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Chemistry of *O*-Silylated Ketene Acetals: Preparation of α-Siloxy Phenyl Sulfides and Methyl 3-(Phenylthio)butyrates from Alkyl Phenyl Sulfoxides

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Treatment of alkyl phenyl sulfoxides (**2a—h**) with *O*-methyl-*O*-*tert*-butyldimethylsilyl ketene acetal (**1a**) in dry acetonitrile in the presence of a catalytic amount of zinc iodide caused a Pummerer-type rearrangement to give α-siloxy phenyl sulfides (**3a—h**) under mild conditions. On the other hand, treatment of the sulfoxide (**2d**) with *O*-methyl-*O*-trimethylsilyl ketene acetals (**1b, c**) under similar conditions gave carbon–carbon bond-formed products, methyl 3-(phenylthio)-butyrates (**8** and **9**).

Keywords——*O*-methyl-*O*-*tert*-butyldimethylsilyl ketene acetal; alkyl phenyl sulfoxide; Pummerer rearrangement; α-siloxy phenyl sulfide; *O*-methyl-*O*-trimethylsilyl ketene acetal; carbon–carbon bond forming reaction; methyl 3-(phenylthio)butyrate; α-siloxy sulfide reaction

In a recent communication,[1] we briefly reported a novel silicon induced Pummerer-type rearrangement of sulfoxides using *O*-methyl-*O*-*tert*-butyldimethylsilyl ketene acetal, which gives α-siloxy sulfides under mild conditions. We present here a full account of this work and additional studies on the reaction of sulfoxides with *O*-methyl-*O*-trimethylsilyl ketene acetals leading to carbon–carbon bond-formed products.

Pummerer-Type Rearrangement of Alkyl Phenyl Sulfoxides (2a—h)

The Pummerer rearrangement of sulfoxides is widely recognized as an important reaction because it provides a means for the facile synthesis of α-substituted sulfides.[2] Although intramolecular silicon induced Pummerer rearrangements (so-called Sila–Pummerer or Silyl Pummerer rearrangement) have been reported[3] recently by the thermal treatment of α-trimethylsilyl sulfoxides, leading to α-siloxy sulfides, no successful silicon induced Pummerer rearrangement of normal sulfoxides having no α-silyl group has been reported. For example, some silylating agents react with sulfoxides to give the elimination products predominantly instead of the rearrangement products, α-siloxy sulfides: the use of iodotrimethylsilane/diisopropylethyl amine[4] or chlorotrimethylsilane in the absence of added base[5] gives α,β-unsaturated sulfides. We have found a new methodology leading to α-siloxy sulfides (**3a—h**) from normal sulfoxides having no α-silyl group by using an effective silylating agent, *O*-methyl-*O*-*tert*-butyldimethylsilyl ketene acetal (**1a**).[6]

The starting sulfoxides (**2a—h**) were prepared by the reported methods[7-9] as outlined in Chart 1. A typical experimental procedure is as follows for the reaction of *O*-methyl-*O*-*tert*-butyldimethylsilyl ketene acetal (**1a**) with methyl phenyl sulfoxide (**2a**). A solution of **2a**, **1a**, and a catalytic amount of zinc iodide in dry acetonitrile was stirred at room temperature for 12 h to give *tert*-butyldimethylsiloxymethyl phenyl sulfide (**3a**). Similarly, other sulfoxides (**2b—h**) were reacted with **1a** to give the corresponding α-siloxy sulfides (**3b—h**). In the case of **2d** and **2h**, the elimination products, α,β-unsaturated sulfides (**4d, h**) were formed as by-

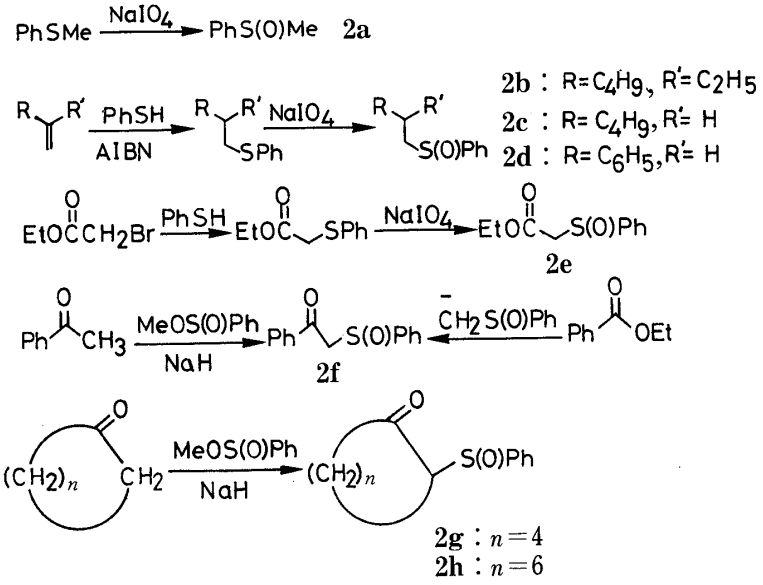

Chart 1

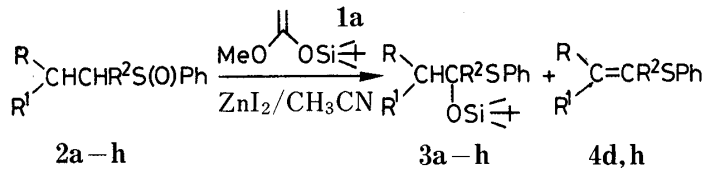

Chart 2

TABLE I. Pummerer Rearrangement of Sulfoxides (**2a—h**)

Sulfoxides	Reaction conditions	Products	Yield (%)
SOPh **2a**	2 eq **1a** r.t. 12 h	SPh **3a**	60
SOPh **2b**	1.5 eq **1a** r.t. 24 h	SPh **3b**	42
SOPh **2c**	2 eq **1a** r.t. 24 h	SPh **3c**	42
Ph SOPh **2d**	1.5 eq **1a** r.t. 20 h	Ph SPh **3d**	55
		Ph SPh **4d**[a]	16
EtOC SOPh **2e**	1.5 eq **1a** r.t. 12 h	EtOC SPh **3e**	42
	1.5 eq **1a** 70 °C 14 h[b]		79
PhC SOPh **2f**	1.2 eq **1a** r.t. 1 h →70 °C 14 h	Ph SPh **3f**	51
SOPh **2g**	1.5 eq **1a** r.t. 1 h →70 °C 14 h	SPh **3g**	75
SOPh **2h**	1.2 eq **1a** r.t. 1 h →70 °C 14 h	SPh **3h**	44
		SPh **4h**	48

a) A mixture of *Z* and *E*-isomers (*Z*/*E*=*ca.* 1/2) was obtained. *b*) The reaction was carried out in the absence of catalyst. r.t.: room temperature.

products. All these products (**3** and **4**) were purified by distillation or recrystallization and characterized by nuclear magnetic resonance (^{1}H-NMR), infrared (IR), exact mass, and analytical data. The reaction conditions and yields are summarized in Table I.

The reaction of alkyl and α-ethoxycarbonyl sulfoxides (**2a—e**) with **1a** presumably proceeds *via* the siloxysulfonium ylid intermediates (B) shown in Chart 3-i: initial silicon transfer from ketene silyl acetal (**1a**) to sulfoxides (**2a—e**) and subsequent abstraction of α-hydrogen by a generated ester enolate anion (A) would give B(↔B′), which then rearranges by the usual Pummerer pathway to give α-siloxy sulfides (**3a—e**) (route a) and, in some cases, α,β-unsaturated sulfide (**4d**) by elimination of *tert*-butyldimethylsilanol (route b). In the case of β-keto sulfoxides (**2f—h**), higher temperature was required for the completion of the reaction: only a trace of the Pummerer products was formed either at room temperature or 70 °C over a long reaction period, but the Pummerer products were the major products after stirring at room temperature for 1 h and then at 70 °C for 14 h. It seems likely that the α-siloxy sulfides (**3f—h**) are produced *via* the intermediacy of the *O*-silylated vinyl sulfoxides (C) (Chart 3-ii). This hypothesis was strongly supported by the isolation of the *O*-silylated vinyl sulfoxide (**5**) after the reaction of **2f** and **1a** at room temperature for 1 h.

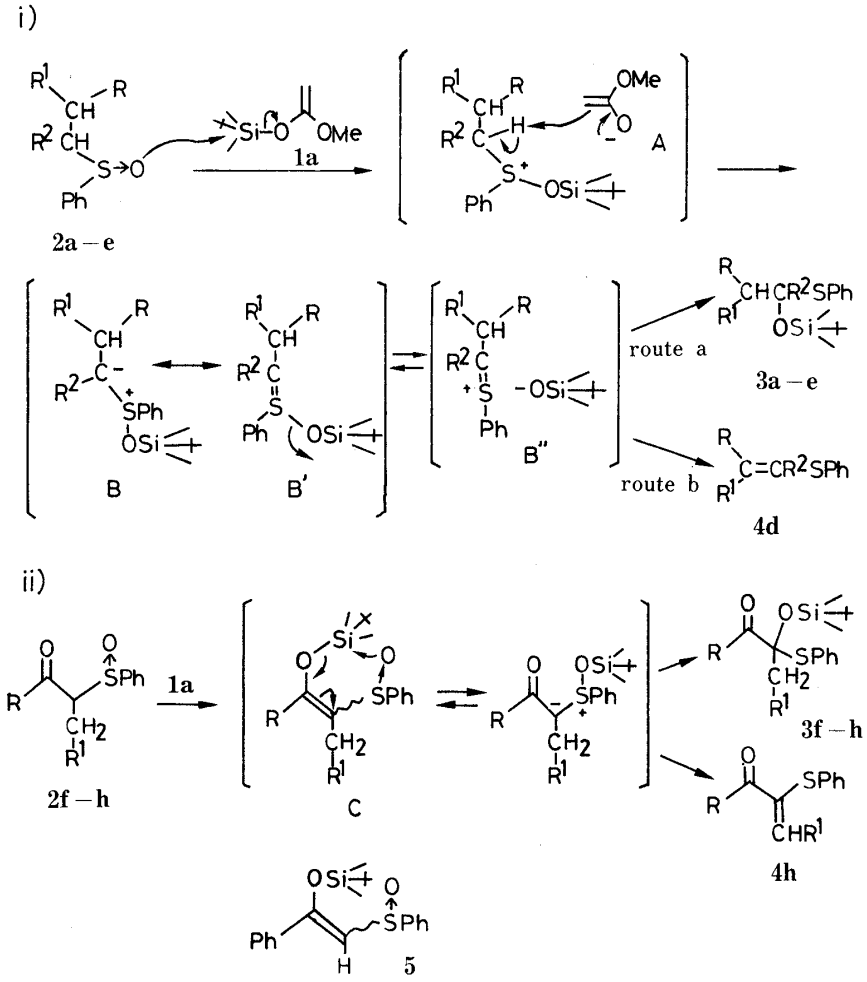

Chart 3

The importance of the α-siloxysulfides (or *O*-silyl hemi thioacetals[10]) is demonstrated by some useful transformations of 2-*tert*-butyldimethylsiloxy-2-(phenylthio)cyclohexanone (**3g**) into 1,2-cyclohexanedione (**6**) and 2-*tert*-butyldimethylsiloxycyclohexanone (**7**) as exemplified in Chart 4. Treatment of **3g** with tetra-*n*-butylammonium fluoride in tetrahydrofuran (THF) at room temperature for 30 min gave **6** in quantitative yield and treatment with Raney nickel

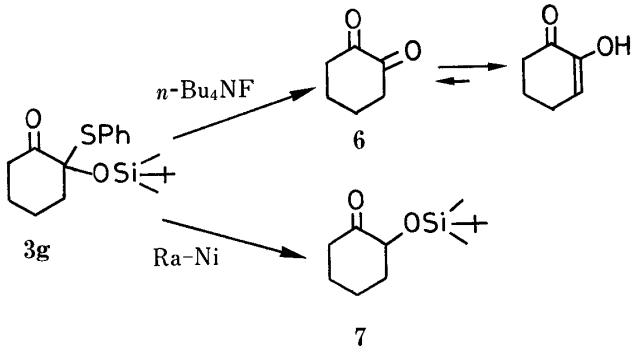

Chart 4

(W2) in ethanol at room temperature for 30 min gave the desulfurized product (**7**) in 61% yield.

Caron–Carbon Bond Forming Reaction of Phenethyl Phenyl Sulfoxide (2d)

When phenethyl phenyl sulfoxide (**2d**) was treated with trimethylsilyl ketene acetals (**1b, c**) instead of *tert*-butyldimethylsilyl ketene acetal (**1a**), somewhat surprisingly the carbon–carbon bond-formed products, methyl 3-(phenylthio)butyrates (**8** and **9**), were obtained in moderate yields. This contrasts with the result that the reaction of **2d** with **1a** gives the Pummerer-type product (**3d**), preferentially (Chart 5), but can reasonably be explained by

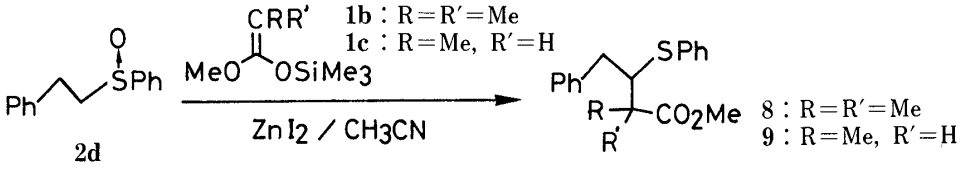

Chart 5

consideration of the common initial intermediate (B′′): the carbon–carbon bond forming reaction of **1b, c** leading to **8** or **9** is greatly facilitated by a strong silicon–oxygen affinity as compared with the carbon–oxygen affinity in the ordinary Pummerer-type reaction. In the case of **1a** having a bulky *tert*-butyl group on silicon, strong steric hindrance causes the siloxy anion to attack the carbon atom of the thionium intermediate (B′′) rather than the silicon atom of the starting reagent (**1a**), as shown in Chart 6.

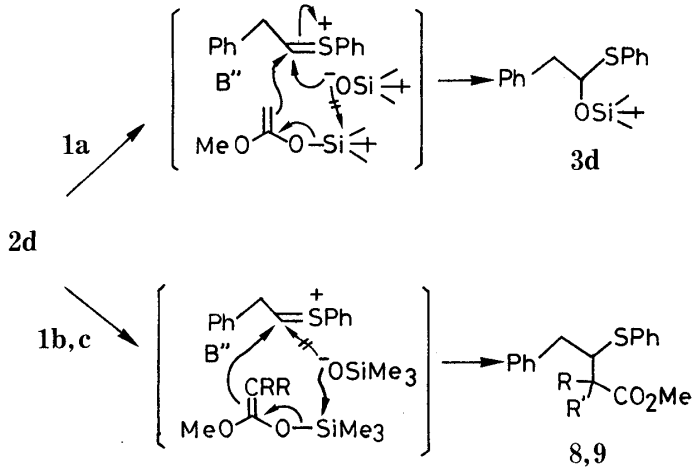

Chart 6

Experimental

All melting and boiling points are uncorrected. IR absorption spectra were recorded on a JASCO IRA-1 spectrometer, and ^{1}H-NMR spectra on a Hitachi R-22 (90 MHz), or a JEOL-JNM-FX 90 Q FT-NMR (90 MHz) spectrometer (with tetramethylsilane as an internal standard). Low- and high-resolution mass spectra (MS) were obtained with a JEOL JMS D-300 instrument, with a direct inlet system.

Alkyl Phenyl Sulfoxides (2a—h)——The sulfoxides (**2a—d**) were obtained from the corresponding sulfides by oxidation with sodium metaperiodate.[8] The β-keto sulfoxides (**2e—h**) were directly obtained[9] in high yields from the corresponding carbonyl compounds by treatment with an equivalent amount of methyl benzenesulfinate and sodium hydride in dry ether at room temperature.

General Procedure for the Preparation of α-Siloxy Phenyl Sulfides (3a—h) and α,β-Unsaturated Sulfides (4d, h)——The following procedure is typical. A solution of the ketene silyl acetal (**1a**, 2.4—4 mmol) in dry acetonitrile (2 ml) was added dropwise to a stirred solution of the sulfoxide (**2**, 2 mmol) and zinc iodide (0.15 mmol) in dry acetonitrile (3 ml) at room temperature under nitrogen. The mixture was stirred at the temperature and for the period indicated in Table I, then partitioned between ether (15 ml) and saturated aqueous $NaHCO_3$ (5 ml). The aqueous layer was extracted with ether (10 ml × 2). The combined extract was washed with saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. The sulfide was isolated by column chromatography on silica gel with *n*-hexane–benzene and purified by distillation under reduced pressure or by recrystallization to give the pure sulfide (**3**) and in some cases, the α,β-unsaturated sulfide (**4**).

***tert*-Butyldimethylsiloxymethyl Phenyl Sulfide (3a)**——This (304 mg) was prepared from **1a** (752 mg, 4 mmol) and methyl phenyl sulfoxide (**2a**, 280 mg, 2 mmol). Distillation under reduced pressure gave pure **3a**, bp 65—70 °C/0.16 mmHg (bath temp). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1065, 835. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 0.07 (s, 6H, Me_2Si), 0.89 (s, 9H, *tert*-BuSi), 5.06 (s, 2H, $PhSCH_2$), 7.0—7.6 (m, 5H, SPh). *Anal.* Calcd for $C_{13}H_{22}OSSi$: C, 61.36; H, 8.71; S, 12.60. Found: C, 61.29; H, 8.74; S, 12.68.

1-*tert*-Butyldimethylsiloxy-2-ethylhexyl Phenyl Sulfide (3b)——This (293 mg) was prepared from **1a** (564 mg, 3 mmol) and 2-ethylhexyl phenyl sulfoxide (**2b**, 484 mg, 2 mmol). Distillation under reduced pressure gave pure **3b**, bp 125—130 °C/0.17 mmHg (bath temp). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1065, 835. ^{1}H-NMR (10% solution in $CDCl_3$) δ: −0.12 (s, 3H, MeSi), −0.06 (s, 3H, MeSi), 0.86 (s, 9H, *tert*-BuSi), 1.1—1.9 (m, 15H, C_7H_{15}), 5.1—5.2 (br s, 1H, CHSPh), 7.1—7.6 (m, 5H, SPh). *Anal.* Calcd for $C_{20}H_{36}OSSi$: C, 68.12; H, 10.29; S, 9.09. Found: C, 67.91; H, 10.09; S, 9.33.

1-*tert*-Butyldimethylsiloxyhexyl Phenyl Sulfide (3c)——This (276 mg) was prepared from **1a** (752 mg, 4 mmol) and hexyl phenyl sulfoxide (**2c**, 420 mg, 2 mmol). Distillation under reduced pressure gave pure **3c**, bp 145—150 °C/0.3 mmHg (bath temp). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1075, 840. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 0.00 (s, 6H, Me_2Si), 0.86 (s, 9H, *tert*-BuSi), 1.1—1.9 (m, 11H, C_5H_{11}), 5.02 (t, 1H, J=5.3 Hz, CHSPh), 7.1—7.6 (m, 5H, SPh). *Anal.* Calcd for $C_{18}H_{32}OSSi$: C, 66.60; H, 9.94; S, 9.88. Found: 66.84; H, 10.14; S, 10.06.

1-*tert*-Butyldimethylsiloxy-2-phenylethyl Phenyl Sulfide (3d) and 2-Phenyl-1-(phenylthio)ethylene (4d)——The sulfoxide (**2d**, 461 mg, 2 mmol) was reacted with **1a** (565 mg, 3 mmol) in the presence of zinc iodide (48 mg, 0.15 mmol) under the conditions described for a typical procedure. The crude residue was chromatographed on silica gel. Elution with *n*-hexane: chloroform = 10 : 1 gave a mixture of stereoisomers of **4d** (Z/E = 1 : 2) in 16% yield (66 mg) and **3d** in 55% yield (371 mg). Distillation of these products under reduced pressure gave pure **3d** and **4d**. **3d**: bp 140—145 °C/0.08 mmHg (bath temp). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1090, 825. ^{1}H-NMR (10% solution in $CDCl_3$) δ: −0.24 (s, 3H, MeSi), −0.07 (s, 3H, MeSi), 0.78 (s, 9H, *tert*-BuSi), 3.01 (d, 1H, J=8 Hz, PhCH–), 3.03 (d, 1H, J=5.5 Hz, PhCH–), 5.13 (dd, 1H, J=8 and 5.5 Hz, CHSPh), 7.0—7.6 (m, 10H, Ph × 2). *Anal.* Calcd for $C_{20}H_{28}OSSi$: C, 69.71; H, 8.19; S, 9.30. Found: C, 69.96; H, 8.25; S, 9.21. **4d**: bp 140—145 °C/0.65 mmHg (bath temp) (lit.[11] 154 °C/0.8 mmHg). All spectral data were identical with those of an authentic sample. The ratio of *Z* and *E* isomers was determined by the reported method.[12]

Ethyl 2-*tert*-Butyldimethylsiloxy-2-(phenylthio)acetate (3e)——This (514 mg) was prepared from **1a** (565 mg, 3 mmol) and ethyl α-(phenylsulfinyl)acetate (**2e**, 424 mg, 2 mmol). Distillation under reduced pressure gave pure **3e**, bp 125—130 °C/0.07 mmHg (bath temp). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740, 840. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 0.05 (s, 6H, Me_2Si), 0.86 (s, 9H, *tert*-BuSi), 1.20 (t, 3H, J=7 Hz, $OCH_2\underline{CH}_3$), 4.10 (q, 2H, J=7 Hz, $OC\underline{H}_2CH_3$), 5.41 (s, 1H, CHSPh), 7.1—7.6 (m, 5H, SPh). *Anal.* Calcd for $C_{16}H_{26}O_3SSi$: C, 58.85; H, 8.03; S, 9.82. Found: C, 58.70; H, 8.04; S, 10.03.

2-*tert*-Butyldimethylsiloxy-2-(phenylthio)acetophenone (3f)——This (366 mg) was prepared from **1a** (453 mg, 2.4 mmol) and α-(phenylsulfinyl)acetophenone (**2f**, 488 mg, 2 mmol). Distillation under reduced pressure gave pure **3f**, bp 160—165 °C/0.14 mmHg (bath temp). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1680, 1105, 840. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 0.00 (s, 3H, MeSi). 0.07 (s, 3H, MeSi), 0.85 (s, 9H, *tert*-BuSi), 5.94 (s, 1H, CHSPh), 7.1—7.6 (m, 8H, ArH), 8.03 (dd, 2H, J=8 and 2 Hz, ArH). *Anal.* Calcd for $C_{20}H_{26}O_2SSi$: C, 66.99; H, 7.31; S, 8.94. Found: C, 66.91; H, 7.30; S, 9.19.

2-*tert*-Butyldimethylsiloxy-2-(phenylthio)cyclohexanone (3g)——This (505 mg) was prepared from **1a** (566 mg, 3 mmol) and α-(phenylsulfinyl)cyclohexanone (**2g**, 444 mg, 2 mmol). Recrystallization from methanol–water gave pure **3g**, mp 64.5—65 °C. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1715, 1120, 835. ^{1}H-NMR (10% solution in $CDCl_3$) δ: −0.11 (s, 3H, MeSi), −0.04 (s, 3H, MeSi), 0.86 (s, 9H, *tert*-BuSi), 1.5—2.8 [m, 8H, $-(CH_2)_4-$], 7.1—7.6 (m, 5H, SPh). *Anal.* Calcd

for $C_{18}H_{28}O_2SSi$: C, 64.24; H, 8.39; S, 9.53. Found: C, 64.44; H, 8.56; S, 9.59.

2-*tert*-Butyldimethylsiloxy-2-(phenylthio)cyclooctanone (3h) and 2-(Phenylthio)-2-cyclooctenone (4h)——The sulfoxide (**2h**, 501 mg, 2 mmol) was reacted with **1a** (452 mg, 2.4 mmol) in the presence of zinc iodide (36 mg, 0.12 mmol) under the conditions described for a typical procedure. The crude residue was chromatographed on silica gel. Elution with *n*-hexane : ethyl acetate = 20 : 1 gave **3h** in 44% yield (328 mg) and **4h** in 48% yield (221 mg). Recrystallization of the α-siloxy sulfide (**3h**) from methanol gave an analytical sample, mp 67—67.5 °C. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1700, 1155, 835. ^{1}H-NMR (10% solution in $CDCl_3$) δ: −0.33 (s, 3H, MeSi), 0.06 (s, 3H, MeSi), 0.90 (s, 9H, *tert*-BuSi), 1.2—2.5 [m, 12H, $-(CH_2)_6-$], 7.0—7.6 (m, 5H, SPh). *Anal.* Calcd for $C_{20}H_{32}O_2SSi$: C, 65.88; H, 8.85; S, 8.79. Found: C, 66.11; H, 9.09; S, 8.72. Distillation of the vinyl sulfide (**4h**) gave a pure sample, bp 110—115 °C/0.15 mmHg (bath temp) (lit.[13] 110 °C/0.3 mmHg). All spectral data were identical with those of an authentic sample.

***β*-*tert*-Butyldimethylsiloxystyryl Phenyl Sulfoxide (5)**——A solution of the ketene silyl acetal (**1a**, 96 mg, 0.51 mmol) in dry acetonitrile (1.5 ml) was added dropwise to a stirred solution of α-(phenylsulfinyl)acetophenone (**2f**, 117 mg, 0.48 mmol) and zinc iodide (8 mg, 0.025 mmol) in dry acetonitrile (2 ml) at room temperature under nitrogen. The mixture was stirred for 1 h under the same conditions and concentrated *in vacuo* to give a 3 : 2 mixture of stereoisomers of **5**. Spectroscopic data of the product were consistent with the proposed structure, but a sample for analysis could not be obtained because the product decomposed during distillation or column chromatography. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1590, 1560, 1080, 1020. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 0.04 (s, 1.8H, MeSi 3/5), 0.09 (s, 1.8H, MeSi 3/5), 0.13 (s, 1.2H, MeSi 2/5), 0.22 (s, 1.2H, MeSi 2/5), 0.88 (s, 5.4H, *tert*-BuSi 3/5), 1.02 (s, 3.6H, *tert*-BuSi 2/5), 5.87 (s, 0.4H, CH = 2/5), 6.04 (s, 0.6H, CH = 3/5), 7.1—8.2 (m, 10H, Ph × 2).

1,2-Cyclohexanedione (6)——A 1 M solution of tetra-*n*-butylammonium fluoride in THF (0.5 ml, 0.5 mmol) was added dropwise to a solution of 2-*tert*-butyldimethylsiloxy-2-(phenylthio)cyclohexanone (**3g**, 167 mg, 0.5 mmol) in dry THF (2 ml) at room temperature under nitrogen. The mixture was stirred at room temperature for 30 min and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel with hexane : ethyl acetate = 3 : 1 to give a quantitative yield (56 mg) of **6**, bp 100—110 °C/30 mmHg (bath temp), which was identical with an authentic sample obtained commercially.

2-*tert*-Butyldimethylsiloxycyclohexanone (7)——A solution of 2-*tert*-butyldimethylsiloxy-2-(phenylthio)-cyclohexanone (**3g**, 167 mg, 0.5 mmol) in ethanol (4 ml) was added to a suspension of Raney nickel (W2, 0.6 g) in ethanol (4 ml). The reaction mixture was stirred at room temperature for 30 min. After removal of the nickel by filtration, the filtrate was concentrated *in vacuo* to give a residue, which was subjected to column chromatography on silica gel with benzene to give **7**. Distillation under reduced pressure gave pure **7**, bp 100—110 °C/20 mmHg (bath temp) (lit.[14] bp 115 °C/16 mmHg). All spectral data were identical with those of an authentic sample.

Methyl 2,2-Dimethyl-4-phenyl-3-(phenylthio)butyrate (8)——The ketene silyl acetal (**1b**, 1.044 g, 6 mmol) was added dropwise to a solution of phenethyl phenyl sulfoxide (**2d**, 460 mg, 2 mmol) and zinc iodide (48 mg, 0.15 mmol) in dry acetonitrile (5 ml) at room temperature under nitrogen. The mixture was heated at 70 °C for 15 min and concentrated under reduced pressure. The residue was partitioned between water (10 ml) and ether (20 ml). The aqueous layer was extracted with ether (10 ml). The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with *n*-hexane : benzene = 2 : 1 to give a 55% yield (345 mg) of the butyrate (**8**) as an oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 1.33 (s, 6H, Me × 2), 2.55—3.15 (m, 2H, CH_2), 3.50 (s, 3H, OMe), 3.4—3.7 (m, 1H, −CHSPh), 6.7—7.25 (m, 10H, Ph × 2). Exact mass Calcd for $C_{19}H_{22}O_2S$: 314.1355. Found: 314.1332.

Methyl 2-Methyl-4-phenyl-3-(phenylthio)butyrate (9)——A 1 : 1 mixture of diastereoisomers of **9** was prepared from **2d** (460 mg, 2 mmol), zinc iodide (48 mg, 0.15 mmol), and the ketene silyl acetal (**1c**, 960 mg, 6 mmol) in dry acetonitrile (5 ml) in 56% yield (336 mg) by a method similar to that described for the preparation of **8**. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 1.31 (d, 3H, J = 7 Hz, CH−C$\underline{H}_3$), 2.5—3.2 (m, 3H, CH_2 and −C$\underline{H}$CH$_3$), 3.50 (s, 1.5H, OMe 1/2), 3.59 (s, 1.5H, OMe 1/2), 3.6—4.0 (m, 1H, CHS), 7.0—7.4 (m, 10H, Ph × 2). Exact mass Calcd for $C_{18}H_{20}O_2S$: 300.1168. Found: 300.1153.

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