Dianion of 6,6-Bis(phenylthio)-1-hexanol (33). *sec*-Butyllithium (2.90 mL, 0.9 M in cyclohexane, 2.6 mmol) was added to a solution of **33** (206 mg, 0.649 mmol) in 65 mL of THF at −78 °C under argon. The resulting solution was stirred for 1 h at −78 °C and for 48 h at 0–3 °C, after which time water (10 mL) was added. The usual workup and purification by flash chromatography (30-mm i.d. column eluted with 5%, 40% followed by 75% ethyl acetate in hexanes) gave, in order of elution, (1) 25.1 mg (18.6%) of a 2.5:1 mixture of *trans*- and *cis*-2-(phenylthio)cyclohexanol (**34**): IR (film) 3625–3125 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.12–2.17 (m, 162, CH_2), 2.49 (br s, 3.5, OH of *cis*-**34**), 2.74–2.82 (m, 10, axial C*H*SPh of *trans*-**34**), 3.00 (br s, 10, OH of *trans*-**34**), 3.33 (td, J = 9.9, 4.2 Hz, 14, axial C*H*O of *trans*-**34** and axial *H*CSPh of *cis*-**34**), 3.75–3.80 (m, 3, equatorial *H*CO of *cis*-**34**), 7.19–7.59 (m, 68, Ph); MS, (15 eV) m/e (rel intensity) 208 (M^+) (46), 110 (100), 98 (27), 81 (32); high-resolution mass spectrum calcd for $C_{12}H_{16}OS$ 208.0922, found 208.0921; (2) 23.2 mg of a 6.0:3.8:1.0 mixture of 6-(phenylthio)-1-hexanol (**36**) (9.0%), 6-(phenylthio)hex-5-en-1-ol (**37**) (trans:cis 1.3:1.0) (5.8%), and 6,6-bis(phenylthio)-1-hexanol (**33**) (1.5%); (3) 5.0 mg (3.7%) of 1,12-dihydroxy-6,7-bis(phenylthio)-6-dodecene (**35**) of undetermined stereochemistry: IR (film) 3650–3125 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.17–1.58 (m, 12 H, CH_2), 2.30

(t, J = 7.8 Hz, 4 H, allylic CH_2), 2.78 (br s, 2 H, OH), 3.57 (t, J = 6.6 Hz, 4 H, CH_2O), 7.20–7.37 (m, 10 H, Ph); MS, (15 eV) m/e (rel intensity) 416 (M^+) (78), 221 (42), 129 (100), 111 (40), 110 (87), 71 (55); high resolution mass spectrum calcd for $C_{24}H_{32}O_2S_2$ 416.1844, found 416.1845; and (4) 39.6 mg (29.3%) of the other isomer of **35**: IR (film) 3650–3100 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.20–1.66 (m, 12 H, CH_2), 2.10 (br s, 2 H, OH), 2.31 (t, J = 7.8 Hz, 4 H, allylic CH_2), 3.56 (t, J = 6.5 Hz, 4 H, CH_2O), 7.21–7.66 (m, 10 H, Ph); MS, (15 eV) m/e (rel intensity) 416 (M^+) (100), 307 (2.8), 306 (3.0), 248 (4.0), 234 (3.4), 233 (4.5), 215 (3.0), 197 (3.2), 186 (4.7), 171 (2.5), 161 (3.8), 147 (3.4), 110 (7.8), 97 (3.5), 95 (5.5), 85 (6.1), 81 (5.9), 71 (6.7), 69 (3.6), 67 (4.1); high resolution mass spectrum calcd for $C_{24}H_{32}O_2S_2$ 416.1844, found 416.1845.

In an attempt to prepare analytically pure samples of **36** and **37**, a portion of the 6.0:3.8:1.0 mixture of **36**, **37**, and **33** was purified by RP-MPLC (10 × 240 mm reverse-phase C_8 column, eluted with 70:30 methanol/water) to give (1) an inseparable (normal and reverse phase HPLC) mixture of **36** and **37** and (2) **33**, as shown by comparison of the 300-MHz ^1H NMR and mass spectrum with those of authentic material.

3,3-Bis(phenylthio)-1-propanol (40). To a stirred solution of bis(phenylthio)methane[1] (2.05 g, 8.83 mmol) in 100 mL of anhydrous THF at −23 °C was added *n*-butyllithium (6.80 mL, 1.30 M in hexane, 8.84 mmol). The resulting yellow solution was stirred for 30 min, at which time ethylene oxide (0.44 mL, 8.8 mmol), condensed from a lecture bottle, was injected with a dry-ice cooled syringe. The solution was stirred for 17 h at 6 °C and was then poured into water, and the mixture was extracted with ether. Rotary evaporation of the dried ($MgSO_4$) ether layer afforded 3.83 g of a crude product mixture. Purification by column chromatography (silica gel, eluted with 20% ethyl acetate in hexanes) afforded 2.2 g (90%) of **40** as a yellow oil: IR (film) 3650–3100 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 1.80–2.10 (m, 2 H, CH_2), 3.05 (br s, 1 H, O*H*), 3.70 (t, J = 6 Hz, 2 H, CH_2O), 4.60 (t, J = 7 Hz, 1 H, $CH(SPh)_2$), 7.05–7.60 (m, 10 H, Ph); MS, (15 eV) m/e (rel intensity) 276 (M^+) (27), 167 (100); high-resolution mass spectrum calcd for $C_{15}H_{16}OS_2$ 276.0643, found 276.0542.

Decomposition of the Dilithio Derivative of 3,3-Bis(phenylthio)-1-propanol (40). *sec*-Butyllithium (1.30 mL, 1.14 M in cyclohexane, 1.48 mmol) was added to a solution of 3,3-bis(phenylthio)-1-propanol (125 mg, 0.452 mmol) in 45 mL of THF at −78 °C under argon. The resulting solution was stirred for 1 h at −78 °C and then at 0–3 °C for 45 h. The reaction was quenched by the addition of water and worked up to produce an ether soluble residue which was purified by flash chromatography (20-mm i.d. silica column, eluted with 20% and 60% ethyl acetate in hexanes followed by ethyl acetate) to give, in order of elution, (1) 23.8 mg of 4.9:1 mixture of 3-(phenylthio)prop-2-en-1-ol (**43**) (*E*:*Z* = 2.7:1) (24.7%) and **40** (3.4%), as determined by comparison of 300-MHz ^1H NMR spectra of the authentic samples (see below); (2) 16.2 mg (21.5%) of (*E*)-1,6-dihydroxy-3,4-bis(phenylthio)-3-hexene (**42**) as a white solid: mp 139–142 °C; IR (KBr) 3550–3100 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.89 (br s, 2 H, O*H*), 2.92 (t, J = 6.3 Hz, 4 H, OCH_2CH_2), 3.80 (t, J = 6.3 Hz, 4 H, OCH_2), 7.23–7.35 (m, 10 H, Ph); MS, (15 eV) m/e (rel intensity) 332 (M^+) (100), 201 (20), 168 (24), 167 (20), 165 (72), 163 (18), 161 (18), 145 (32), 137 (21), 110 (50); high-resolution mass spectrum calcd for $C_{18}H_{20}O_2S_2$ 332.0905, found 332.0905; and (3) 16.5 mg (21.9%) of (*Z*)-1,6-dihydroxy-3,4-bis(phenylthio)-3-hexene (**41**) as a white solid: mp 71–75 °C; IR (KBr) 3500–3100 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.67 (t, J = 5.5 Hz, 4 H, OCH_2CH_2), 3.75 (br t, J = 5.5 Hz, 6 H, $HOCH_2$), 7.21–7.40 (m, 10 H, Ph); MS, (15 eV) m/e (rel intensity) 332 (M^+) (100), 237 (3.4), 222 (13), 204 (4.4), 192 (9.5), 191 (5.5), 187 (3.4), 186 (3.5), 161 (9.5), 149 (5.8), 147 (4.4); high-resolution mass spectrum calcd for $C_{18}H_{20}O_2S_2$ 332.0905, found 332.0905. The stereochemistry assigned to **41** and **42** is not certain and is based on the fact that both methylene groups of the trans isomer **42** absorb at lower field than those of the cis isomer; it is quite usual for protons on groups having a cis relationship to phenylthio groups to absorb at lower fields than those on groups having a trans relationship.

Isolation of *cis*- and *trans*-3-(Phenylthio)prop-2-en-1-ol (43) from Large Scale Preparation of 3,3-Bis(phenylthio)-1-propanol (40). *n*-Butyllithium (44.0 mL, 1.30 M in hexane, 57.2 mmol) was added to a solution of bis(phenylthio)methane (13.0 g, 56.1 mmol) in 875 mL of anhydrous THF at −23 °C under an argon atmosphere. The resulting yellow solution was stirred for 30 min, and then ethylene oxide (2.80 mL, 56.1 mmol), condensed from a lecture bottle, was added with a dry-ice cooled syringe. The solution was stirred for 48 h at 0–5 °C and then poured into 200 mL of water. The usual workup followed by column chromatography of the crude product mixture (500 g of silica gel, eluted with 5% ethyl acetate in hexanes, followed by 20% ethyl acetate in hexanes) gave 13.5 g of a yellow oil, homogeneous by silica gel TLC but which produced two spots upon RP-TLC analysis (30% water in methanol). Further separation of a small portion of this mixture by RP-MPLC (25 × 310 mm Lobar RP-8 column, eluted with 30% water in methanol) gave 29.4 mg of a 2.8:1 mixture of cis and trans vinyl sulfides as the more mobile component: IR (film) 3600–3100 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.64 (br s, 1 H, OH), 4.21 (d, J = 5.9 Hz, 2 H, trans CH_2), 4.38 (d, J = 6.1 Hz, 2 H, cis CH_2), 5.91–6.01 (m, 1 H, cis and trans PhSCH=C*H*), 6.37 (dt, J = 9.5, 1.2 Hz, 1 H, cis PhSC*H*=C), 6.47 (dt, J = 15, 1.4 Hz, 1 H, trans PhSC*H*=C), 7.23–7.40 (m, 5 H, Ph); MS, (15 eV) m/e (rel intensity) 166 (M^+) (52), 149 (2), 147 (3), 137 (3), 135 (5), 123 (4), 110 (100), 89 (4), 47 (6); high-resolution mass spectrum calcd for $C_9H_{10}OS$ 166.0452, found 166.0451. The slower moving component consisted of a yellow oil whose 300-MHz NMR spectra was identical with that of the previously isolated 3,3-bis(phenylthio)-1-propanol.

Ethyl 3,3-Bis(phenylthio)propionate (46). The procedure of Tilak et al.[33] was used. A solution of ethyl propiolate (0.50 mL, 4.9 mmol), thiophenol (1.2 mL, 12 mmol), and a catalytic amount of piperidine (4 drops) in 15 mL of benzene was heated at reflux under argon for 24 h to produce, after workup and purification by column chromatography (150 g of silica gel, eluted with 5% ethyl acetate in hexanes), 1.15 g (73.4%) of **46** as a colorless oil.

1,1-Dideuterio-3,3-bis(phenylthio)-1-propanol (40d). Ethyl 3,3-bis(phenylthio)propionate (0.297 g, 0.934 mmol) was added to a slurry of lithium tetradeuterioaluminate (0.067 g, 1.58 mmol) in 10 mL of anhydrous ether at −23 °C under argon. The resulting solution was stirred for 1 h at −23 °C and for 14 h at 0 °C, after which time analysis by TLC showed that approximately one half of the starting material still remained. An additional aliquot of lithium tetradeuterioaluminate (0.117 g, 2.79 mmol) in 5 mL of ether was added, the resultant mixture was heated at reflux for 1 h, the mixture was cooled to ambient temperature, and the reaction was quenched by slow, sequential addition of 0.20 mL of water and 0.20 mL of 15% aqueous NaOH, followed by 0.55 mL of water to form a granular precipitate. The resulting solution was diluted with ether and filtered. The filtrate was dried ($MgSO_4$), filtered, concentrated, and purified by column chromatography (20 g of silica gel, eluted with 20% ethyl acetate in hexanes) to give 0.236 g (90.8%) of **40d** as a yellow oil: IR (film) 3700–3100, 2215, 2110 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.01 (d, J = 7.1 Hz, 2 H, CH_2), 4.62 (t, J = 7.1 Hz, 1 H, $CH(SPh)_2$), 7.10–7.47 (m, 10 H, Ph); MS, (15 eV) m/e (rel intensity) 278 (M^+) (14), 169 (M^+ − SPh) (100), 137 (46); high-resolution mass spectrum calcd for $C_{15}H_{14}D_2OS_2$ 278.0768, found 278.0768.

Decomposition of the Dilithio Derivative of 1,1-Dideuterio-3,3-bis(phenylthio)-1-propanol (40d). *sec*-Butyllithium (1.35 mL, 1.24 M in cyclohexane, 1.67 mmol) was added to a solution of **40d** (0.202 g, 0.726 mmol) and TMEDA (0.55 mL, 3.6 mmol) in 72.5 mL of THF at −78 °C under argon. The resulting solution was stirred for 1 h at −78 °C and then at 0–4 °C for 17 h. The reaction was quenched by the addition of 5.0 mL of water and worked up to give 0.161 g of the crude product mixture. Analysis by 300-MHz NMR spectra indicated a 7:5:1.3:2.5 ratio of **40d**: (*E*) and (*Z*) **43d**:**42**:**41**, with the 3-(phenylthio)prop-2-en-1-ol (**43d**) arising exclusively by 1,2-hydride shift; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.25 (br s, 11, OH), 2.05 (d, J = 7.1 Hz, 20, $(PhS)_2CHCH_2$ of **40d**), 2.64 (s, 10, $PhSCCH_2$ of the cis dimer **41**), 2.88 (s, 6, $PhSCCH_2$ of the trans dimer **42**), 3.17 (br s, 8, OH), 4.65 (t, J = 7.1 Hz, 7, $(PhS)_2CH$), 5.94 (d, J = 15.3 Hz, 5, (*E*)- and (*Z*)-PhSCH=C*H*), 6.32 (d, J = 9.6 Hz, 1, (*Z*)-PhSC*H*=CH), 6.43 (d, J = 15 Hz, 4, (*E*)-PhSC*H*=CH), 7.18–7.52 (m, 158, Ph).

Acknowledgment. We thank the National Science Foundation for general support of this work (CHE 8210245) and for providing the funds for purchase of the 300-MHz Bruker NMR instrument used in this study (CHE 7905185). We also thank Dr. Alvin Marcus for recording the mass spectra.

Supplementary Material Available: IR and 300-MHz ^1H NMR spectral data, mass spectrometric data, and determined exact masses for compounds **16**, **18–21**, **26**, **30**, **33**, and **47**. Spectral and mass spectrometric data for *trans*-2-(phenylthio)-3,4,4a,5,6,7,8,8a-octahydro-2*H*-chromene. NMR and mass spectrometric data as well as exact mass for the mixture of **36** and **37**. NMR data for several mixtures reported as products (4 pages). Ordering information is given on any current masthead page.

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