Introduction of the 2-(Phenylthio)ethyl, 2-(Phenylsulfinyl)ethyl, and 2,2-Bis(phenylthio)ethyl Substituents into Cyclic Ketones

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Introduction

Although a variety of methods exist for introducing a terminally oxygenated two-carbon side chain α to a ketone, the related installation of a two-carbon side chain bearing sulfur functionality is difficult. During the course of our investigations of pinacol-terminated cationic cyclizations,[2] we required this latter transformation in order to form cyclization initiators such as **1** from the corresponding cyclic ketone (Figure 1). The keto phenyl sulfoxides **2**, keto phenyl sulfides **3**, and keto diphenyl thioacetals **4** are obvious progenitors of the α-thiocarbenium ions **1**. Only a few routes to ketones of this type have been reported. The reaction of episulfonium ions with enoxysilanes and silyl ketene acetals to produce ketones and esters containing a substituted 2-(phenylthio)ethyl substituent has been disclosed,[3] yet the unsubstituted ethylene-derived episulfonium ion was reported to be particularly unreactive.[4] The alkylation of various enolates with vinyl sulfoxides to produce keto sulfoxides analogous to **2** has also been described.[5] However, a recent report by Haynes[6] suggests that overalkylation and cyclobutanol formation limit the generality of this approach to 2-sulfinylethyl ketones.

In an effort to develop reliable routes to thionium ion precursors for Prins-pinacol cyclizations, we reinvestigated the conversion of cyclic ketones to derivatives **2-4**. The results of this study, which led to practical methods to prepare these potentially valuable intermediates, are described.

Results and Discussion

Introduction of the 2-(Phenylsulfinyl)ethyl and 2-(Phenylthio)ethyl Side Chains. The addition of phenyl vinyl sulfoxide to the lithium enolates of cyclic ketones at −78 °C, followed by gradual warming to room temperature, afforded mixtures of the desired (phenylsulfinyl)ethyl-substituted ketones **2** and variable amounts of the corresponding bicyclic alcohol. Although only trace amounts of the cyclobutanol product were typically produced, substantial amounts of **5** were seen in the reactions of the monoethylene ketal of 1,4-cyclohexanedione (eq 1).

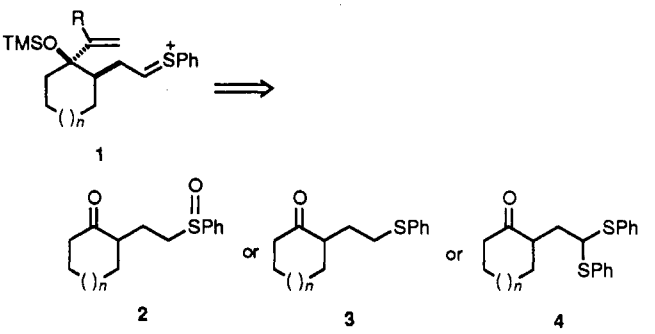
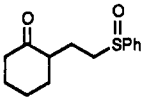
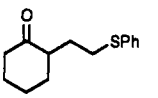
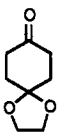
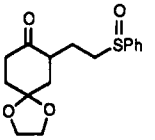
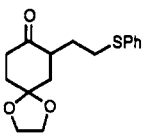
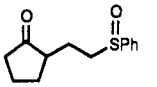
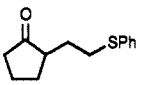
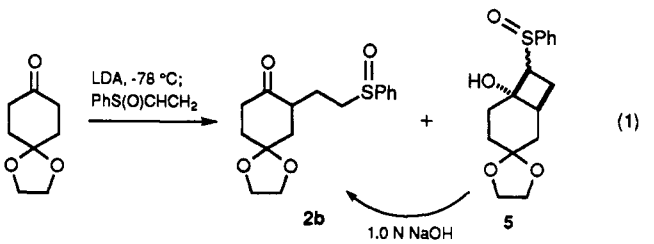


Figure 1.

Table I. Introduction of the 2-(Phenylsulfinyl)ethyl and 2-(Phenylthio)ethyl Substituents

ketone	product (yield)	
	 **2a** (86%)	 **3a** (95%)
	 **2b** (93%)	 **3b** (95%)
	 **2c** (63%)	 **3c** (93%)



(1)

Alcohol **5**, however, was converted in excellent yield to the (phenylsulfinyl)ethyl-substituted ketone **2b** upon treatment with dilute base. Thus, allowing the reactions of phenyl vinyl sulfoxide with lithium enolates to warm to room temperature followed by the addition of 1.0 N NaOH provided optimized yields of the sulfinyl ketones **2a-c** with virtually none of the bicyclic alcohol being detectable (Table I).

Phenyl sulfoxides have been converted to diphenyl thioacetals by the Pummerer reaction,[7] but our efforts to transform **2a** to the corresponding dithioacetal were unsuccessful. Treatment of **2a** with trifluoroacetic anhydride (TFAA) in dichloromethane at 0 °C for 30 min, followed by the addition of thiophenol, surprisingly

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(2) For related reactions of oxocarbenium ions, see: Hirst, G. C.; Howard, P. N.; Overman, L. E. *J. Am. Chem. Soc.* **1989**, *111*, 1514.

(3) (a) Patel, S. K.; Paterson, I. *Tetrahedron Lett.* **1983**, *24*, 1315. (b) Ibragimov, M. A.; Smit, W. A. *Tetrahedron Lett.* **1983**, *24*, 961. (c) Toshimitsu, A.; Hirosawa, C.; Tanimoto, S. *Chem. Lett.* **1992**, 239.

(4) We have also observed that basic lithium enolates could not be directly alkylated with β-bromo sulfides; elimination of HBr to afford vinylsulfides occurs instead.

(5) (a) Seki, K.; Ohnuma, T.; Oishi, T.; Ban, Y. *Tetrahedron Lett.* **1975**, 723. (b) Brown, P. J.; Jones, D. N.; Khan, M. A.; Meanwell, N. A. *Tetrahedron Lett.* **1983**, *24*, 405. The conjugate addition of the anions of malonates and β-keto esters to vinyl sulfoxides is more common. For example, see: (c) Tsuchihashi, G.; Mitamura, S.; Inoue, S.; Ogura, K. *Tetrahedron Lett.* **1973**, 323. (d) Koppel, G. A.; Kinnick, M. D. *J. Chem. Soc., Chem. Commun.* **1975**, 473.

(6) Haynes, R. K.; Loughlin, W. A.; Hambley, T. W. *J. Org. Chem.* **1991**, 5785.

(7) Tanikaga, R.; Hiraki, Y.; Ono, N.; Kaji, A. *J. Chem. Soc., Chem. Commun.* **1980**, 41.

0022-3263/93/1958-6476$04.00/0

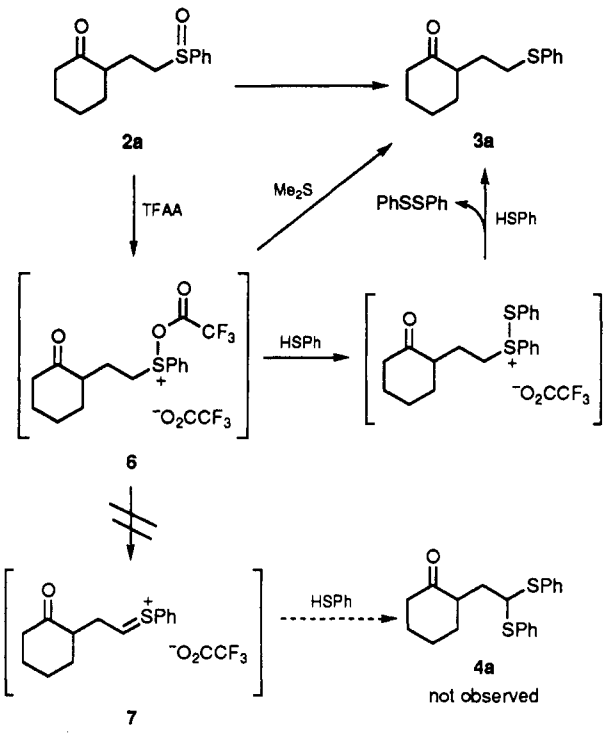


Figure 2.

afforded sulfide **3a** and diphenyl disulfide in modest yield, with no trace of **4a** being produced (Figure 2).

Adducts **6** are likely involved in the conversion of keto sulfoxide **2a** to keto sulfide **3a** as outlined in Figure 2.[8] Stabilization of **6** by coordination of the carbonyl oxygen to the electron-deficient sulfur may be responsible for the failure of **6** to decompose to thionium ion **7**. The deoxygenation of **2a** could be optimized by adding dimethyl sulfide,[8] which produced sulfide **3a** in nearly quantitative yield. This high-yielding two-step sequence of enolate alkylation with phenyl vinyl sulfoxide followed by sulfoxide reduction provides a practical method for the introduction of a (phenylthio)ethyl group α to a ketone (Table I).

Introduction of a 2,2-Bis(phenylthio)ethyl Side Chain. Since a two-carbon side chain containing a dithioacetal group could not be developed from a sulfoxide precursor, we examined formation of this unit from an α allylated ketone, intermediates that are readily available from cyclic ketones by enolate alkylation or Claisen rearrangement.[9] Indeed, when 2-allylcyclohexanone (**8a**) was treated sequentially at −78 °C in dichloromethane with ozone and triphenylphosphine, followed by warming to 0 °C and *in situ* treatment of the resulting aldehyde with thiophenol and $MgBr_2{\cdot}Et_2O$, dithioacetal **4a** was formed in 70% yield. It is necessary to apply vacuum (~10–15 mm) for a few minutes to the reaction flask prior to the addition of thiophenol and $MgBr_2{\cdot}Et_2O$ to prevent the formation of side products that incorporate formaldehyde.

Results of applying this one pot sequence to three representative allylated ketones are summarized in Table II. The dithioacetalization is notably selective, even for the aldehyde intermediate derived from ketone **8b** which

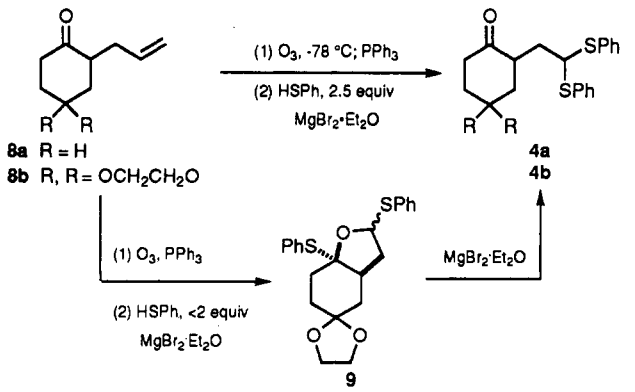
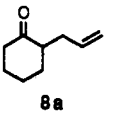
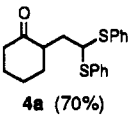
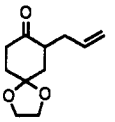
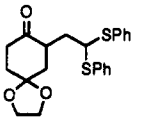
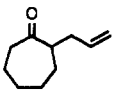
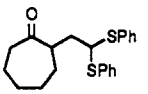


Figure 3.

Table II. Introduction of the 2,2-Bis(phenylthio)ethyl Substituent

ketone	product (yield)
 **8a**	 **4a** (70%)
 **8b**	 **4b** (77%)
 **8c**	 **4c** (60%)

contains three potentially reactive functionalities. This result is somewhat surprising given that $MgBr_2{\cdot}Et_2O$ has been described as a highly selective reagent for the conversion of ketals into dithioketals in the presence of ketones.[10] The high chemoselectivity in the formation of **4b** appears to be the result of thermodynamic control.

When $MgBr_2{\cdot}Et_2O$ was employed as the limiting reagent in the acetalization of the aldehyde intermediate derived from **8b**, two separable diastereomers of the cyclic monothioacetal **9** were isolated along with dithioacetal **4b**. Treatment of both diastereomers of **9** with additional $MgBr_2{\cdot}Et_2O$ resulted in the exclusive formation of **4b**. When 2.5 equiv of $MgBr_2{\cdot}Et_2O$ were employed in the initial thioacetalization only trace quantities of **9** were observed and a 77% yield of **4b** was realized (Table II).

Conclusion

Lithium enolates of cyclic ketones can be alkylated with phenylvinyl sulfoxide in good yield to afford ketones containing the 2-(phenylsulfinyl)ethyl substituent. These keto sulfoxides are converted to the corresponding sulfides in high yield by reaction with TFAA/dimethyl sulfide. This two-step sequence provides a practical method for introducing at the α position of cyclic ketones a 2-thioethyl group. A convenient one pot procedure for converting α-allyl ketones to 2,2-bis(phenylthio)ethyl-substituted ketones was also developed. Although this study focused exclusively on cyclic ketones, the procedures developed should also be useful for functionalization of acyclic ketones.

(8) (a) Tanikaga, R.; Nakayama, K.; Tanaka, K.; Kaji, A. *Chem. Lett.* **1977**, 395. (b) Tanikaga, R.; Tanaka, K.; Kaji, A. *J. Chem. Soc., Chem. Commun.* **1978**, 865.

(9) (a) Stork, G.; Brizzolara, H.; Landesman, H.; Szmuszkovicz, J.; Terrell, R. *J. Am. Chem. Soc.* **1963**, *85*, 207. (b) Lorette, N. B.; Howard, W. L. *J. Org. Chem.* **1961**, *26*, 3112.

(10) Park, J. H.; Kim, S. *Chem. Lett.* **1989**, 629.

Experimental Procedures

General Procedure for the Alkylation of Ketones with Phenyl Vinyl Sulfoxide. To a 1.0 M THF solution of diisopropylamine (1.05 equiv) cooled to −78 °C under N_2 was added *n*-butyllithium (1.0 equiv, 2.5 M in hexane) dropwise by syringe. The resulting colorless solution was stirred for 30 min at −78 °C. A 0.35 M THF solution of the ketone (1.0 equiv) then was added dropwise by cannula to the LDA solution at −78 °C, and the cooling bath was removed. Stirring was continued for 1 h to give a cream-colored solution. This solution then was cooled to −78 °C, a 1.0 M THF solution of phenyl vinyl sulfoxide (1.05 equiv) was added dropwise by cannula, and the reaction was allowed to warm to 25 °C over 5 h to give a light yellow solution. Aqueous NaOH (1.0 N, same volume as the reaction) was added, and the resulting mixture was stirred at 25 °C for 1 h. This mixture was extracted with ethyl acetate, dried (Na_2SO_4), filtered, and concentrated and the residue chromatographed on silica gel to afford the keto sulfoxide product.

2-[2-(Phenylsulfinyl)ethyl]cyclohexanone (2a). Following this general procedure, cyclohexanone (1.03 g, 10.5 mmol), diisopropylamine (1.11 g, 11.0 mmol), *n*-butyllithium (4.13 mL, 10.5 mmol of a 2.54 M solution), and phenyl vinyl sulfoxide (1.67 g, 11.0 mmol) were employed to produce, after purification on silica gel (1:3 hexane–EtOAc), 2.26 g (86%) of a crystalline, inseparable mixture of the two diastereomers of ketone **2a**, which was homogeneous by TLC analysis: mp 83–84 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.4–7.7 (m, 5H), 2.98 (ddd, J = 5.5, 10.7, 13.0 Hz), 2.89 (m), 2.72 (ddd, J = 5.2, 10.5, 13.0 Hz, 2H), 1.3–2.55 (m, 11 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.0, 211.9, 143.8, 143.2, 130.74, 130.67, 129.0, 123.83, 123.75, 55.0, 54.1, 49.6, 49.1, 42.0, 34.3, 34.2, 27.79, 27.75, 24.90, 24.85, 22.9, 21.8; IR (film) 2934, 2881, 1702, 1478, 1445, 1042 cm^{-1}; MS (CI) m/e calcd for $C_{14}H_{19}O_2S$ 251.1107, found: 251.1092 (MH^+). Anal. Calcd for $C_{14}H_{18}O_2S$: C, 67.17; H, 7.25. Found: C, 67.20; H, 7.26. This reaction was also carried out on a 60 mmol scale in 77% yield.

2-[2-(Phenylsulfinyl)ethyl]-1,4-cyclohexanedione Monoethylene ketal (2b). Following the general procedure, 1,4-cyclohexanedione *mono*ethylene ketal (780 mg, 5.0 mmol), diisopropylamine (530 mg, 5.25 mmol), *n*-butyllithium (1.92 mL, 5.0 mmol of a 2.60 M solution), and phenyl vinyl sulfoxide (798 mg, 5.25 mmol) were employed to produce, after purification on silica gel (EtOAc), 1.44 g (93%) of an inseparable mixture of the two diastereomers of ketone **2b** as a colorless oil, which was homogeneous by TLC analysis: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.4–7.7 (m, 5H), 4.00 (m, 4H), 2.98 (ddd, J = 5.2, 11.1, 13.0 Hz), 2.80–2.95 (m, 2H), 2.55–2.75 (m, 2H), 2.35 (app quintet, J = 2.6 Hz), 2.32 (app quintet, J = 2.65 Hz), 1.6–2.2 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.3, 210.2, 143.9, 143.5, 130.8, 130.7, 129.0, 123.9, 123.8, 106.9, 64.6, 64.5, 54.8, 54.2, 45.5, 45.0, 40.8, 40.7, 38.03, 37.97, 34.5, 22.4, 21.5; IR (film) 2958, 2887, 1716, 1478, 1444; MS (CI) m/e calcd for $C_{16}H_{21}O_4S$ 309.1161, found 309.1136 (MH^+).

2-[2-(Phenylsulfinyl)ethyl]cyclopentanone (2c). Following the general procedure, cyclopentanone (420 mg, 5.0 mmol), diisopropylamine (530 mg, 5.25 mmol), *n*-butyllithium (1.92 mL, 5.0 mmol of a 2.60 M solution), and phenyl vinyl sulfoxide (800 mg, 5.25 mmol) were employed to produce, after purification on silica gel (EtOAc), 738 mg (63%) of an inseparable mixture of the two diastereomers of ketone **2c** as a colorless oil, which was homogeneous by TLC analysis: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.4–7.7 (m, 5H), 2.85 (m), 2.77 (ddd, J = 4.9, 10.5, 13.1 Hz, 2H), 1.4–2.3 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 219.8, 219.6, 143.5, 143.3, 130.9, 130.8, 129.1, 123.9, 54.8, 54.4, 47.7, 47.4, 37.8, 37.7, 29.6, 29.5, 22.5, 21.9, 20.4; IR (film) 2961, 2875, 1736, 1478, 1444, 1405 cm^{-1}; MS (EI) m/e calcd for $C_{13}H_{16}O_2S$ 236.0871, found 236.0870 (M^+).

General Procedure for the Reduction of Keto Sulfoxides to Keto Sulfides. A solution of the keto sulfoxide (1.0 equiv) and dimethyl sulfide (1.5 equiv) in CH_2Cl_2 (0.5 M in keto sulfoxide) was cooled to 0 °C, and trifluoroacetic anhydride (1.2 equiv) was added by syringe. The resulting light peach-colored solution was stirred at 0 °C for 1 h and then was quenched with aqueous $NaHCO_3$ (4× the reaction volume). This mixture was extracted with ethyl acetate, dried (Na_2SO_4), filtered, and concentrated and the residue chromatographed on silica gel to afford the keto sulfide product.

2-[2-(Phenylthio)ethyl]cyclohexanone (3a). Following the general procedure, keto sulfoxide **2a** (500 mg, 2.0 mmol), dimethyl sulfide (186 mg, 3.0 mmol), and trifluoroacetic anhydride (504 mg, 2.4 mmol) were employed to produce, after purification on silica gel (9:1 hexane–EtOAc), 443 mg (95%) of sulfide **3a** as a colorless oil, which was homogeneous by TLC analysis: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.1–7.4 (m, 5H), 2.9–3.1 (m, 2H), 1.3–2.6 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.5, 136.4, 128.8, 125.6, 49.2, 42.1, 34.1, 31.1, 29.1, 27.9, 25.1; IR (film) 3058, 2934, 2860, 1708, 1584, 1481, 1448, 1439 cm^{-1}; MS (EI) m/e calcd for $C_{14}H_{18}OS$ 234.1078, found 234.1069 (M^+). Anal. Calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74. Found: C, 71.85; H, 7.75.

2-[2-(Phenylthio)ethyl]-1,4-cyclohexanedione Monoethylene Ketal (3b). Following the general procedure, keto sulfoxide **2b** (200 mg, 0.65 mmol), dimethyl sulfide (60 mg, 0.98 mmol), and trifluoroacetic anhydride (164 mg, 0.78 mmol) were employed to produce, after purification on silica gel (2:1 hexane–EtOAc), 180 mg (95%) of sulfide **3b** as a colorless oil, which was homogeneous by TLC analysis: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.1–7.4 (m, 5H), 3.99 (m, 4H), 2.8–3.05 (m, 3H), 2.64 (dt, J = 6.2, 14.0 Hz, 1H), 2.34 (ddd, J = 3.0, 5.0, 14.2 Hz, 1H), 1.86–2.20 (m, 4H), 1.71 (t, J = 13.1 Hz, 1H), 1.48 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.8, 136.1, 128.7, 125.6, 107.0, 64.6, 64.4, 44.9, 40.5, 38.1, 34.5, 30.7, 28.7; IR (film) 2957, 2835, 1712, 1584, 1481, 1440 cm^{-1}; MS (EI) m/e calcd for $C_{16}H_{20}O_3S$ 292.1133, found: 292.1139 (M^+). Anal. Calcd for $C_{16}H_{20}O_3S$: C, 65.73; H, 6.89. Found: C, 65.74; H, 6.96.

2-[2-(Phenylthio)ethyl]cyclopentanone(3c). Following the general procedure, keto sulfoxide **2c** (138 mg, 0.58 mmol), dimethyl sulfide (60 mg, 0.98 mmol), and trifluoroacetic anhydride (164 mg, 0.78 mmol) were employed to produce, after purification on silica gel (9:1 hexane–EtOAc), 120 mg (93%) of sulfide **3c** as a colorless oil, which was homogeneous by TLC analysis: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.1–7.4 (m, 5H), 2.9–3.1 (m, 2H), 1.95–2.35 (m, 6H), 1.7–1.85 (m, 1H), 1.4–1.65 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 220.4, 136.0, 129.0, 128.8, 125.8, 47.9, 37.8, 31.6, 29.4, 29.1, 20.5; IR (film) 1735, 1584, 1481, 1438 cm^{-1}; MS (EI) m/e calcd for $C_{13}H_{16}OS$ 220.0922, found 220.0925 (M^+). Anal. Calcd for $C_{13}H_{16}OS$: C, 70.87; H, 7.32. Found: C, 70.61; H, 7.33.

General Procedure for the Ozonolysis/Dithioacetalization of Allylated Ketones. A solution of the allylated ketone[9] (1.0 equiv) in dichloromethane (0.2 M) was cooled to −78 °C, and O_3 was bubbled through until a blue color appeared. While the temperature was maintained at −78 °C, N_2 was bubbled through this solution for 0.5 h to give a colorless solution. Under a steady stream of argon, Ph_3P (1.5 equiv) was added, the resulting solution was placed in an ice bath, and N_2 was bubbled through the solution with stirring for 0.5 h. The gas inlet then was replaced with a glass stopper, and vacuum (~10–15 mm) was applied to the reaction for 5 min at 0 °C to remove formaldehyde. The vacuum then was bled with Ar, and thiophenol (2.2 equiv) and $MgBr_2{\cdot}Et_2O$[11] (2.5 equiv of a 2.0 M Et_2O solution) were injected by syringe. The ice bath then was removed, stirring was continued for 15–20 h, and the reaction was quenched with $NaHCO_3$ (5× the reaction volume). The mixture then was extracted with ethyl acetate, dried (Na_2SO_4), filtered, and concentrated and the residue chromatographed on silica gel to afford the dithioacetal product.

2-[2,2-Bis(phenylthio)ethyl]cyclohexanone (4a). Following the general procedure, 2-(2-propenyl)cyclohexanone (500 mg, 3.6 mmol), Ph_3P (1.42 g, 5.4 mmol), thiophenol (876 mg, 8.0 mmol), and $MgBr_2{\cdot}Et_2O$ (3.1 mL of a 2.6 M solution, 8.0 mmol) were used to produce, after purification on silica gel (9:1 hexane–EtOAc), 872 mg (70%) of dithioacetal **4a** as an oil, which solidified on standing and was homogeneous by TLC analysis: mp 61–63 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.1–7.6 (m, 10 H), 4.67 (dd, J = 5.9, 9.2 Hz, 1H), 2.8–2.9 (m, 1H), 1.2–2.5 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.3, 134.2, 133.6, 132.5, 132.0, 128.8, 127.6, 127.3, 55.4, 48.0, 42.1, 36.3, 34.4, 27.9, 25.1; IR (film) 3073, 3058, 2934, 1707, 1583, 1481, 1447, 1439 cm^{-1}; MS (CI) m/e calcd for $C_{20}H_{22}OS_2$ 342.1114, found 342.1121 (M^+). Anal. Calcd for

(11) Freshly prepared from magnesium turnings and 1,2-dibromoethane.

$C_{20}H_{22}OS_2$: C, 70.13; H, 6.47. Found: C, 70.17; H, 6.48. This reaction was also carried out on 50 mmol scale in 61% yield.

2-[2,2-Bis(phenylthio)ethyl]cyclohexanone 4-(Ethylene Ketal) (4b). Following the general procedure, 2-(2-propenyl)-cyclohexanedione 4-(ethylene ketal) (250 mg, 1.3 mmol), Ph_3P (501 mg, 1.9 mmol), thiophenol (310 mg, 2.8 mmol), and $MgBr_2 \cdot Et_2O$ (1.6 mL of a 2.0 M solution, 3.2 mmol) were used to produce, after purification on silica gel (4:1 hexane–EtOAc), 395 mg (77%) of dithioacetal **4b** as a colorless oil, which was homogeneous by TLC analysis: ^1H NMR (300 MHz, $CDCl_3$) δ 7.4–7.55 (m, 4H), 7.2–7.35 (m, 6H), 4.63 (dd, J = 6.2, 9.1 Hz, 1H), 3.99 (m, 4H), 3.26 (m, 1H), 2.64 (dt, J = 6.3, 14.0 Hz, 1H), 2.43 (tt, J = 6.3, 7.9 Hz, 1H), 2.31 (ddd, J = 2.7, 4.8, 14.1 Hz, 1H), 1.85–2.05 (m, 3H), 1.65 (t, J = 13.1 Hz, 1H), 1.50 (ddd, J = 4.8, 9.2, 14.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.8, 134.1, 133.4, 132.9, 132.2, 128.8, 127.8, 127.4, 107.0, 64.7, 64.6, 55.6, 43.9, 40.8, 38.2, 35.8, 34.6; IR (film) 2955, 2886, 1713, 1583, 1480, 1475, 1438 cm^{-1}; MS (CI) m/e calcd for $C_{22}H_{25}O_3S_2$ 401.1245, found : 401.1226 ($M + H^+$). Anal. Calcd for $C_{22}H_{24}O_3S_2$: C, 65.97; H, 6.04. Found: C, 66.01; H, 6.06.

2-[2,2-Bis(phenylthio)ethyl]cycloheptanone (4c). Following the general procedure, 2-(2-propenyl)cycloheptanone (760 mg, 5.0 mmol), Ph_3P (1.97 g, 7.5 mmol), thiophenol (1.15 g, 10.5 mmol), and $MgBr_2 \cdot Et_2O$ (6.25 mL of a 2.0 M solution, 12.5 mmol) were used to produce, after purification on silica gel (9:1 hexane–EtOAc), 1.06 g (60%) of dithioacetal **4c** as a colorless oil, which was homogeneous by TLC analysis: ^1H NMR (300 MHz, $CDCl_3$) δ 7.4–7.5 (m, 4H), 7.2–7.35 (m, 6H), 4.49 (dd, J = 5, 6, 9.5 Hz, 1H), 3.11 (m, 1H), 2.34–2.45 (m, 3H), 1.55–1.90 (m, 6H), 1.38–1.51 (m, 1H), 1.15–1.32 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.0, 134.2, 133.8, 132.6, 132.3, 128.9, 127.7, 127.5, 55.9, 49.0, 43.2, 38.6, 31.9, 28.8, 23.7; IR (film) 3058, 2929, 2854, 1701, 1583, 1480, 1454, 1439 cm^{-1}; MS (EI) m/e calcd for $C_{21}H_{24}OS_2$ 356.1269, found 356.1282 (M^+). Anal. Calcd for $C_{21}H_{24}OS_2$: C, 70.74; H, 6.78. Found: C, 70.84; H, 6.78.

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Supplementary Material Available: ^1H and ^{13}C NMR spectra of **2b** and **2c** (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.