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TETRAHEDRON

Tandem Reductive Lithiations - Carbanionic Cyclizations Yielding Sulfur Stabilized Cyclopropyl- and Cyclobutylcarbinyllithiums[1]

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Abstract: Reductive lithiation of 1,4- or 1,5-bis(phenylthio)-1-alkenes with an aromatic radical-anion results in replacement with a lithium atom of only that phenylthio group which is attached to the sp^3 carbon atom. The resulting carbanion executes an intramolecular nucleophilic addition to the vinyl sulfide group, usually at -78 °C, leading to a phenylthio-stabilized cyclopropyl- or cyclobutylcarbinyllithium. The substrates were prepared by Wittig or Peterson olefination of carbonyl compounds which were in turn generated by conjugate addition of thiophenol or of the cuprate of a phenylthio-stabilized carbanion to an α,β-unsaturated carbonyl compound.

INTRODUCTION

Reductive lithiation of phenyl thioethers with aromatic radical-anions[2] is an exceptionally general method of organolithium production . The generality is due to the ready availability of the substrates and the fact that, unlike the conventional method of organolithium preparation, electrophile removal, the less stable the organolithium the greater the ease of its generation by reductive lithiation. We have recently reported the preparation of homoallyllithiums[3] and bishomoallyllithiums,[4] which all have unactivated alkene functional groups, and the rearrangements of some of them to less substituted ones via cyclopropylcarbinyllithium and cyclobutylcarbinyllithium intermediates, respectively. Our earlier work showed that vinyl sulfides undergo reductive lithiation far more slowly than do saturated phenyl thioethers even though the product vinyllithiums are far more stable than alkyllithiums.[5] Thus, selective reductive lithiation is likely in a molecule with both types of phenylthio groups. A phenylthio group substituted at the terminal alkene carbon atom will be reductively removed far more slowly than another phenylthio group attached to a saturated carbon atom in the same molecule and the vinyl sulfide thus functions as an activated alkene with regard to intramolecular nucleophilic attack. Carbanionic cyclizations of olefinic alkyllithiums or vinyllithiums, leading to 5-membered rings[6,7] or to 3- and 4-membered ring systems possessing an anion-stabilizing group,[8] have been well studied. However, only primary or benzylic tertiary organolithiums have been used in carbanionic cyclizations reported to date, because unstabilized secondary and tertiary organolithiums can not be produced by the lithium-halogen or lithium-selenium exchange methods of organolithium generation. Herein, we report a new synthesis of usefully functionalized cyclopropanes and cyclobutanes utilizing carbanionic ring closures of olefinic primary and tertiary alkyllithiums in which phenylthio groups serve two distinct functions, the precursor of the carbanionic nucleophile and the substituent that activates the alkene electrophile toward nucleophilic attack.

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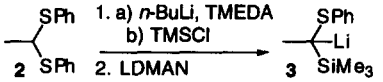
RESULTS AND DISCUSSION

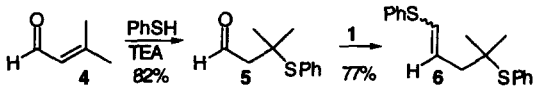
Preparation of 1,4- and 1,5-bis(phenylthio)-1-alkenes.

1,4-bis(phenylthio)-1-alkenes are the substrates for reductive cyclizations leading to phenylthio-stabilized cyclopropylcarbinyllithiums. Peterson olefination[9] of β-phenylthio carbonyl compound **5**, which was in turn generated by conjugate addition of thiophenol to enal **4** in the presence of triethylamine, gave sulfide **6** as a typical 1,4-bis(phenylthio)alkene (Scheme 1). Enal **9** was prepared by the formylation method developed in our laboratory[5] while the others are commercially available. THF was the usual solvent in the 1,4-additions. However neat thiophenol was used in the reaction of crowded enal **9** since the addition was very slow in THF. Peterson reagent **1** was formed by deprotonation of commercially available (phenylthiomethyl)trimethylsilane (eq 1). Deprotonation of the thioacetal of acetaldehyde followed by silylation and reductive lithiation gave the Peterson reagent **3** (eq 2).[10] Peterson reagents **1** and **3** reacted with carbonyl compounds to give vinyl sulfides directly. A good yield was usually obtained from Peterson olefination of β-(phenylthio)aldehydes. However, the Peterson or Johnson-Peterson procedure[11] gave a low yield for ketone **12** due to elimination of thiophenol. The results of the preparation of 1,4-bis(phenylthio)-1-alkenes are summarized in Table 1.

(1)

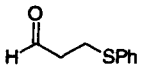
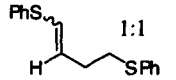
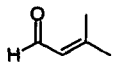
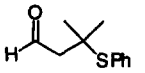
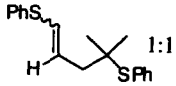
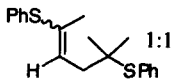
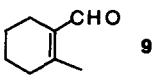
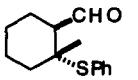
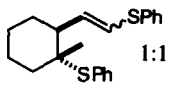
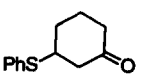
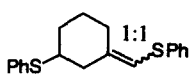


(2)



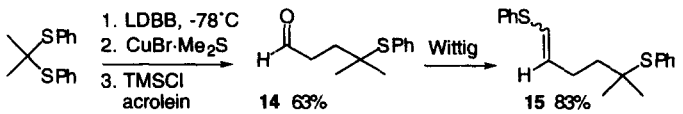
Scheme 1

Table 1. Preparation of 1,4-Bis(phenylthio)-1-alkenes

Enone or Enal	Addition Product (% yield)		Olefination Product (% yield)	
		*a*		**7** (70 for two steps)
 **4**		**5** (82)		**6** (77)
				**8** (70)
 **9**		**10** (86) [b]		**11** (87)
		**12** (90)		**13** (40)

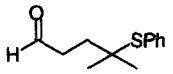
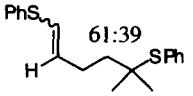
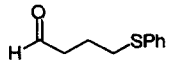
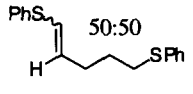
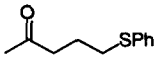
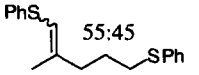
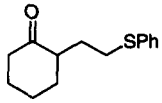
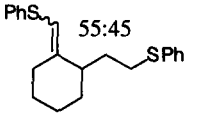
[a] Used directly in next step. [b] Based on consumed **9**; see Experimental Section.

1,5-Bis(phenylthio)-1-alkenes are precursors of phenylthio-stabilized cyclobutylcarbinyllithiums produced by reductive ring closure. Their preparation is illustrated by a typical example in Scheme 2.[4,12] The reductive lithiation of the thioacetal[13] of acetone with lithium 4,4'-di-*tert*-butylbiphenylide (LDBB) provides a phenylthio-stabilized organolithium which is converted to a cuprate by the addition of cuprous bromide-dimethyl sulfide complex. Because of the presence of lithium thiophenoxide in the solution, the resulting "mixed" cuprate incorporates a thiophenoxide group and allows full stoichiometric utilization of the organolithium species.[14] This cuprate adds to acrolein in a conjugate fashion in the presence of trimethylsilyl chloride (TMSCl) at -78 °C. The resulting silyl enol ether is hydrolyzed to the corresponding γ-phenylthio aldehyde **14** during work up. The Wittig reagent $Ph_3P{=}CHSPh$[15] reacted well with aldehydes **14** and **16**, but not with the ketones. However, Peterson olefination with reagent **1** gave satisfactory yields of **19** and **21** starting from ketones **18** and **20**, respectively. The results of the preparation of 1,5-bis(phenylthio)-1-alkenes are summarized in Table 2.



Scheme 2

Table 2. Preparation of 1,5-Bis(phenylthio)-1-alkenes

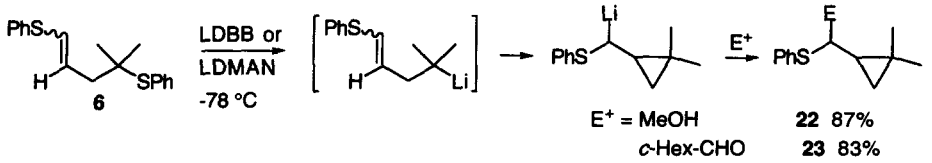
Thioacetal	1,4-Addition Product (% yield)		Olefination Product (% yield)	
		**14** (61)		**15** (83 Wittig)
		**16** (54)		**17** (81 Wittig)
		**18**[a] (93)		**19** (71 Peterson)
		**20** (80)		**21** (65 Peterson)

[a] Prepared by the reaction of NaSPh and commercial 5-chloropentane-2-one instead of by 1,4-addition.

Reductive Cyclizations of 1,4- and 1,5-Bis(phenylthio)-1-alkenes.

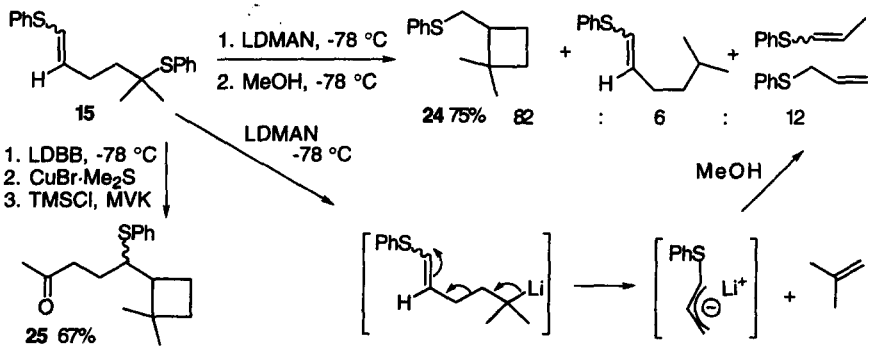
A typical cyclization reaction is shown in Scheme 3. Substrate **6** was added to preformed LDBB or lithium 1-(dimethylamino)naphthalenide[16] (LDMAN) in THF at -78 °C and after the solution had been stirred for 15 min, the electrophile was added. Only cyclopropane product **22** or **23** was detected by GC-MS. It can

be concluded that the chemoselectivity of the reduction in the first step is exclusive in that only the phenylthio group attached to the saturated carbon atom was replaced by a lithium atom. With the phenylthio group activating the double bond and stabilizing the cyclized organolithium, the ring closure resulting from the nucleophilic attack of the carbanion on the proximal carbon atom of the alkene in Scheme 3 is greatly accelerated as compared to the 1,2- and 1,3-vinyl rearrangements that occur via cyclopropylcarbinyllithiums and cyclobutylcarbinyllithiums only at higher temperatures.[3,4] Furthermore, and most importantly, when the ring closed cycloalkylcarbinyllithium is stabilized by a phenylthio group, the ring remains closed unlike the cyclized intermediates from the homoallyllithiums[3] and bishomoallyllithiums.[4]



Scheme 3

The reductive cyclization of 1,5-bis(phenylthio)alkene **15** provided a phenylthio-stabilized cyclobutylcarbinyllithium which was (1) protonated with methanol to produce in 75% yield cyclobutane **24** and (2) as its heterocuprate, added in a conjugate fashion to methyl vinyl ketone to produce the adduct **25** as a 1.2 : 1.0 mixture of diastereomers in 67% yield (Scheme 4); the mixed cuprate was generated by treatment with $CuBr{\cdot}Me_2S$ and contained the thiophenoxide group, which was formed in the reductive lithiation. Four minor products were detected by GC-MS analysis of the crude reaction mixture after the methanol quench. Three of the products constituted about 12% of the total product by GC integration and had $M^+=150$; these are very probably the isomeric fragmentation products the structures and likely mode of generation of which are shown in Scheme 4. The other minor product, constituting about ~6% of the total, is isomeric with **24** and is assumed to be protonated, uncyclized tertiary organolithium as depicted in Scheme 4.

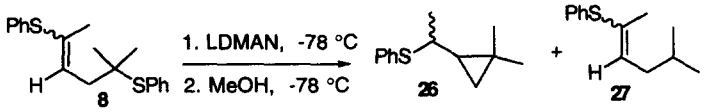


Scheme 4

The effect of an alkyl group substituted at the terminal alkene carbon atom on the ease of cyclization was studied. Both uncyclized and cyclized products were present when an electrophile was added to the reaction mixture following the reductive lithiation of sulfide **8** at -78 °C (eq 3). The methyl group substituted at the double bond thus inhibited the cyclization in comparison with the reaction in Scheme 3. However, when the

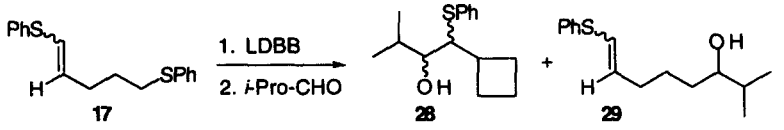
organolithium was allowed to warm to -60 °C, cyclization was virtually complete.

When a primary rather than a more reactive tertiary carbanion is used in the cyclization to a 4-membered ring, the ring closure is also less favorable than that in Scheme 4 as shown for the reductive lithiation of **17** at -78 °C in eq 4. However, when the organolithium from **17** is warmed to -60 °C, cyclization appears to be complete. The fact that no fragmentation products were detected in this case is evidence that fragmentation in the case of the tertiary analogue (Scheme 4) is an anionic process rather than a radical process[17] (followed by reduction) since the less stable primary radical would be expected to fragment faster; a carbanionic fragmentation would be expected to be faster in the case of the less stable tertiary anion, as observed.



(3)

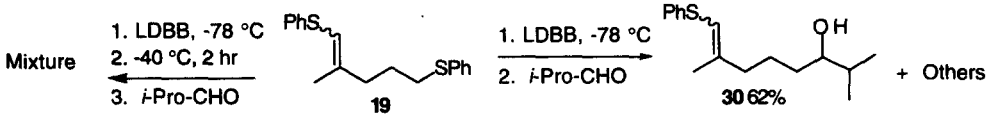
-78 °C, 10 min	45%	36% (23:77)
-60 °C, 30 min	75% (55:45)	0%



(4)

-78 °C, 10 min	29%	47% (30:70)
-60 °C, 30 min	69%	0%

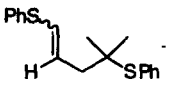
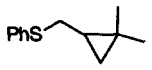
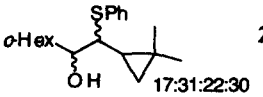
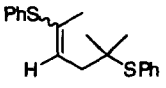
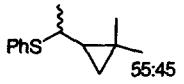
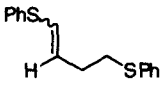
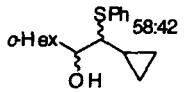
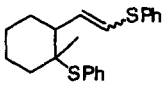
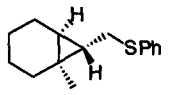
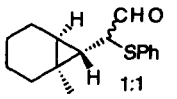
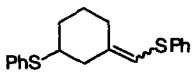
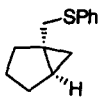
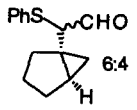
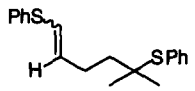
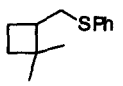
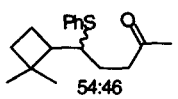
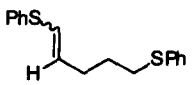
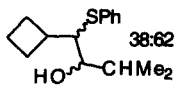
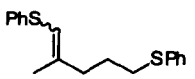
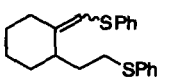
The reductive lithiation of 1,5-bis(phenylthio)-1-alkene **19**, with disubstitution at the proximal terminus of the alkene, followed by addition of an aldehyde gave mainly the uncyclized **30** and some unidentified products (Scheme 5). Thus, proximal alkyl substitution at the alkene appears to be deleterious to the cyclization. In another experiment, the reaction mixture resulting from reductive lithiation was warmed to -40 °C for 2 hr before the aldehyde was added; an inseparable mixture resulted. According to GC-MS, **30** was absent, but there were other peaks with the same molecular weight; these could be cyclized products but may very well be the products from 1,5-proton transfers. A similar result was obtained for the reaction of **21**, another example in which alkyl substitution at the proximal alkene terminus inhibits ring closure.



Scheme 5

The results of the reductive cyclizations are summarized in Table 3. The phenylthio-stabilized cyclopropylcarbinyllithium in the reductive cyclization of **11** was formed stereoselectively according to the stereochemistry of the cyclopropane products **32** and **33** as determined by NOE experiments (see Experimental Section).

Table 3. Cyclizations of 1,4- and 1,5-Bis(phenylthio)-1-alkenes

Substrate	Electrophile	Cyclized Product (yield)
 **6**	MeOH	 **22** (87)
	c-Hex-CHO	 **23** (83)
 **8**	MeOH	 **26**[a] (75)
 **7**	*c*-Hex-CHO	 **31**[a] (81)
 **11**	Methanol	 **32**[a] (83)
	Ethyl Formate	 **33** (79)
 **13**	Methanol	 **34** (86)
	Ethyl Formate	 **35** (71)
 **15**	MeOH	 **24** (75)
	MVK (after cuprate formation)	 **25** (67)
 **17**	*i*-Pro-CHO	 **28**[a] (69)
 **19**	*i*-Pro-CHO	Mixture[a]
 **21**	MeOH	Mixture[a]

[a] After warm up: see text

CONCLUSIONS

A new and fairly general method is presented for the production of cyclopropyl- and cyclobutylcarbinyl carbanions bearing a phenylthio group at the carbanionic site. Carbanionic cyclizations result when reductive lithiation of 1,4- and 1,5-bis(phenylthio)-1-alkenes with aromatic radical-anions generate sp^3 carbanions that add in an intramolecular fashion to the vinyl sulfide, often at -78 °C, the temperature of the reductive lithiation. In the formation of 4-membered rings in which the open chain carbanion is primary or in which it is tertiary but there is an alkyl group at the vinyl terminus bearing the phenylthio group, slightly elevated temperatures are required for cyclization of the carbanion. Alkyl substitution at the proximal vinyl terminus inhibits cyclization of the anion to a cyclobutylcarbinyl carbanion.

It had earlier been shown in analogous systems, but lacking the vinyl phenylthio substituent, that cyclizations also occur. However, elevated temperatures are required and the cyclizations are reversible, often leading to 1,2- or 1,3-vinyl rearrangements.[3,4] The present system provides a dramatic demonstration of the great selectivity of reductive lithiation in the sense that phenylthio groups attached to sp^3 carbon atoms are reductively removed far faster than those attached to sp^2 carbon atoms, undoubtedly as a consequence of the far greater stability of sp^3 radicals. The presence of the very versatile phenylthio group in the cyclized carbanion adds greatly to the potential synthetic utility of this method.

EXPERIMENTAL SECTION

The general procedures and analytical techniques are the same as those described earlier.[4]

1,4-Bis(phenylthio)-4-methylpent-1-ene (6). To a solution of (phenylthiomethyl)trimethylsilane (1.96 g, 10.0 mmol) in 20 mL of THF at 0 °C, *n*-BuLi (1.45 M in hexanes, 7.5 mL, 11 mmol) was added dropwise. After 30 min of being stirred at 0 °C, the reaction mixture was cooled to -78 °C and 3-phenylthio-3-methylbutanal[3] (**5**, 1.94 g, 10 mmol, in 5 mL of THF) was added dropwise. The mixture was stirred at -78 °C for 30 min, allowed to warm to 0 °C, and 25 mL of saturated NaCl was added. The organic materials were extracted with diethyl ether (3 x 30 mL). The combined organic layer was dried over $MgSO_4$. The solvent was removed by rotary evaporation. Flash chromatography (hexanes) gave 2.30 g (77%) of the titled product as a yellow oil. Based on ^1H NMR spectroscopy, the two geometric isomers were formed in the ratio of about 1:1. ^1H NMR ($CDCl_3$): δ 7.57-7.17 (m, 10H), 6.40-6.03 (m, 2H), 2.43 (dd, J_1 = 7.1 Hz, J_2 = 1.2 Hz, 1H), 2.34 (d, J = 7.0 Hz, 1H), 1.30 (s, 3H), 1.26 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 137.51, 136.03, 131.81, 128.93, 128.76, 128.48, 126.22, 125.29, 124.51, 49.01, 48.50, 45.74, 41.22, 28.59, 28.43; HRMS: calc. for $C_{12}H_{15}S$ $(M\text{-}SPh)^+$ 191.0894, found 191.0894.

1,4-Bis(phenylthio)but-1-ene (7). To the mixture of thiophenol (11.0 g, 100 mmol) and triethylamine (0.5 mL) in 15 mL of THF at 0 °C, acrolein (8.40 g, 100 mmol) was added dropwise. After being stirred at room temperature for 1 hr, the reaction mixture was washed with 5% $NaHCO_3$. The organic layer was dried over $MgSO_4$ and the solvent was removed by rotary evaporation to give 3-phenylthiopropanal (16.1 g), which was immediately used in the next step without further purification. To a solution of (phenylthiomethyl)trimethylsilane (9.8 g, 50 mmol) in 100 mL of THF at 0 °C, *n*-BuLi (1.45 M in hexanes, 37 mL, 55 mmol) was added dropwise. After 30 min of stirring at 0 °C, the reaction mixture was cooled to -78 °C and the crude 3-phenylthiopropanal (8.0 g, 50 mmol, in 10 mL of THF) was added dropwise. The reaction mixture was stirred at -78 °C for 30 min and after it was allowed to warm to 0 °C and 100 mL of saturated NaCl was added. The organic materials were extracted with diethyl ether (3 x 150 mL). The combined organic layer was dried over $MgSO_4$. The solvent was removed by rotary evaporation. Distillation, 160 °C / 0.2 mm Hg, provided the titled product as a colorless oil, 9.50 g, 70%. Based on ^1H NMR spectroscopy, the two geometric isomers were formed in the ratio of about 1:1. ^1H NMR ($CDCl_3$): δ 7.40-7.20 (m, 10H), 6.30 (d, J = 9.3 Hz, 0.5H), 6.22 (d, J = 15.0 Hz, 0.5H), 6.00-5.84 (m, 1H), 3.07-2.99 (m, 2H), 2.64-2.14 (m, 2H); ^{13}C NMR

($CDCl_3$): δ 136.80, 136.74, 135.81, 135.73, 129.24, 129.17, 128.89, 128.81, 126.26, 125.94, 125.87, 123.54, 32.90, 32.71, 32.51, 28.63; HRMS: calc. for $C_{16}H_{16}S_2$ (M^+) 272.0693, found 272.0679.

2,5-Bis(phenylthio)-5-methylhex-2-ene (8). To a preformed LDMAN solution (20 mmol, in 45 mL of THF) at -78 °C, 1,1-bis(phenylthio)-1-trimethylsilylethane[18] (3.18 g, 10 mmol, in 5 mL of THF) was added dropwise. The dark-green color of LDMAN turned to dark-red. After 15 min of stirring, 3-phenylthio-3-methylbutanal (1.94 g, 10 mmol, in 5 mL of THF) was added. The reaction mixture was stirred at -78 °C for 30 min, allowed to warm to 0 °C, and 45 mL of saturated NaCl was added. The organic materials were extracted with diethyl ether (3 x 50 mL). The combined organic layer was washed with 5% HCl and brine and dried over $MgSO_4$. The solvent was removed by rotary evaporation. Flash chromatography (hexanes) gave 2.18 g (70%) of the titled product as a yellow oil. Based on ^1H NMR, the two geometric isomers are formed in the ratio of about 1:1. ^1H NMR ($CDCl_3$): δ 7.56-7.19 (m, 10H), 6.10-5.98 (m, 1H), 2.53 (d, J = 7.1 Hz, 1H), 2.31 (d, J = 7.5 Hz, 1H), 1.97 (s, 1.5H), 1.86 (s, 1.5H), 1.27 (s, 3H), 1.26 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 132.53, 130.00, 129.52, 127.12, 127.00, 126.35, 126.25, 126.00, 125.80, 125.64, 125.44, 123.92, 123.83, 123.76, 123.70, 123.50, 121.589, 121.37; 44.08, 37.16, 36.58, 23.84, 23.54, 19.62, 13.44; HRMS: calc. for $C_{13}H_{17}S$ $(M\text{-}SPh)^+$ 205.1051, found 205.1061.

***E*-2-Methyl-2-(phenylthio)cyclohexanecarboxaldehyde (10).** A mixture of 2-methyl-1-cyclohexenecarboxaldehyde[19] (**9**, 1.30 g, 10.5 mmol, prepared as in ref. 5), TEA (0.5 mL) and excess thiophenol (2 mL) was stirred at ambient temperature under argon overnight. GC-MS analysis showed that two isomers of the product formed in the ratio 2:1 and only a trace of starting aldehyde present. The reaction mixture was washed with 5% NaOH (3 x 25 mL) and then 5% $NaHCO_3$. The solvent was removed by rotary evaporation. The minor isomer mostly decomposed to the starting aldehyde during work up and completely disappeared in chromatographic separation according to TLC. Flash chromatography (2% AcOEt / hexanes) gave 0.60 g of starting aldehyde and 1.34 g (86%, based on consumed starting material) of isomerically pure product as a light yellow oil. ^1H NMR ($CDCl_3$): δ 10.14 (d, J = 2.2 Hz, 1H), 7.56-7.27 (m, 5H), 2.38-2.33 (m, 1H), 1.83-1.04 (m, 8 H), 1.37 (s, 3H); NOE: No NOE signal between the methyl group and the methinyl proton of the cyclohexane ring. ^{13}C NMR ($CDCl_3$): δ 204.36, 137.84, 129.88, 129.01, 128.53, 54.78, 49.66, 39.53, 23.78, 23.13, 22.18, 20.60; HRMS: calc. for $C_{14}H_{18}OS$ (M^+) 234.1078, found 234.1081.

1-Methyl-1-phenylthio-2-(2-phenylthioeth-1-enyl)cyclohexane (11). The procedure was the same as that for **6** except that 2-phenylthio-2-methylcyclohexanecarboxaldehyde (**10**, 1.00 g, 4.27 mmol) was used instead of 3-phenylthio-3-methylbutanal. Flash chromatography (hexanes) gave the titled product as a yellow oil, 1.26 g, 87%. Based on the ^1H NMR spectrum, the two geometric isomers are formed in a ratio of about 1:1. ^1H NMR ($CDCl_3$): δ 7.57-7.17 (m, 10H), 6.35-5.98 (m, 2H), 2.79-2.33 (m, 0.5H), 2.41-2.33 (m, 0.5H), 1.80-1.21 (m, 8 H), 1.32 (s, 1.5H), 1.24 (s, 1.5H); ^{13}C NMR ($CDCl_3$): δ 137.91, 137.81, 137.62, 136.45, 136.32, 134.10, 130.89, 128.88, 128.82, 128.65, 128.56, 128.43, 128.33, 128.24, 126.06, 125.94, 123.32, 122.28, 52.38, 52.15, 48.18, 45.01, 39.39, 39.11, 28.77, 24.68, 24.56, 22.53, 20.75; HRMS: calc. for $C_{21}H_{24}S_2$ (M^+) 340.1319, found 340.1353.

3-(Phenylthio)cyclohexanone (12). To a mixture of thiophenol (11.0 g, 100 mmol) and triethylamine (0.5 mL) in 15 mL of THF at 0 °C, was added dropwise cyclohexenone (9.60 g, 100 mmol). After being stirred at room temperature overnight, the reaction mixture was washed with 5% NaOH (3 x 50 mL), and then 5% $NaHCO_3$. The organic phase was dried over $MgSO_4$ and concentrated by rotary evaporation. Distillation (135 °C/0.1 mm Hg) provided 18.0 g (90%) of the titled product as a colorless oil. ^1H NMR ($CDCl_3$): δ 7.44-7.25 (m, 5H), 3.42 (m, 1H), 2.71 (m, 1 H), 2.44-2.08 (m, 5 H), 1.80-1.62 (m, 2 H); ^{13}C NMR ($CDCl_3$): δ 208.46, 133.02, 132.95, 128.99, 127.62, 47.53, 45.87, 40.73, 30.96, 23.84; HRMS: calc. for $C_{12}H_{14}OS$ (M^+) 206.0765, found 206.0760.

1-(Phenylthio)methylidene-3-(phenylthio)cyclohexane (13). The same procedure was followed as that for **6** except that 3-(phenylthio)cyclohexanone (**12**, 4.94 g, 24 mmol) was used instead of 3-phenylthio-3-methylbutanal. Flash chromatography (hexanes) gave 3.00 g (40%) the titled product as a yellow

oil. Based on the ^{1}H NMR spectrum, the two geometric isomers are formed in the ratio of about 1:1. ^{1}H NMR ($CDCl_3$): δ 7.45-7.16 (m, 10H), 6.00 (s, 0.5H), 5.93 (s, 0.5H), 3.27-3.10 (m, 1.5 H), 2.70-2.66 (m, 1 H), 2.36-1.91 (m, 4.5 H), 1.64-1.46 (m, 2 H); 143.76, 143.37, 136.90, 136.77, 134.46, 134.32, 131.98, 131.60, 128.72, 128.66, 127.89, 126.78, 126.58, 125.57, 114.91, 114.85, 46.68, 46.20, 42.32, 36.39, 35.43, 32.57, 32.45, 29.37, 26.40, 25.36; HRMS: calc. for $C_{19}H_{20}S_2$ (M^+) 312.1006, found 312.0955.

1,5-Bis(phenylthio)-5-methylhex-1-ene (15). To a suspension of triphenyl [(phenylthio)-methyl]phosphonium chloride (2.63 g, 7.43 mmol) in 30 mL of THF at 0 °C, *n*-butyllithium (1.6 M in hexanes, 4.3 mL, 6.9 mmol) was added dropwise. After being stirred at 0 °C for 15 min, the resulting orange solution was cooled to -78 °C and 4-methyl-4-(phenylthio)pentan-1-one[4] (**14**, 1.03 g, 4.95 mmol) in 10 mL of THF was added. After being stirred at -78 °C for 15 min, the mixture was warmed to room temperature, stirred for 30 min., and the reaction was quenched with about 1 mL of methanol. The mixture was poured into 100 mL of pentane and filtered through silica gel to remove triphenylphosphine oxide. Flash chromatography (hexanes) provided 1.29 g (83%) of the titled product as a yellow oil. Based on capillary GC and ^{1}H NMR, the two geometric isomers were formed in the ratio of 61 : 39. ^{1}H NMR ($CDCl_3$): δ 7.56 - 7.18 (m, 10H), 6.90 (m, 0.39H), 6.18 (m, 1H), 5.80 (m, 0.61H), 2.52 - 2.36 (m, 2H), 1.61 - 1.54 (m, 2 H), 1.27 (s, 3.66H), 1.25 (s, 2.34H). ^{13}C NMR ($CDCl_3$): δ 137.55, 137.45, 136.68, 136.44, 136.31, 132.93, 132.08, 128.93, 128.72, 128.65, 128.45, 128.37, 126.10, 126.04, 122.91, 121.10, 48.98, 48.88, 41.05, 31.56, 28.62, 24.96. IR (neat, NaCl): 3059.5 (m), 2961.1 (s), 2926.4 (s), 1718.8 (m), 1583.8 (m), 1473.8 (s), 1439.1 (s), 1363.8 (m), 1120.8 (m), 1089.9 (m), 1068.7 (m), 1024.3 (s), 750.4 (s), 738.8 (s), 692.5 (s) cm^{-1}; HRMS: calc. for $C_{19}H_{22}S_2$ 314.1107, found 314.1135.

4-(Phenylthio)butanal (16). To a solution of LDBB (40 mmol, in 70 mL of THF) at -78 °C, was added bis(phenylthio)methane (4.64 g, 20 mmol, in 15 mL of THF). After the reaction mixture had been stirred at -78 °C for 15 min, copper bromide-dimethyl sulfide complex was added fast and with increased argon flow. The cuprate formation was carried out by stirring the reaction mixture at -78 °C for 3 hr. TMSCl (3.4 mL, 23 mmol) was added and then acrolein (1.20 mL, 18.0 mmol). The mixture was stirred at -78 °C over night. Saturated NH_4Cl (100 mL) and tetrabutylammonium fluoride (~ 1 mL) were added after the mixture had been allowed to warm to 0 °C. The mixture was stirred at room temperature for about 45 min after which all of the silyl enol ether was hydrolyzed to the carbonyl compound according to TLC. The mixture was filtered through celite 545 to remove copper salt. The organic materials were extracted by ether (3 x 100 mL) and the organic layer was dried over $MgSO_4$. The solvent was removed by rotary evaporation. Flash chromatography (3% AcOEt / hexanes) gave recovered DBB and 1.75 g (54%) of the titled product as a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 9.77 (s, 1 H), 7.47 - 7.16 (m, 5H), 2.98 (t, J = 6.9 Hz, 2H), 2.83 (t, J = 7.1 Hz, 2H, $COCH_2$), 2.00-1.91 (m, 2 H); HRMS: calc. for $C_{10}H_{12}OS$ (M^+) 180.0609, found 180.0596.

1, 5-Bis(phenylthio)pent-1-ene (17). The procedure was the same as that for **15** except that 4-(phenylthio)butanal (**16**, 0.954 g, 5.30 mmol) was used instead of **14**. Flash chromatography (hexanes) provided the titled product as a yellow oil, 1.21 g, 80%. Based on the ^{1}H NMR spectrum, the two geometric isomers were formed in the ratio of 50 : 50 ^{1}H NMR ($CDCl_3$): δ 7.48 -7.21 (m, 10H), 6.21 (m, 1H), 5.92 (m, 0.5H), 5.82 (m, 0.5H), 2.99 - 2.93 (m, 2H), 2.60 -2.28 (m, 2H), 1.99 - 1.76 (m, 2 H); HRMS: calc. for $C_{17}H_{18}S_2$ (M^+) 286.0849, found 286.0802.

5-(Phenylthio)pentan-2-one (18). NaOH (0.78 g, 20.0 mmol) and thiophenol (2.10 mL, 20.0 mmol) were dissolved in 30 mL of water, and 5-chloropentan-2-one (2.41 g, 20.0 mmol) was added to the solution at room temperature. The reaction mixture was heated at about 80 °C for 30 min. Ether was added to the reaction mixture after it was allowed to cool to room temperature. The organic materials were extracted with ether and the combined organic layer was dried over anhydrous $MgSO_4$. After the solvent was removed by rotary evaporation, the product (1.81 g, 93%) did not require further purification. ^{1}H NMR ($CDCl_3$): δ 7.35 - 7.14 (m, 5H), 2.94 (t, J = 7.0 Hz, 2H), 2.60 (t, J = 7.1 Hz, 2 H), 2.13 (s, 3H), 1.97 (m, 2 H); HRMS: calc. for $C_{11}H_{14}OS$ (M^+) 194.0765, found 194.0760.

1, 5-Bis(phenylthio)-2-methylpent-1-ene (19). The procedure was the same as that for **17** except that 5-(phenylthio)pentan-2-one (**18**, 1.64 g, 8.47 mmol) was added to the organolithium instead of **16**. Flash chromatography (pure hexanes) provided **19** as a yellow oil, 1.80 g, 71%. Based on the ^{1}H NMR spectrum, the two geometric isomers were formed in the ratio of 55 : 45. ^{1}H NMR ($CDCl_3$): δ 7.36 - 7.15 (m, 10H), 5.98 (s, 1H), 2.94 (t, J = 7.3 Hz, 2H), 2.45 (t, J = 7.5 Hz, 1.1H), 2.33 (t, J = 7.4 Hz, 0.9H), 1.88 - 1.76 (m, 2H), 1.87 (d, J = 1.1 Hz, 1.65H), 1.84 (s, 1.35H); CI MS using isobutane: $C_{18}H_{21}S_2$ $(M+1)^+$ 301.

2-(2-Phenylthioethyl)cyclohexanone (20). The procedure was the same as that for **16** except that 2-methylenecyclohexanone[20] (2.2 g, 20 mmol) was used as the electrophile. Bis(phenylthio)-methane (3.48 g, 15 mmol) was added to LDBB in order to generate the sulfur-stabilized organolithium to be added to the cuprate. Flash chromatography (3% AcOEt / hexanes) gave recovered DBB and 2.80 g (80%) of the titled product as a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.36 - 7.13 (m, 5H), 2.98 (m, 2H), 2.53 (m, 1 H), 2.41 - 2.25 (m, 2H, $COCH_2$), 2.21 - 1.22 (m, 8 H); HRMS: calc. for $C_{14}H_{18}OS$ (M^+) 234.1078, found 234.1080.

2-[2-(Phenylthio)ethyl]-1-(phenylthio)methylenecyclohexane (21). To a solution of (phenylthio)methyltrimethylsilane (3.60 g, 18.4 mmol) in 15 mL of THF at 0 °C, *n*-butyllithium (1.6 M in hexanes, 12.5 mL, 19 mmol) was added dropwise. After 30 min of stirring, a solution of 2-[2-(phenylthio)ethyl]cyclohexan-1-one (**20**, 4.30 g, 18.4 mmol) in 5 mL of THF was added dropwise. The mixture was stirred at 0 °C for 30 min before 20 mL of saturated NaCl was added. The organic materials were extracted with ether (3 x 25 mL) and the combined organic layer was dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation. Flash chromatography (hexanes) provided **21** as a yellow oil, 4.30 g, 65%. Based on ^{1}H NMR, the two geometric isomers were formed in the ratio of 55 : 45. ^{1}H NMR ($CDCl_3$): δ 7.34 - 7.12 (m, 10H), 5.99 (s, 0.55H), 5.91 (s, 0.45H), 3.16 (m, 0.55H), 2.99 - 2.81 (m, 2H), 2.45 (m, 1H), 2.31 (m, 0.45H), 2.22 (m, 0.45H), 2.06 - 1.51 (m, 8.55 H); CI MS using isobutane: $C_{21}H_{24}S_2$ $(M+1)^+$ 341.

2,2-Dimethyl-1-(phenylthio)methylcyclopropane (22). To an LDMAN solution (3.6 mmol, in 12 mL of THF) at -78 °C under argon, 1,4-bis(phenylthio)-4-methylpent-1-ene (**6**, 540 mg, 1.80 mmol, in 2 mL of THF) was added dropwise. At the end of the addition, the dark-blue solution color changed to red. After the mixture had been stirred at -78 °C for 15 min, 0.5 mL of MeOH was added via syringe. The mixture was allowed to warm to room temperature and H_2O (10 mL) was added. The organic materials were extracted with Et_2O (3 x 15 mL). The combined organic layer was washed with 5% HCl (to remove DMAN) and brine, and then dried over $MgSO_4$. The solvent was removed by rotary evaporation. Flash chromatography (hexanes) provided **22** as a pale yellow oil, 294 mg, 85%. ^{1}H NMR ($CDCl_3$): δ 7.51-7.14 (m, 5H), 2.98 - 2.89 (m, 2H), 1.06 (s, 3H), 1.04 (s, 3H), 0.93-0.80 (m, 1H), 0.57-0.52 (dd, J_1 = 8.5 Hz, J_2 = 4.5 Hz, 1H), 0.17-0.10 (dd, J_1 = 8.5 Hz, J_2 = 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 137.26, 129.24, 128.66, 125.65, 35.30, 27.10, 23.52, 20.70, 19.76, 16.97. HRMS: calc. for $C_{12}H_{16}S$ (M^+) 192.0973, found 192.0979.

1-Cyclohexyl-2-(2,2-dimethylcyclopropyl)-2-(phenylthio)ethanol (23). To a solution of LDBB (1.90 mmol, in 6 mL of THF) at -78 °C under argon, 1,4-bis(phenylthio)-4-methylpent-1-ene (**6**, 285 mg, 0.95 mmol, in 1 mL of THF) was added dropwise. At the end of the addition, the dark-blue color of the solution changed to red. After the reaction mixture had been stirred at -78 °C for 15 min, cyclohexanecarboxaldehyde (145 μL, 1.20 mmol) was added. The mixture was stirred at -78 °C for 15 min and allowed to warm to room temperature before 5 mL of H_2O was added. The organic materials were extracted with Et_2O (3 x 10 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed by rotary evaporation. Flash chromatography (2% AcOEt / hexanes) provided the titled product **23** (GC ratio: 17:31:22:30) as a pale yellow oil, 240 mg, 83%. ^{1}H NMR ($CDCl_3$): δ 7.55-7.23 (m, 5H), 3.36 -3.08 (m, 2H), 2.08-1.92 (m, 1H, methine proton of cyclohexane), 1.74-1.54 (m, 5 H), 1.30-0.83 (m, 12 H), 0.70-0.53 (m, 1H), 0.34-0.26 (m, 2H). HRMS: calc. for $C_{19}H_{24}OS$ (M^+) 340.1861, found 304.1904.

2,2-Dimethyl-1-(phenylthio)methylcyclobutane (24). A solution of LDMAN (1.6 mmol) in 6 mL of THF, prepared freshly at -55 °C, was cooled to -78 °C and treated with 1,5-bis(phenylthio)-5-methylhex-1-ene (**15**, 251 mg, 0.80 mmol, in 2 mL of THF). After being stirred at -78°C for 10 min, the

reaction was quenched with 0.5 mL of methanol. The mixture was allowed to warm to room temperature and 5 mL of water was added. The organic materials were extracted with ether (3 x 20 mL) and the combined organic layer was washed with 5% HCl to remove DMAN and dried over $MgSO_4$. Solvent removal and flash chromatography (hexanes) provided 123 mg (75%) of the titled product as a colorless oil. ^1H NMR ($CDCl_3$): δ 7.39-7.13 (m, 5H), 3.05 - 2.84 (m, 2H), 2.22 (m, 1 H), 1.98 (m, 1 H), 1.68 - 1.53 (m, 3 H), 1.00 (s, 3H), 1.08 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 137.26, 128.82 (2), 125.58, 42.86, 38.22, 35.26, 32.31, 30.42, 22.57, 22.03; IR (neat, NaCl): 3059.5 (m), 2951.5 (s), 2880.1 (s), 2862.7 (s), 1583.8 (m), 1479.6 (m), 1464.2 (m), 1439.1 (m), 1381.2 (m), 1365.8 (m), 1259.7 (m), 1089.9 (m), 1026.3 (m), 736.9 (s), 690.6 (m) cm^{-1}; HRMS: calc. for $C_{13}H_{18}S$ (M^+) 206.1148, found 206.1138.

5-(2,2-Dimethylcyclobutyl)-5-phenylthio-2-pentanone (25) A solution of LDBB (1.5 mmol), freshly prepared in THF (6 mL) at 0 °C, was cooled to -78 °C and treated with 1,5-bis(phenylthio)-5-methylhex-1-ene (**15**, 235 mg, 0.75 mmol, in 2 mL of THF). After the solution had been stirred for 10 min at -78 °C, copper bromide-dimethyl sulfide complex was quickly added under increased argon flow. The cuprate formation was insured by stirring the reaction mixture at -78 °C for 3 hr. Trimethylsilyl chloride (3.0 mL, 23 mmol) was then added followed by the methyl vinyl ketone (80 μL, 0.95 mmol). The mixture was stirred at -78 °C overnight. Aqueous 5% sodium hydroxide solution (5 mL) and about 0.5 mL of tetrabutylammonium hydroxide were added and the mixture was allowed to warm to 0 °C. It was stirred at room temperature for about 45 min in order to hydrolyze all of the silyl enol ether to the ketone product. After the mixture had been filtered through celite to remove the copper salts, the organic materials were extracted with ether (3 x 10 mL) and the organic layer was dried over $MgSO_4$. The solvent was removed by rotary evaporation. Flash chromatography (2% AcOEt / hexanes) provided two diastereomers, **A** and **B**, of the titled product, both as pale yellow oils. Diastereomer **A** (63 mg, 31%): ^1H NMR ($CDCl_3$): δ 7.45 - 7.18 (m, 5H), 3.15 (m, 1H), 2.70 (m, 1 H), 2.54 - 1.25 (m, 8H), 2.03 (s, 3H), 1.19 (s, 3H), 1.16 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 208.75, 135.06, 131.76, 128.88, 126.72, 49.14, 47.07, 39.32, 38.56, 31.96, 31.12, 29.95, 25.33, 22.45, 21.35; IR (neat, NaCl): 30611.4 (m), 2951.5 (s), 2862.7 (s), 2357.3 (m), 1718.8 (s), 1583.8 (m), 1475.7 (m), 1466.1 (m), 1439.1 (m), 1367.7 (s), 1286.7 (m), 1253.9 (m), 1155.5 (m), 746.5 (m), 692.5 (m) cm^{-1}; HRMS: calc. for $C_{17}H_{24}OS$ 276.1548, found 276.1550. Diastereomer **B** (75 mg, 36%): ^1H NMR ($CDCl_3$): δ7.40 - 7.23 (m, 5H), 3.03 - 2.95 (m, 1H), 2.84-2.65 (m, 2H), 2.08 (s, 3H), 2.04-1.22 9 (m, 7H), 1.10 (s, 3H), 1.05 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 208.62, 134.37, 133.22, 128.85, 127.20, 51.99, 48.62, 40.28, 38.82, 31.77, 31.08, 30.12, 26.88, 22.70, 21.68; IR (NaCl, neat) 2953.4 (s), 2862.7 (m), 1716.9 (s), 1583.8 (m), 1479.6 (m), 1467.2 (m), 1439.1 (m), 1365.8 (s), 1288.6 (m), 1248.1 (m), 1157.4 (m), 1089.9 (m), 1024.3 (m), 744.6 (s), 692.5 (s) cm^{-1}; HRMS: calc. for $C_{17}H_{24}OS$ 276.1548, found 276.1540.

1,1-Dimethyl-2-[1-(phenylthio)ethyl]cyclopropane (26). To a solution of LDMAN (2.0 mmol) at -78 °C, 2,5-bis(phenylthio)-5-methylhex-2-ene (**8**, 314 mg, 1.00 mmol, in 2 mL of THF) was added dropwise. At the end of the addition, the dark-blue color of the solution changed to red. After the reaction mixture had been warmed to -60 °C for 30 min, MeOH (0.5 mL) was added via syringe. The mixture was allowed to warm to room temperature before H_2O (10 mL) was added. The mixture was extracted with Et_2O (3 x 15 mL). The combined organic layer was washed with 5% HCl (to remove DMAN) and brine, and dried over $MgSO_4$. Removal of solvent by rotary evaporation and flash chromatography (hexanes) provided diastereomers **A** and **B** of **26**, both as pale yellow oils. **A** (105 mg, 41%): ^1H NMR ($CDCl_3$): δ 7.45-6.83 (m, 5H), 2.62-2.52 (m, 1H), 1.31 (d, J = 6.6 Hz, 3H), 0.99 (s, 3H), 0.93 (s, 3H), 0.64-0.56 (m, 1H), 0.33 (dd, J_1 = 8.7 Hz, J_2 = 4.3 Hz, 1H), -0.17 (dd, J_1 = J_2 = 5.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 135.83, 133.89, 128.90, 127.22, 45.67, 31.53, 27.20, 22.21, 20.24, 19.99, 17.43; HRMS: calc. for $C_{13}H_{18}S$ (M^+) 206.1129, found 206.1106. **B** (70 mg, 34%): 7.49-7.42 (m, 2H), 7.06-6.95 (m, 3H), 2.79-2.69 (m, 1H), 1.30 (d, J= 6.5 Hz, 3H), 0.89 (s, 3H), 0.86 (s, 3H), 0.66-0.56 (m, 1H), 0.46 (dd, J_1 = 7.4 Hz, J_2 = 3.8 Hz, 1H), 0.15 (dd, J_1 = J_2 = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 135.97, 133.50, 128.90, 127.06, 46.12, 31.39, 27.44, 22.90, 21.16, 19.98, 17.69; HRMS: calc. for $C_{13}H_{18}S$ (M^+) 206.1129, found 206.1160.

5-Methyl-2-(phenylthio)hex-2-ene (27). The same procedure as that for **22** was followed except that 2,5-bis(phenylthio)-5-methylhex-2-ene (**8**, 157 mg, 0.50 mmol) instead of **6** was added to LDMAN. Flash chromatography (hexanes) provided **26** (46 mg, 45%) and 37 mg (36%) the titled product as a pale yellow oil. Based on ^{1}H NMR, the two geometric isomers were formed in the ratio of 23:77. ^{1}H NMR ($CDCl_3$): δ 7.53-7.17 (m, 5H), 5.94-5.83 (m, 1H), 2.24 (dd, $J_1 = J_2 = 6.9$ Hz, 0.5H), 2.03 (dd, $J_1 = J_2 = 7.1$ Hz, 1.5H), 1.93 (d, J = 1.0 Hz, 0.75H), 1.88 (s, 2.25H), 1.78-1.66 (m, 1 H), 0.94 (d, J = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 135.52, 134.87, 130.15, 130.05, 129.11, 128.92, 128.85, 126.33, 39.04, 38.46, 28.70, 22.45, 18.24; HRMS: calc. for $C_{13}H_{18}S$ (M^+) 206.1129, found 206.1106.

1-Cyclobutyl-3-methyl-1-(phenylthio)butan-2-ol (28). The procedure used was the same as that for **29** (see below) except that 1,5-bis(phenylthio)pent-1-ene (**17**, 178 mg, 0.623 mmol) was added to LDBB and the mixture was warmed to -60 °C for 30 min before isobutyraldehyde was added. Flash chromatography (2% AcOEt / hexanes) gave DBB and 108 mg (69%) of the product. Based on capillary GC, the two diastereomers were formed in the ratio of 38 : 62. ^{1}H NMR ($CDCl_3$): δ 7.49 - 7.19 (m, 5H), 3.40 (dd, J = 8.7 Hz, 2.8 Hz, 1H), 3.19 (m, 1H), 2.67 (m, 1H), 2.33 -1.75 (m, 8H), 0.97 - 0.66 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 135.59, 135.13, 132.72, 131.86, 129.01, 128.88, 127.10, 126.94, 77.51, 76.86, 61.89, 59.91, 35.46, 31.45, 30.49, 29.73, 29.28, 28.43, 28.11, 28.05, 19.80, 19.59, 19.38, 18.87, 18.14, 17.47; IR (neat, NaCl): 3483.9 (m, br), 2963.0 (s), 2870.4 (s), 1583.8 (m), 1479.6 (s), 1439.1 (s), 1388.9 (m), 1253.9 (m), 1088.9 (m), 1068.7 (m), 1051.3 (m), 1024.3 (m), 985.7 (m), 738.8 (s), 692.5 (s) cm^{-1}; HRMS: calc. for $C_{15}H_{22}OS$ (M^+) 250.1392, found 250.1386.

***trans*- & *cis*-2-Methyl-8-(phenylthio)oct-7-en-3-ol (29).** The procedure used was the same as that for **23** except that 1,5-bis(phenylthio)pent-1-ene (**17**, 200 mg, 0.700 mmol) instead of **6** was added to LDBB and the electrophile was isobutyraldehyde. Flash chromatography gave recovered DBB, **28** (51 mg, 29%) and 82 mg (47%) of **29** as a pale yellow oil (GC ratio: 30:70). ^{1}H NMR ($CDCl_3$): δ 7.36 - 7.17 (m, 5H), 6.12 (m, 1H), 5.84 (m, 1H), 3.39 (m, 1H), 2.32 - 2.17 (m, 2H), 1.71 - 1.36 (m, 6H), 0.97 - 0.85 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 137.17, 136.45, 136.32, 133.22, 128.91, 128.66, 128.37, 126.10, 126.00, 122.90, 121.05, 76.39, 33.53, 33.42, 33.06, 29.05, 25.44, 18.83, 17.15; IR (neat, NaCl): 3406.7 (m, br), 3059.5 (m), 2932.2 (s), 1713.0 (m), 1583.8 (m), 1479.6 (m), 1439.1 (m), 1385.1 (m), 1367.7 (m), 1089.9 (m), 1068.7 (m), 1024.3 (m), 980.0 (m), 738.8 (m), 690.6 (m) cm^{-1}; HRMS: calc. for $C_{15}H_{22}OS$ (M^+) 250.1392, found 250.1387.

2,7-Dimethyl-8-(phenylthio)oct-7-en-3-ol (30). The procedure used was the same as that for **28** except that 1,5-bis(phenylthio)-2-methylpent-1-ene (**19**, 205 mg, 0.684 mmol) instead of **17** was added to LDBB. Flash chromatography (5% AcOEt / hexanes) gave recovered DBB and 93 mg (62%) of **30** as a yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.31 - 7.14 (m, 5H), 5.94 (m, 1H), 3.39 (m, 1H), 2.32 (m, 1.1H), 2.20 (m, 0.90H), 1.89 (d, J = 1.3 Hz, 1.65H), 1.86 (s, 1.35H), 1.74 - 1.25 (m, 6H), 0.94 - 0.89 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 143.67, 142.99, 137.42, 137.30, 128.82, 127.85, 127.74, 125.53, 115.68, 115.53, 76.44, 76.38, 39.34, 33.65, 33.55, 33.45, 24. 19, 24.04, 23.16, 18.83, 17.99, 17.15; CI MS using isobutane: $C_{16}H_{25}OS$ $(M+1)^+$ 265.

1-Cyclohexyl-2-cyclopropyl-2-(phenylthio)ethanol (31). A solution of LDBB (3.7 mmol), preformed in 10 mL of THF at 0 °C, was cooled to -78 °C and treated with 1,4-bis(phenylthio)but-1-ene (**7**) (500 mg, 1.85 mmol, in 1 mL of THF). The color of the mixture changed from dark-blue to dark-red immediately at the end of the addition. The mixture was warmed to -60 °C for 30 min and then cooled to -78 °C. Cyclohexanecarboxaldehyde (254 μL, 2.1 mmol) was added via syringe. The resulting pale yellow solution was stirred at -78 °C for 15 min, warmed to 0 °C, and quenched with 10 mL of H_2O. The mixture was extracted with ether (3 x 20 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and the solvent removed by rotary evaporation. Flash chromatography (3% AcOEt / hexanes) gave recovered DBB and 411 mg (81%) of the **31** as a pale yellow oil. Based on ^{1}H NMR, the two diastereomers were formed in the ratio of 42:58. ^{1}H NMR ($CDCl_3$): δ 7.54 - 7.21 (m, 5H), 3.50 (d, J = 5.7 Hz, 0.42H), 3.35 (dd, $J_1 = 8.5$ Hz,

J_2 = 2.8 Hz, 0.58H), 2.89 (dd, J_1 = 9.9 Hz, J_2 = 2.8 Hz, 0.58H), 2.54 (dd, J_1 = 9.6 Hz, J_2 = 6.1 Hz, 0.42H), 2.41 (s, br, 1H, OH), 2.04 (m, 1H), 1.89 - 0.29 (m, 15 H); ^{13}C NMR ($CDCl_3$): δ 146.51, 134.31, 132.21, 129.01, 128.75, 127.98, 127.75, 127.23, 78.03, 76.05, 58.39, 40.34, 39.63, 29.60, 29.41, 26.37, 26.37, 25.91, 25.85, 9.79, 7.41, 4.27. HRMS: calc. for $C_{17}H_{24}OS$ (M^+) 276.1548, found 276.1576.

1-Methyl-7-*exo*-(phenylthio)methyl[4.1.0]heptane (32). The procedure used was the same as that for **22** except that 1-methyl-1-phenylthio-2-(2-phenylthioethenyl)cyclohexane (**11**, 132 mg, 0.39 mmol) was added to the LDMAN instead of **6**. Flash chromatography (hexanes) gave 75 mg (83%) of the titled product as a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.97-7.14 (m, 5H), 3.30-2.90 (m, 2H), 1.87-1.00 (m, 8H), 1.08 (s, 3H), 0.75 (m, 1H), 0.53 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 137.41, 129.40, 128.72, 125.71, 35.47, 32.29, 26.69, 25.95, 23.62, 21.96, 21.61, 21.09, 20.61; HRMS: calc. for $C_{15}H_{20}S$ (M^+) 232.1286, found 232.1290. NOE: A strong NOE signal was observed between the methyl group (1.08 ppm) and one of the cyclopropane protons (0.53 ppm), but no NOE effect was observed between the methyl (1.08 ppm) and the other cyclopropane proton (0.75 ppm), nor between the two cyclopropane protons (0.75 ppm and 0.53 ppm).

1-Methyl-7-*exo*-(1-phenylthio-2-oxoethyl)[4.1.0]heptane (33). A solution of LDBB (0.55 mmol), freshly prepared in THF (5 mL) at 0 °C, was treated with **11** (94 mg, 0.27 mmol) in THF (1 mL) at -78 °C. The color of the solution changed from dark green to dark red immediately at the end of the addition. After being stirred for 15 min, the organolithium solution was cannulated to a precooled solution of ethyl formate (81 μL, 1.00 mmol) in 3 mL of THF (3 mL) at -78 °C. The mixture was stirred at -78 °C for 30 min before being quenched with 5 mL of water. It was extracted with ether (3 x 10 mL) and the organic layer was dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation. Flash chromatography (1% AcOEt / Hex) gave recovered DBB and 57 mg (79%) of **33** as a pale yellow oil. Based on the ^{1}H NMR spectrum, the two diastereomers were formed in the ratio of about 1:1. ^{1}H NMR ($CDCl_3$): δ 9.42 (d, J = 4.6 Hz, 1H), 7.41-7.17 (m, 5H), 3.23 (dd, J_1 = 10.7 Hz, J_2 = 4.4 Hz, 0.5H), 3.14 (dd, J_1 = 10.4 Hz, J_2 = 4.5 Hz, 0.5H), 2.00-1.13 (m, 8H), 1.25 (s, 1.5H), 1.09 (s, 1.5H), 0.85-0.80 (m, 0.5H), 0.71-0.63 (m, 1.5H); ^{13}C NMR ($CDCl_3$): δ 189.39., 127.87, 126.84, 126.73, 124.60, 123.83, 122.82, 53.59, 53.43, 26.86, 20.24, 19.86, 19.59, 18.33, 18.07, 17.37, 17.17, 16.88, 16.10, 16.04, 15.70, 15.58, 15.26; IR (neat, NaCl): 2909.0 (s), 1703.4 (s), 737.1 (s), 686.7 (m), 661.7 (m); HRMS: calc. for $C_{16}H_{20}OS$ (M^+) 260.1235, found 260.1255.

1-(Phenylthio)methyl[3.1.0]hexane (34). The procedure was the same as that for **22** except that **13** (295 mg, 0.95 mmol) was added to LDMAN instead of **6**. Flash chromatography (hexanes) gave 165 mg (86%) of **34** as a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.37-7.13 (m, 5H), 3.15 (two d, AB system, J = 12.5 Hz, 2H), 1.82-1.07 (m, 6H), 0.89-0.77 (m, 1H), 0.50 (dd, ABX system, J_1 = J_1 = 4.9 Hz, 1H), 0.41 (dd, ABX system, J_1 = 8.1 Hz, J_2 = 4.9 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 137.72, 129.16, 128.69, 125.64, 41.73, 31.09, 27.98, 27.59, 24.26, 21.42, 13.04; HRMS: calc. for $C_{13}H_{16}S$ (M^+) 204.0973, found 204.0988.

1-(1-Phenylthio-2-oxoethyl)[3.1.0]hexane (35). The procedure was the same as that for **33** except that **13** (235 mg, 0.750 mmol) instead of **11** was added to LDBB . Flash chromatography (1% AcOEt / hex) gave recovered DBB and 125 mg (71%) the titled product as a pale yellow oil. Based on the ^{1}H NMR spectrum, the two diastereomers were formed in the ratio of about 40:60. ^{1}H NMR ($CDCl_3$): δ 9.44 (m, 1H), 7.39-7.26 (m, 5H), 3.54 (d, J = 5.1 Hz, 0.4H), 3.50 (d, J = 5.2 Hz, 0.6H), 1.91-1.19 (m, 6H), 0.95-0.83 (m, 2H), 0.68-0.59 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 195.62, 195.26, 133.05, 132.99, 132.05, 131.78, 129.11, 127.65, 127.58, 63.44, 62.24, 29.87, 28.92, 27.60, 27.50, 27.24, 27.01, 23.36, 22.68, 20.96, 20.77, 12.26, 11.39; IR (neat, NaCl): 2920.6 (m), 2849.2 (m), 1709.1 (s), 1469.9 (m), 1429.4 (m), 1062.9 (m), 1020.5 (m), 736.9 (m), 686.7 (m); HRMS: calc. for $C_{14}H_{16}OS$ (M^+) 232.0922, found 232.0925.

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