[Methoxy(phenylthio)methyl]lithium and [Methoxy(phenylthio)(trimethylsilyl)methyl]lithium. Convenient Reagents for the Facile Conversion of Aldehydes, Ketones, and 3-Alkoxy Enones into Ketene *O,S*-Acetal Derivatives†

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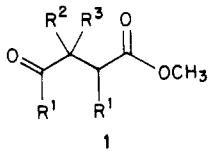
The title organometallics have been found to react in the 1,2-sense with a variety of carbonyl compounds to provide *O,S*-acetal and ketene *O,S*-acetal derivatives in high yield. The β,γ-unsaturated *O,S*-acetals obtained via the reaction of [methoxy(phenylthio)methyl]lithium with 3-alkoxy enones are readily convertible to structurally diverse γ-keto esters and their derivatives by way of an efficient alkylation–hydrolysis sequence.

In projected syntheses of the antineoplastic sesquiterpene quadrone (**2**)[1] and the Sceletium alkaloid mesembrine (**6**)[2] (Scheme I)[3] we required a concise and general procedure for the preparation of β-substituted-γ-keto esters of the type **1**. Intermediates such as **1** were predicted



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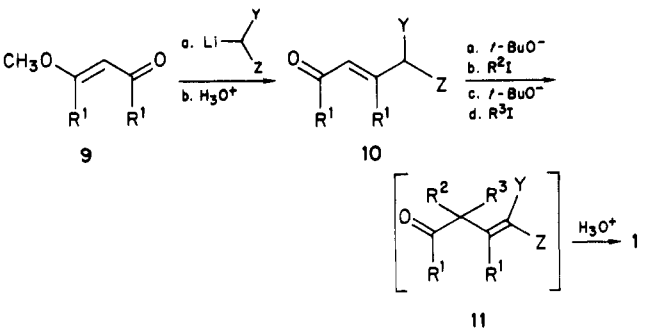
to be available by way of a three-step sequence involving the conversion of a β-alkoxy enone (e.g., **9**) to the intermediate **10** via exposure to an appropriate formyl anion equivalent.[4,5] Base-mediated alkylation of **10** followed by alcoholysis of the resultant ketene acetal derivative **11** was expected to give rise to the corresponding γ-keto ester **1**. Herein we report the full details of the preparative scope and synthetic limitations of the preceding method in addition to those of an operationally related procedure for the homologation of carbonyl compounds.[6]

Scheme I



Results

The initial phases of our studies were directed at the preparation of the dithioacetal **15a** and the investigation of its alkylation reactions. The dithioacetal **15a** was easily prepared (77% yield) by treatment of 3-ethoxycyclohex-2-en-1-one (**12**) with [bis(thiomethyl)methyl]lithium (**13**) (0 °C, 3.5 h) followed by aqueous acid.[4] The bisalkylation of the dithioacetal **15a** with reactive halides (e.g., methallyl iodide) utilizing potassium *tert*-butoxide or potassium hydride in THF proceeded with reasonable α-selectivity to provide the ketene dithioacetal **16a**.[7] Unfortunately, the tetrasubstituted dithioacetal moiety present in **16a** proved surprisingly resistant to hydrolysis. As a consequence, it was necessary to employ mercuric chloride in aqueous methanol at reflux to effect the cleavage of this structural subunit. In the synthesis intermediates we specifically desired to prepare there existed functional groups which were incompatible with these hydrolytic conditions. Accordingly, treatment of **16a** in this manner resulted in the isomerization and, to a lesser extent, hydration of the pendant alkene moieties. We reasoned that intermediates bearing the ketene *O,S*-acetal function would be much more susceptible to hydrolytic cleavage under a *number* of complementary reaction conditions.[8,9] Compounds of this variety were expected to be available via the selective α-alkylation of the corresponding enones (e.g., **15b**), which were predicted to be accessible from 3-alkoxy

† This manuscript is dedicated to the memory of Professor Robert V. Stevens.

(1) Ranieri, R. L.; Calton, G. J. *Tetrahedron Lett.* **1978**, 499.
(2) Jeffs, P. W.; Capps, T.; Johnson, D. B.; Karle, J. M.; Martin, N. H.; Rauckman, B. *J. Org. Chem.* **1974**, *39*, 2703.
(3) An account of the application of this methodology to the syntheses of these natural products will appear elsewhere.
(4) Quesada, M. L.; Schlessinger, R. H. *Synth. Commun.* **1976**, *6*, 555.
(5) Grosserode, R. S.; Tobin, P. S.; Wheeler, D. M. S. *Synth. Commun.* **1976**, *6*, 377.
(6) Hackett, S.; Livinghouse, T. *Tetrahedron Lett.* **1984**, *25*, 3539.
(7) Kende, A. S.; Constantinides, D.; Lee, S. J.; Liebeskind, L. *Tetrahedron Lett.* **1975**, 405.
(8) Hershfield, R.; Yeager, M. J.; Schmir, G. L. *J. Org. Chem.* **1975**, *40*, 2940.
(9) de Groot, Ae.; Jansen, B. J. M. *Tetrahedron Lett.* **1981**, 887.

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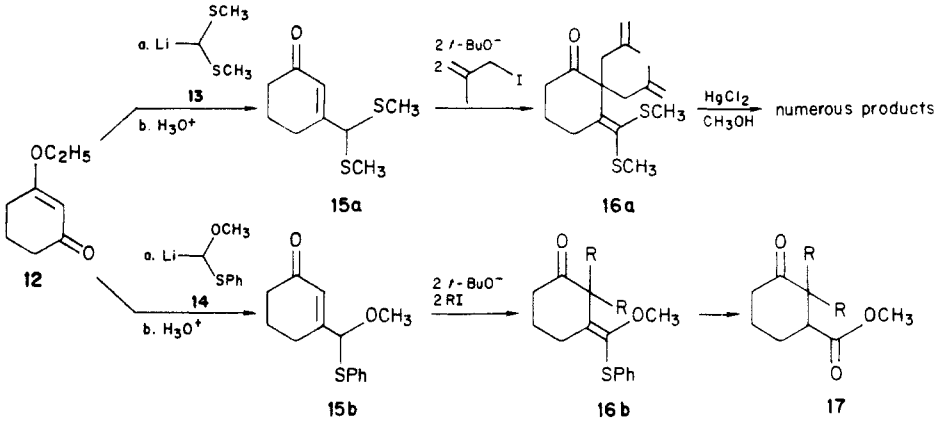
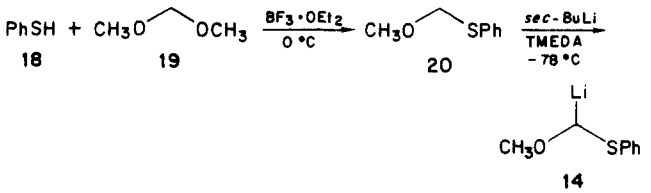
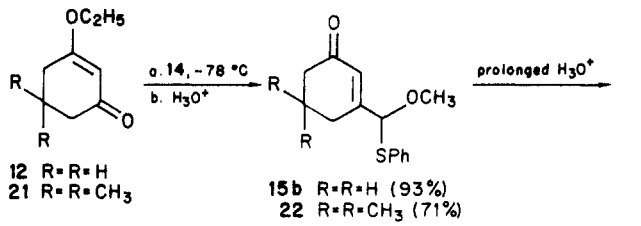


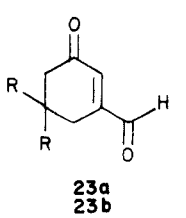
enones (e.g., **12**) and the organometallic **14**.

The reported synthetic procedure for methoxy(phenylthio)methane (**20**), the direct precursor to **14**, involves the treatment of chloromethyl methyl ether (a potent carcinogen) with thiophenoxide ion.[9,11] We have found that this useful *O,S*-acetal can be prepared economically on a multimole scale in 96% yield by the action of 1 equiv of boron trifluoride etherate on a solution of thiophenol (**18**) in dimethoxymethane (**19**) maintained at 0 °C.

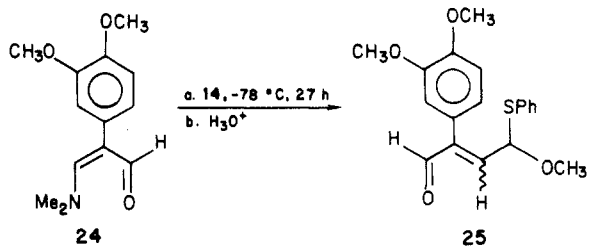


Lithiation of the *O,S*-acetal **20** occurred *cleanly* without attendant decomposition by employing *sec*-butyllithium (−78 °C, 2 h) in the presence of 1.1 equiv of the additive TMEDA.[12] The union of the lithiated derivative **14** with representative 3-alkoxy enones was straightforward. Slow addition of the 3-ethoxycyclohexenones **12** or **21** to 1.0 equiv of the lithiated derivative **14** in THF (−78→25 °C) followed by the addition of the reaction mixture to cold 10% aqueous H_2SO_4 and immediate extraction with ether afforded the adducts **15b** and **22** in 93% and 71% yield, respectively, after purification. As expected, prolonged



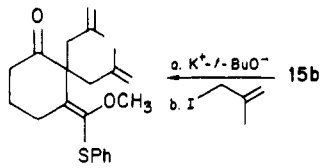


treatment of the reaction mixtures with aqueous acid resulted in the formation of varying quantities of the corresponding keto aldehydes **23a,b**. A better indication of the preparative scope of this synthetic transformation was provided by the reaction of the lithiated derivative **14** with a representative vinylogous amide. Treatment of 3-(dimethylamino)-2-(3,4-dimethoxyphenyl)prop-2-en-1-al (**24**)[13] with **14** (−78 °C, THF, 24 h) followed by hydrolysis with aqueous acid furnished the crystalline enal **25** in 63% yield.



The utilization of lithium diisopropylamide in THF either with or without HMPA for the metalation and subsequent alkylation of the carbonyl compounds **15b** and **22** was readily determined to be experimentally ineffective.[14] Moreover, potassium hexamethyldisilazide[15] was found to offer no preparative advantages over the use of potassium *tert*-butoxide in the above regard. It was ultimately determined that simple treatment of the enones **15b** or **22** with the appropriate quantity of a THF solution of freshly sublimed potassium *tert*-butoxide (0 °C, 0.5 h) followed by the requisite mono- or dihalide afforded symmetrically γ-disubstituted ketene *O,S*-acetals **26** and **28** in 77% and 64% overall yield, respectively. In these instances the production of the *E* isomers was accompanied to a minor extent (ca. 5%) by the formation of the corresponding *Z* isomers. Regiospecific symmetrical bisfunctionalizations of the Michael variety were also achievable using the intermediates **22** and **25**. To this end, treatment of the enone **22** with methyl acrylate (4.0 equiv) in the presence of a catalytic quantity of potassium *tert*-butoxide gave the adduct **29** in 73% yield. The enal **25** was converted into the projected mesembrine precursor **27** in 91% yield by the sequential treatment of **25** with methyl vinyl ketone (1.2 equiv) and DBN (0.2 equiv) followed by 0.03 N ethanolic NaOEt (0.5 equiv, reflux, 24 h). It is noteworthy, but not entirely surprising, that attempts to effect "unsymmetrical" dialkylations of the intermediates **15b** and **22** gave product mixtures to varying extents.[16] Specifically, sequential exposure of **15b** to 1.0 equiv of potassium *tert*-butoxide followed by 1 equiv of

(10) Trost, B. M.; Miller, C. H. *J. Am. Chem. Soc.* **1975**, *97*, 7182.
(11) Brown, H. C.; Imai, T. *J. Am. Chem. Soc.* **1983**, *105*, 6285.
(12) Beak, P.; Brown, R. A. *J. Org. Chem.* **1982**, *47*, 34.
(13) Coppola, G. M.; Hardtmann, G. E.; Huegi, B. S. *Heterocycles* **1974**, *11*, 51.
(14) In our hands, the use of LDA under a variety of different reaction conditions led to incomplete alkylation.
(15) Brown, C. A. *J. Org. Chem.* **1974**, *39*, 3913.
(16) The selective monoalkylation of extended dienolate ions has been a long-standing problem which has been partially resolved through the use of metallo enamines: Stork, G.; Benaim, J. *J. Am. Chem. Soc.* **1971**, *93*, 5938.



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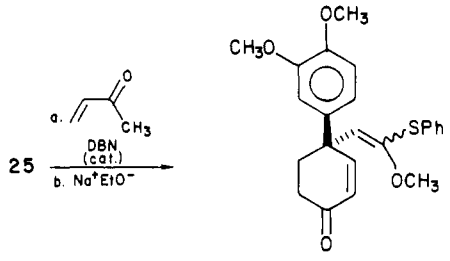

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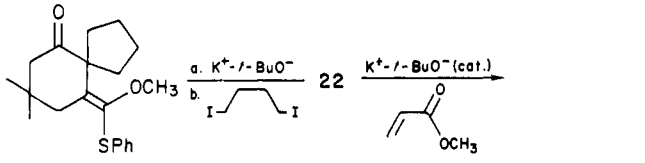

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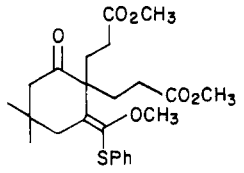

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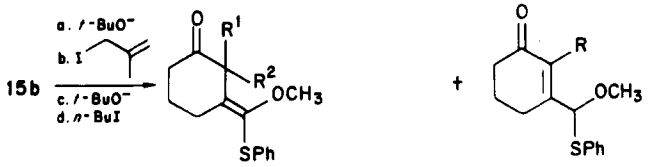
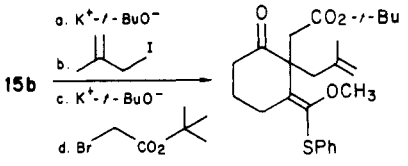
methallyl iodide (−78→0 °C) and subsequently a further 1.0 equiv of potassium *tert*-butoxide followed by *n*-butyl iodide provided the unsymmetrical dialkylation product **30a** in 43% purified yield. Also isolated from this reaction



30a, R^1 = methallyl; R^2 = *n*-Bu
30b, R^1 = R^2 = methallyl
30c, R^1 = R^2 = *n*-Bu

31a, R = methallyl
31b, R = *n*-Bu



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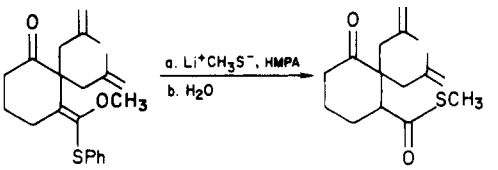
were the symmetrical dialkylation products **30b** (6%) and **30c** (6%) as well as the monoalkylation products **31a** (3%) and **31b** (9%).[17] In a similar vein, sequential deprotonation–alkylation of **15b** (K^+-O-*t*-Bu 1.0 equiv, $IC H_2C(CH_3)=CH_2$, K^+-O-*t*-Bu 1.0 equiv, $BrCH_2CO_2$-*t*-Bu) furnished the crystalline product **32** (42% isolated).

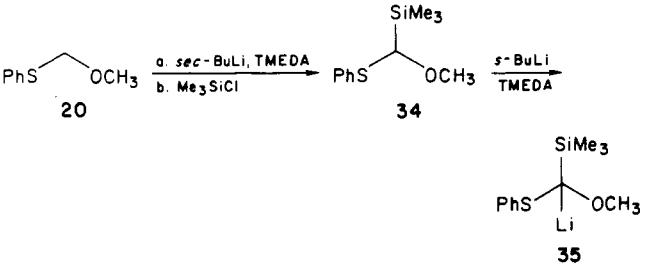
An exceptionally mild procedure was subsequently developed for the nucleophilic cleavage of ketene *O*-methyl *S*-acetal moieties. To this end treatment of the alkylation product **26** with lithium thiomethoxide (HMPA, 25 °C)[18] furnished the crystalline thio ester **33** directly in (82%)



26 33

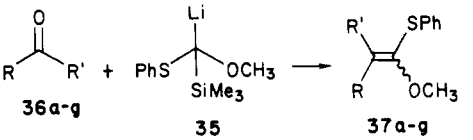
yield. Alternatively, the hydrolysis of ketene *O*,*S*-acetals could be accomplished conveniently by exposure to iodotrimethylsilane followed by filtration through a bed of activity 3 alumina[19] or by mercuric chloride mediated methanolysis at 25 °C.[20]

The remarkably facile cleavage of the ketene *O*,*S*-acetal **26** suggested that a carbonyl homologation procedure involving this functional assembly might be quite useful. We have therefore developed a Peterson-type olefination procedure for the preparation of these intermediates.[21-25] To this end, the silylated *O*,*S*-acetal **34** was prepared in



35

96.5% isolated yield by the exposure of **20** to *sec*-butyllithium (TMEDA, THF, −78 °C, 2 h) followed by the addition of chlorotrimethylsilane (2.0 equiv, −78→25 °C). In complete accord with our previous observations, the silylated *O*,*S*-acetal **34** was efficiently lithiated by *sec*-butyllithium in the presence of TMEDA at −78 °C to generate the organometallic **35**. The treatment of a variety of aldehydes and ketones (e.g., **36a–g**) with **35** (THF, −78→25



36a-g 35 37a-g

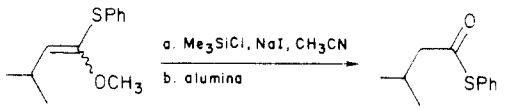
°C) furnished the corresponding ketene *O*,*S*-acetals **37a–g** in good to excellent yields.[26] The successful homologation of crotonaldehyde (**36c**) was particularly noteworthy in this regard. For this substrate, the desired homologation event occurred to the exclusion of the possible competing side reactions of conjugate addition and γ-deprotonation. In all instances, the ketene *O*,*S*-acetals synthesized in this manner were product mixtures in which the *E* isomer was formed as the predominant product. Homologation of the ketones **36d** and **36e** was accompanied, to a *minor extent* (ca. 7–11%), by competing deprotonation. With 1-carvone (**36f**), the homologation procedure was complicated by extensive deprotonation (e.g., 21%) as well as other side reactions. These experimental observations are summarized in Table I.

(17) Several attempts to further enhance the formation of the desired unsymmetrical alkylation product **30a** were unsuccessful.

(18) Bartlett, P. A.; Johnson, W. S. *Tetrahedron Lett.* **1970**, 4459.
(19) Kosarych, Z.; Cohen, T. *Tetrahedron Lett.* **1980**, *21*, 3959.
(20) de Groot, A.; Jansen, B. J. M. *Synth. Commun.* **1983**, 985.
(21) Grobel, B. T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 852.
(22) Mikolajczyk, M.; Grzejszczak, S.; Zatorski, A.; Mlotkowska, B.; Gross, H.; Costisella, *Tetrahedron* **1978**, *34*, 3081.
(23) Jones, P. F.; Cappert, M. F. *J. Chem. Soc., Chem. Commun.* **1972**, 526.
(24) Corey, E. J.; Markl, G. *Tetrahedron Lett.* **1967**, 3201.
(25) Cohen, T.; Gapinski, R. E.; Hutchins, R. R. *J. Org. Chem.* **1979**, *44*, 3599.

(26) Mixtures of *E* and *Z* isomers were formed in all instances involving the condensation of **35** with carbonyl compounds.

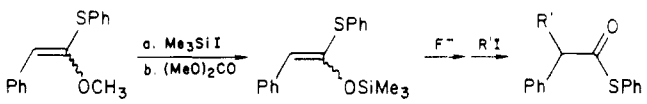
Ketene *O,S*-acetals have been reported to undergo acid-catalyzed methanolysis in the presence of hydrogen chloride and mercuric chloride.[20] We required cleavage procedures which could be executed under neutral or mildly acidic reaction conditions. Accordingly, exposure of the ketene *O,S*-acetal **37g** to chlorotrimethylsilane (1.2



37g 38

equiv) and sodium iodide (1.2 equiv) in dry acetonitrile (25 °C, 5 min) and subsequent filtration of the reaction mixture through alumina (activity 3)[19] afforded the phenyl thio ester **38** in 90% yield.

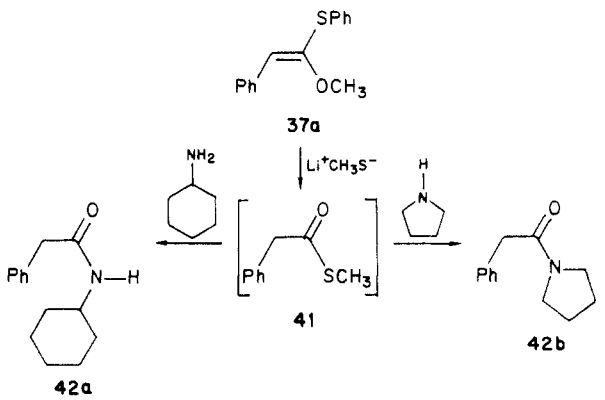
The synthetic utility of silyl enol ethers in fluoride-mediated alkylation reactions[27] as well as aldol and Michael reactions[28,29] catalyzed by Lewis acids has been generally recognized. In principle, the conversion of ketene *O,S*-acetals to the corresponding ***O***-trimethylsilyl derivatives would permit the execution of these and other synthetic operations (e.g., **37a** → **40**). After numerous trials the



37a 39 40

following procedure for the conversion of ketene *O,S*-acetals into their silyl enol ether counterparts was determined to be optimum. Treatment of the ketene *O,S*-acetal **37a** with freshly distilled iodotrimethylsilane (2.0 equiv, CH_3CN, 80 °C, 20 h) and subsequent quenching ($(CH_3O)_2C{=}O$, 2.0 equiv, 25 °C)[30] followed by purification provided the ketene *O*-silyl, *S*-acetal **39** as a mixture of geometrical isomers.[31]

A useful and revealing modification of the nucleophilic cleavage procedure previously utilized for the preparation of the thio ester **33** was subsequently developed for the direct conversion of ketene *O,S*-acetals into carboxamides. In this connection, sequential treatment of **37a** with lithium thiomethoxide in HMPA followed by the addition of



representative amines (e.g., cyclohexylamine or pyrrolidine, 3 equiv) furnished the corresponding carboxamides **42a** (94%) and **42b** (95%) by way of the thio ester **41**.

The high yields and apparent scope attributable to the foregoing homologation procedure are particularly noteworthy. These factors, considered in light of the demonstrated synthetic utility of intermediates possessing the ketene *O,S*-acetal moiety, strongly suggest that this method will be a valuable addition to existing literature procedures for the one-carbon homologation of carbonyl compounds into carboxylic acid derivatives.

Experimental Section

Melting points were determined on an electrothermal capillary melting point apparatus and are uncorrected. Infrared spectra were run on a Beckman Model 4250 infrared spectrometer. ^1H NMR spectra were obtained on Varian HFT-80 and Nicolet NT-300 spectrometers. ^{13}C NMR spectra were recorded on a Nicolet NT-300 spectrometer. Microanalyses were performed at MHW Laboratories, Phoenix, AZ. Mass spectra were determined with a AEI MS-30 mass spectrometer at an ionizing voltage of 70 eV.

Methoxy(phenylthio)methane (20). A flame-dried 500-mL three-necked flask equipped with a magnetic stirring bar, N_2 inlet, low-temperature thermometer, and rubber septum was charged with 250 mL of dry dimethoxymethane and 30 mL of thiophenol (0.29 mol). To this solution was added 36 mL of boron trifluoride etherate (0.29 mol) at −78 °C. The reaction mixture was warmed to 0 °C and stirred for an additional $1^2/_3$ h. The reaction mixture was then treated with 200 mL of 10% aqueous KOH solution. The mixture was stirred a few minutes and then poured into 200 mL of ether and extracted. The organic layer was then successively washed with H_2O and saturated brine and then dried overnight with Na_2SO_4. The solvent was evaporated in vacuo, and the crude product was purified by bulb-to-bulb distillation to afford 42.79 g of methoxythiophenylmethane (**20**) (bp 40 °C, 0.04 mm) (96%) as a colorless oil: NMR ($CDCl_3/Me_4Si$) δ 3.45 (3 H, s, CH_3O), 5.00 (2 H, s, CH_2), 7.36 (5 H, Ar CH); IR (film) cm^{-1} 3062 (Ar CH), 3040–2710 (CH envelope), 1590 (aromatic C=C).

3-[Methoxy(phenylthio)methyl]cyclohex-2-en-1-one (15b). A three-necked, 1-L flask equipped with a magnetic stirring bar, low-temperature thermometer, nitrogen inlet adaptor, and rubber septum was flame-dried under nitrogen. After having been cooled to room temperature, the flask was charged with 22.69 g of methoxy(phenylthio)methane (**20**) (147 mmol) in 300 mL of dry THF. To this solution was added 23.26 mL of TMEDA (154 mmol) and 10 mg of 1,10-phenanthroline. Then, *sec*-butyllithium in cyclohexane was added at −78 °C, until a color change was indicated, whereupon 99.4 mL of *sec*-BuLi (1.48 M in cyclohexane, 147 mmol) was added dropwise at a rate to maintain the temperature below −70 °C (~30 min). The reaction mixture was then allowed to stir at −78 °C for 3 h. A solution of 19.64 g of 3-ethoxycyclohex-2-en-1-one (**12**) (140 mmol) in 100 mL of dry THF was then added, maintaining the temperature below −70 °C. The mixture was subsequently allowed to warm to room temperature overnight and was then added to petroleum ether and 150 mL of 10% aqueous H_2SO_4. The layers were separated, and the aqueous layer was extracted with an additional 100 mL of petroleum ether. The combined organic fractions were sequentially washed with 5% $NaHCO_3$, H_2O, and saturated brine and then dried over Na_2SO_4. The solvent was evaporated in vacuo, and the crude product was purified by bulb-to-bulb distillation to afford 42.79 g (93%) of the enone **15b** as an oil (bp 105 °C, 0.05 mm): NMR ($CDCl_3/Me_4Si$) δ 1.93 (2 H, m, CH_2), 2.24 (3 H, complex m, CH_2), 2.56 (1 H, d of d of d, J = 17.8, 6.1 Hz, CH_2), 3.59 (3 H, S, CH_3O), 5.00 (1 H, br s, CH), 5.74 (1 H, br s, vinyl CH), 7.29 (3 H, complex m, Ar CH), 7.33 (2 H, complex m, Ar CH); IR (film) cm^{-1} 3060 (Ar CH), 3000–2820 (CH envelope), 1680 (C=O). Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.49. Found: C, 67.71; H, 6.70.

3-[Methoxy(phenylthio)methyl]-5,5-dimethylcyclohex-2-en-1-one (22). A flame-dried, 200-mL three-necked flask equipped with a magnetic stirring bar, low-temperature thermometer, ni-

(27) Kuwajima, I.; Nakamura, E. *J. Am. Chem. Soc.* **1975**, *97*, 3257.
(28) Mukaiyama, T.; Banno, K.; Narasaka, K. *J. Am. Chem. Soc.* **1974**, *96*, 7503.
(29) Saigo, K.; Osaki, M.; Mukaiyama, T. *Chem. Lett.* **1976**, 163. An investigation is currently underway to ascertain the utility of ketene *O*-silyl S-acetals in $TiCl_4$-mediated aldol and Michael condensation reactions.
(30) The optimum reaction conditions entailed the use of dimethyl carbonate as an iodotrimethylsilane scavenger subsequent to the desilylation of the ketene *O,S*-acetal.
(31) In addition, 8% of *S*-phenyl thioacetate was formed via hydrolysis of the ketene *O*-silyl *S*-acetal.

trogen inlet adaptor, and rubber septum was charged with 6.59 g of methoxy(phenylthio)methane (**20**) (42.72 mmol) in 85 mL of dry THF. To this solution was added 7.09 mL of TMEDA (46.99 mmol) and 5 mg of 1,10-phenanthroline. The reaction mixture was cooled to −78 °C, and *sec*-BuLi in cyclohexane was added dropwise via syringe until a color change was indicated. The reaction mixture was then treated with 30.0 mL of *sec*-BuLi (1.44 M in cyclohexane, 43.20 mmol) at a rate to maintain the temperature below −70 °C. The reaction mixture was allowed to stir at −78 °C for an additional 3 h. Then, 7.19 g of 3-ethoxy-5,5-dimethylcyclohex-2-en-1-one (**21**) (42.72 mmol) was added in 35 mL of dry THF, maintaining a temperature of −70 °C. The reaction flask was packed in a dry ice–acetone bath and allowed to warm slowly to room temperature overnight. The solution was diluted with ether and 10% aqueous H_2SO_4. The aqueous layer was separated and subsequently extracted with ether. The combined ether extracts were sequentially washed with aqueous 5% $NaHCO_3$ solution, H_2O, and saturated NaCl and dried overnight (Na_2SO_4). After evaporation of the ether in vacuo, the residue was purified by bulb-to-bulb distillation (88 °C, 0.025 mm) to separate a mixture of the starting enone and methoxy(phenylthio)methane from the less volatile product. The residue was filtered through a bed of silica gel (25% ethyl acetate–hexane for elution) to provide 8.33 g (71%) of the enone **22** as an oil: ^{13}C NMR δ 199.65, 156.74, 133.87, 131.61, 128.85, 128.39, 124.16, 91.80, 56.58, 51.38, 40.47, 33.59, 28.58, 28.04; ^1H NMR ($CDCl_3/Me_4Si$) δ 0.97 (3 H, s, CH_3), 1.02 (3 H, s, CH_3), 2.10 (1 H, d, J = 16.0 Hz, CH_2), 2.14 (1 H, d, J = 18.1 Hz, CH_2), 2.18 (1 H, d, J = 16.0 Hz, CH_2), 2.44 (1 H, d, J = 18.1 Hz, CH_2), 3.57 (3 H, s, OCH_3), 4.97 (1 H, br s, CH), 5.83 (1 H, br s, vinyl CH), 7.28 (3 H, complex m, Ar CH), 7.39 (2 H, complex m, Ar CH); IR (neat) cm^{-1} 3060 (Ar CH), 3010–2790 (CH envelope), 1670 (C=O). Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29. Found: C, 69.33; H, 7.18.

3-[Methoxy(phenylthio)methyl]-2-(3,4-dimethoxyphenyl)prop-2-en-1-al (25). A flame-dried, 100-mL three-necked flask equipped with a magnetic stirring bar, low-temperature thermometer, nitrogen inlet adaptor, and rubber septum was charged with 1.974 g of methoxy(phenylthio)methane (**20**) (12.80 mmol) in 25 mL of dry THF and 1.93 mL of TMEDA (12.80 mmol). The reaction mixture was then treated with 8.29 mL of *sec*-BuLi (1.48 M in cyclohexane, 12.27 mmol) so as to maintain the temperature below −70 °C. After being stirred at −78 °C for an additional 2.5 h, the solution was diluted with 50 mL of dry THF, and 1.93 g of the solid vinylogous amide **24** (8.2 mmol) was added in one portion without solvent. The reaction mixture was then stirred at −78 °C for an additional 27 h. After being warmed to room temperature, the solution was poured into 10% H_2SO_4 and was extracted 3 times with ether. The combined ether fractions were then washed with saturated $NaHCO_3$, H_2O, saturated brine and then dried over Na_2SO_4. Evaporation of the ether in vacuo left a solid which was recrystallized from 10% ethyl acetate–hexane to furnish 2.29 g (63%) of the enal **25** as a white solid, mp 101–103.5 °C: NMR ($CDCl_3/Me_4Si$) δ 3.51 (3 H, s, CH_3O), 3.86 (3 H, s, CH_3O), 3.91 (3 H, s, CH_3O), 5.31 (1 H, d, J = 9.24 Hz, CH), 6.37 (1 H, d, J = 9.24 Hz, vinyl CH), 6.86 (3 H, complex m, Ar CH), 7.34 (3 H, complex m, Ar CH), 7.48 (2 H, complex m, Ar CH), 9.49 (1 H, s, CHO); IR (CCl_4) cm^{-1} 3100–2700 (aliphatic envelope), 1700 (C=O). Anal. Calcd for $C_{19}H_{20}O_4S$: C, 66.24; H, 5.86. Found: C, 66.14; H, 6.05.

2,2-Bis[2-(carbomethoxy)ethyl]-3-[methoxy(phenylthio)methylene]-5,5-dimethylcyclohexan-1-one (29). A three-necked flask equipped with a serum cap, canula inlet, nitrogen outlet adapter, and magnetic stirring bar was charged with 0.159 g of the enone **22** (0.58 mmol) and 2.3 mL of dry THF. To this solution was added 0.065 mL of potassium *tert*-butoxide (1.77 M in THF, 0.115 mmol) at −30 °C. After being warmed to 0 °C and stirred for 30 min, the mixture was again cooled to −30 °C, whereupon 0.26 mL of methyl acrylate (2.88 mmol) was passed into the reaction mixture in the vapor phase via the canula in a stream of nitrogen. After the methyl acrylate had all been evaporatively transferred, the canula was removed, and the solution was allowed to slowly warm to room temperature. The mixture was poured into saturated aqueous NH_4Cl solution and extracted with 3 portions of ether. The combined ether extracts were washed with H_2O and saturated aqueous brine and then dried over Na_2SO_4. Evaporation of the solvents in vacuo left 0.242 g of an oil which was subsequently submitted to chromatography on silica gel with 20% ethyl acetate–hexane for elution to afford 0.188 g of the keto diester **29** as an oil (73%): NMR ($CDCl_3/Me_4Si$) δ 1.00 (6 H, s, CH_3), 1.63 (2 H, s, CH_2), 2.23 (4 H, complex m, CH_2), 2.34 (4 H, complex m, CH_2), 2.64 (2 H, s, CH_2), 3.54 (3 H, s, CH_3O), 3.66 (6 H, s, CH_3O), 7.28 (5 H, complex m, Ar CH); IR (film) cm^{-1} 3140–2745 (CH envelope), 1735 (C=O), 1705 (C=O). Anal. Calcd for $C_{24}H_{32}O_6S$: C, 64.26; H, 7.19. Found: C, 64.17; H, 7.22.

4-(3,4-Dimethoxyphenyl)-4-[(*E*)-2-methoxy-2-(phenylthio)vinyl]cyclohex-2-en-1-one (27). A 10-mL, round-bottomed flask equipped with a serum cap, nitrogen inlet, and magnetic stirring bar was charged with 0.192 g of the enal **25** (0.56 mmol) and 6 mL of dry THF. The resultant solution was cooled to −30 °C, and 0.014 mL of DBN (0.11 mmol) was added. The reaction mixture was then treated with 0.043 g of methyl vinyl ketone (0.61 mmol). The solution was allowed to slowly warm to room temperature and then stirred for an additional 10 h. To this solution was added 9.3 mL of sodium ethoxide in ethanol (0.03 N, 0.28 mmol), and the mixture was then heated at reflux for 24 h. The resultant mixture was then poured into aqueous 1 M citric acid and extracted with ether (2 × 50 mL). The combined organic fractions were sequentially washed with 10% aqueous $NaHCO_3$ and saturated NaCl and then dried over Na_2SO_4. The solvents were evaporated in vacuo, and the crude product was purified by column chromatography on silica gel (30% ethyl acetate–hexane for elution) to provide 0.171 g of the *E* isomer of the enone **27** and 0.031 g of the corresponding *Z* isomer (91% combined yield). ***E* isomer**: NMR ($CDCl_3/Me_4Si$) δ 2.40 (4 H, complex m, CH_2), 3.32 (3 H, s, CH_3O), 3.88 (3 H, s, CH_3O), 3.90 (3 H, s, CH_3O), 5.73 d (1 H, s, vinyl), 6.15 (1 H, d, J = 10 Hz, vinyl), 6.90 (3 H, complex m, Ar CH), 7.33 (5 H, complex m, Ar CH), 7.36 (1 H, d, J = 10 Hz, vinyl); IR (film) cm^{-1} 3160–2700 (CH envelope), 1680 (C=O); high resolution mass spectrum calcd for $C_{23}H_{24}O_4S$ M^+ 396.1395, found M^+ 396.1388. ***Z* isomer**: NMR ($CDCl_3/Me_4Si$) δ 2.40 (4 H, complex m, CH_2), 3.65 (3 H, s, CH_3O), 3.87 (3 H, s, CH_3O), 3.90 (3 H, s, CH_3O), 5.66 (1 H, s, vinyl), 6.15 (1 H, d, J = 10 Hz, vinyl), 6.88 (3 H, m, Ar CH), 7.23 (5 H, m, Ar CH), 7.53 (1 H, d, J = 10 Hz, vinyl); IR (film) cm^{-1} 3100–2720 (CH envelope), 1680 (C=O); high resolution mass spectrum calcd for $C_{23}H_{24}O_4S$ M^+ 396.1393, found M^+ 396.1381.

2,2-Bis(2-methylprop-2-en-1-yl)-3-[(*E*)-methoxy(phenylthio)methylene]cyclohexan-1-one (26). A 10-mL, round-bottomed flask equipped with a magnetic stirring bar, nitrogen inlet adaptor, and rubber septum was flame-dried under nitrogen. After cooling to room temperature, the flask was charged with 0.145 g of the enone **15b** (0.58 mmol) in 2.5 mL of dry THF. To this solution was added 0.30 mL of potassium *tert*-butoxide (1.93 M in THF, 0.584 mmol) dropwise over 2 min at −78 °C. The mixture was then warmed to 0 °C for 35 min. The solution was cooled to −78 °C, and 0.064 mL of methallyl iodide (0.58 mmol) was added in one portion. The mixture was slowly allowed to warm to 25 °C and was stirred at this temperature for 1 h. The above sequence of deprotonation and alkylation was subsequently repeated in an identical manner. The reaction mixture was then diluted with ether and saturated aqueous NH_4Cl solution. The organic layer was separated, and the aqueous layer was extracted with two additional portions of ether. The combined ether extracts were sequentially washed with H_2O and saturated aqueous brine and dried over Na_2SO_4. The solvents were evaporated in vacuo, and the crude product was chromatographed on silica gel (2.5% ethyl acetate–hexane for elution) to give 0.148 g (71%) of the ketone **26** and 0.0128 g (6%) of the corresponding *Z* isomer. ***E* isomer**: NMR ($CDCl_3/Me_4Si$) δ 1.68 (6 H, br s, allylic CH_3), 1.80 (2 H, apparant t of t, J = 6.4 Hz, CH_2), 2.40 (2 H, apparant t, J = 6.9 Hz, CH_2), 2.70 (2 H, d, J = 13.3 Hz, allylic CH_2), 2.75 (2 H, m, CH_2), 2.84 (2 H, d, J = 13.3 Hz, allylic CH_2), 3.61 (3 H, s, CH_3O), 4.62 (2 H, br s, vinyl), 4.79 (2 H, br s, vinyl); IR (film) cm^{-1} 3088 (Ar CH), 3030–2750 (CH envelope), 1702 (C=O). Anal. Calcd for $C_{22}H_{28}O_2S$: C, 74.10; H, 7.92. Found: C, 74.24; H, 7.72. ***Z* isomer**: NMR ($CDCl_3/Me_4Si$) δ 1.64 (6 H, br s, allylic CH), 1.81 (2 H, apparent t of t, J = 6.5 Hz), 2.42 (2 H, apparent t, J = 6.8 Hz, CH_2), 2.65 (2 H, m, CH_2), 2.76 (2 H, d, J = 13.6, allylic CH_2), 3.09 (2 H, d, J = 13.6, allylic CH_2), 3.49 (3 H, s, CH_3O),

4.63 (2 H, br s, vinyl), 4.77 (2 H, br s, vinyl), 7.14 (5 H, complex m, Ar CH); IR (film) cm^{-1} 3080 (Ar CH), 2980–2815 (CH envelope), 1708 (C=O). Anal. Calcd for $C_{22}H_{28}O_2S$: C, 74.12; H, 7.92. Found: C, 74.21; H, 7.87.

10-[(*E*)-Methoxy(phenylthio)methylene]spiro[4,5]decan-6-one (28). A 10-mL, round-bottomed flask equipped with a magnetic stirring bar, nitrogen inlet adaptor, and rubber septum was flame-dried under nitrogen. After being cooled to room temperature, the flask was charged with 0.179 g of the enone **22** (0.65 mmol) in 2.6 mL of dry THF. To this solution was added 0.39 mL of potassium *tert*-butoxide (1.83 M in THF, 0.71 mmol) dropwise over 2 min at −78 °C. The mixture was warmed to 0 °C and stirred for 35 min. Then, 0.047 mL of diiodobutane (0.36 mmol) was added at −78 °C. The solution was allowed to slowly warm to 0 °C and was then stirred at 0 °C for 2 h and at room temperature for 15 h. The foregoing sequence of deprotonation (t-BuO^-K^+, 0.71 mmol) and alkylation (diiodobutane, 0.36 mmol) was then repeated in an identical manner at −78 °C, and the resultant mixture was allowed to warm to room temperature overnight with stirring. The reaction mixture was then diluted with ether, and saturated aqueous NH_4Cl solution was added. The organic layer was separated, and the aqueous layer was extracted with two additional portions of ether. The ether extracts were combined and sequentially washed with H_2O followed by saturated aqueous brine and dried over $MgSO_4$. The solvent was evaporated in vacuo, and the crude product was chromatographed on silica gel (5% ethyl acetate–hexane for elution) to give 0.136 g (64%) of the ketone **28** and a trace of the corresponding *Z* isomer which were separable by HPLC. ***E* isomer**: NMR ($CDCl_3/Me_4Si$) δ 1.02 (6 H, s, CH_3), 1.68 (2 H, m, CH_2), 1.82 (2 H, m, CH_2), 1.95 (2 H, m, CH_2), 2.14 (2 H, m, CH_2), 2.31 (2 H, s, CH_2), 2.54 (2 H, s, CH_2), 3.52 (3 H, s, CH_3O), 7.18 (1 H, m, Ar CH), 7.28 (4 H, m, Ar CH); IR (film) cm^{-1} 3070 (Ar CH), 3040–2760 (CH envelope), 1712 (C=O). Anal. Calcd for $C_{20}H_{26}OS$: C, 72.69; H, 7.93. Found: C, 72.80; H, 7.95. ***Z* isomer**: NMR ($CDCl_3/Me_4Si$) δ 1.08 (6 H, s, CH_3), 1.63 (2 H, m, CH_2), 1.88 (2 H, m, CH_2), 2.04 (2, m, CH_2), 2.18 (2 H, m, CH_2), 2.36 (2 H, s, CH_2), 2.41 (2 H, s, CH_2), 3.47 (3 H, s, CH_3O), 7.19 (1 H, m, Ar CH), 7.30 (4 H, m, Ar CH); IR (film) cm^{-1} 3059 (Ar CH), 3025–2740 (CH envelope), 1709 (C=O). Anal. Calcd for $C_{20}H_{26}OS$: C, 72.69; H, 7.93. Found: C, 72.51; H, 8.13.

2-Butyl-2-(2-methylprop-2-en-1-yl)-3-[(*E*)-methoxy(phenylthio)methylene]cyclohexan-1-one (30a). A flame-dried 25-mL three-necked round-bottomed flask equipped with a magnetic stirring bar, low-temperature thermometer, nitrogen inlet adaptor, and rubber septum was charged with 0.441 g of the enone **15b** (1.78 mmol) in 7.1 mL of dry THF. The solution was cooled to −78° C, and 1.08 mL of potassium *tert*-butoxide (1.63 M in THF, 1.78 mmol) was added dropwise over 2 min. The mixture was warmed to 0 °C and stirred for 40 min. The solution was then cooled to −78 °C, and 0.194 mL of methallyl iodide (1.78 mmol) was added over 1 min. The solution was then allowed to slowly warm to room temperature over a 6-h period. The reaction mixture was again cooled to −78 °C, and an additional 1.09 mL of potassium *tert*-butoxide in THF (1.78 mmol) was added. The mixture was again warmed to 0 °C, stirred for 40 min, and recooled to −78 °C. The reaction mixture was then treated with 0.20 mL of *n*-butyl iodide (1.78 mmol) over 1 min and was allowed to slowly warm to room temperature. After being stirred for an additional 36 h, the mixture was poured into saturated aqueous NH_4Cl solution and was extracted 3 times with ether. The combined ether extracts were washed with H_2O and saturated aqueous brine and dried over Na_2SO_4. Evaporation of the ether in vacuo and submission of the residue to chromatography on silica gel (3% ethyl acetate–hexane for elution) gave 0.274 g (43%) of the ketone **30a** as of an oil: NMR ($CDCl_3/Me_4Si$) δ 0.88 (3 H, t, J = 7.0 Hz, CH_3), 1.07 (2 H, complex m, CH_2), 1.27 (2 H, complex m, CH_2), 1.67 (3 H, br s, CH_3), 1.82 (2 H, complex m, CH_2), 1.92 (1 H, d of t, J = 8.9 Hz, 4.0, CH_2), 2.08 (1 H, d of t, J = 8.9 Hz, 4.0, CH_2), 2.40 (2 H, apparent t, J = 6.9 Hz, CH_2), 2.69 (1 H, d, J = 13.5 Hz, allylic CH_2), 2.74 (2 H, m, CH_2), 2.72 (1 H, d, J = 13.5, allylic CH_2), 3.56 (3 H, s, CH_3O), 4.65 (1 H, br s, vinyl), 4.76 (1 H, br s, vinyl), 7.19 (1 H, m, Ar CH), 7.32 (4 H, m, Ar CH); IR (film) cm^{-1} 3080 (Ar CH), 3015–2840 (CH envelope), 1704 (C=O). Anal. Calcd for $C_{22}H_{30}O_2S$: C, 73.70; H, 8.43. Found: C, 73.65; H, 8.45.

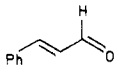
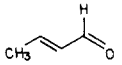
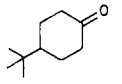
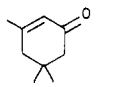
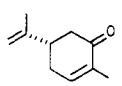
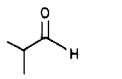
2-[(*tert*-Butoxycarbonyl)methyl]-2-(2-methylprop-2-en-1-yl)-3-[(*E*)-methoxy(phenylthio)methylene]cyclohexan-1-one (32). The keto ester **32** was prepared in an analogous manner in 42% isolated yield: NMR ($CDCl_3/Me_4Si$) δ 1.41 (9 H, s, $(CH_3)_3C$), 1.71 (3 H, br s, allylic CH_3), 1.83 (1 H, complex m, CH_2), 1.95 (1 H, complex m, CH_2), 2.43 (1 H, m, CH_2), 2.49 (1 H, d, J = 12.0 Hz, allylic CH_2), 2.65 (1 H, m, CH_2), 2.67 (1 H, d, J = 12.0 Hz, allylic CH_2), 2.85 (1 H, m, CH_2), 3.20 (1 H, d, J = 16.6 Hz, CH_2), 3.26 (1 H, d, J = 16.6 Hz, CH_2), 3.56 (3 H, s, CH_3O), 4.66 (1 H, br s, vinyl), 4.85 (1 H, br s, vinyl), 7.18 (1 H, Ar CH), 7.29 (4 H, m, Ar CH); IR (film) cm^{-1} 3080 (Ar CH), 3040–2780 (CH envelope), 1735 (C=O), 1710 (C=O). Anal. Calcd for $C_{24}H_{32}O_4S$: C, 69.20; H, 7.74. Found: C, 68.98; H, 7.79.

2,2-Bis(2-methylprop-2-en-1-yl)-3-[(methylthio)carbonyl]cyclohexan-1-one (33). A three-necked, round-bottomed flask equipped with a nitrogen inlet adaptor, dry ice condensor, serum cap, and magnetic stirring bar was charged with 0.120 g of lithium hydride (15 mmol) under an atmosphere of nitrogen. The flask was maintained at room temperature while 4.72 mL of methanethiol in HMPA (6.36 M, 30 mmol) was added. The reaction mixture was then treated with 0.356 g of the ketene *O,S*-acetal (**26**) (1 mmol) dissolved in 1 mL of HMPA. The solution was then stirred at 25 °C for $3^1/_2$ h and was subsequently poured into pentane and saturated aqueous NH_4Cl. The pentane layer was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of the solvents in vacuo, the crude product was chromatographed on silica gel (2% ethyl acetate–hexane for elution). The thio ester **33** (0.230 g) was isolated as a white crystalline solid upon removal of the solvent, mp 70.0–71.0 °C (82%): NMR ($CDCl_3/Me_4Si$) δ 1.64 (3 H, br s, CH_3), 1.70 (3 H, br s, CH_3), 1.79 (1 H, complex m, CH_2), 2.05 (4 H, complex m, CH_2), 2.27 (3 H, s, CH_3S), 2.39 (1 H, d, J = 15.1 Hz, CH_2), 2.51 (1 H, d with fine structure, J = 14.9 Hz, CH_2), 2.53 (1 H, m, CH_2), 2.68 (1 H, d, J = 14.9 Hz, CH_2), 2.90 (1 H, d, J = 15.1 Hz, CH_2), 3.24 (1 H, d of d, J = 8.6, 4.4 Hz, CH), 4.65 (1 H, br s, vinyl), 4.68 (1 H, br s, vinyl), 4.84 (1 H, s with fine splitting, vinyl), 4.88 (1 H, br s, vinyl); IR (film) cm^{-1} 3100–2700 (CH envelope), 1710 (C=O), (1690 C=O). Anal. Calcd for $C_{16}H_{24}O_2S$: C, 68.53; H, 8.63. Found: C, 68.77; H, 8.54.

Methoxy(phenylthio)(trimethylsilyl)methane (34). A flame-dried, three-necked round-bottomed flask equipped with a magnetic stirring bar, low-temperature thermometer, nitrogen inlet, and rubber septum was charged with 6.940 g of methoxy(phenylthio)methane (**20**) (45.0 mmol) and 10 mg of 1,10-phenanthroline in 200 mL of dry THF. To this solution was added 7.47 mL of freshly distilled TMEDA (49.5 mmol). The reaction mixture was cooled to −78 °C, and *sec*-BuLi was added dropwise until a color change was observed. The solution was then treated with 35.7 mL of *sec*-BuLi (1.30 M in cyclohexane, 46.4 mmol) so as to maintain the reaction temperature below −70 °C. The solution was stirred at −78 °C for 2 h whereupon 7.01 mL of freshly distilled chlorotrimethylsilane (55.2 mmol) was added in one portion. The reaction mixture was allowed to warm to room temperature and stirred overnight. The mixture was then diluted with pentane, and saturated NH_4Cl solution was added. After partitioning, the aqueous layer was extracted a second time with pentane, and the combined organic layers were washed with H_2O and saturated brine and dried over Na_2SO_4. Evaporation of the solvent in vacuo left an oil. The crude product was purified by bulb-to-bulb distillation (bp 65–70 °C/0.35 mm) to furnish 9.834 g of methoxy(phenylthio)(trimethylsilyl)methane (**34**) (96.5%) as a colorless oil: NMR ($CDCl_3/Me_4Si$) δ 0.09 (9 H, s, $Si(CH_3)_3$), 3.27 (3 H, s, CH_3O), 4.43 (1 H, s, CH), 7.12 (3 H, m, Ar CH), 7.24 (2 H, m, Ar CH); IR (film) cm^{-1} 3060, 3075 (Ar CH), 3025–2740 (CH envelope), 1585 (Ar C=C). Anal. Calcd for $C_{11}H_{18}OSiS$: C, 58.36; H, 8.01. Found: C, 58.13; H, 8.15.

(*E*)-1-Methoxy-3-methyl-1-(phenylthio)but-1-ene (37g). To a flame-dried, three-necked round-bottomed flask equipped with a magnetic stirring bar, low-temperature thermometer, rubber septum, and nitrogen inlet was added 0.996 g of methoxy(phenylthio)(trimethylsilyl)methane (**34**) (4.40 mmol) and 5 mg of 1,10-phenanthroline in 10 mL of dry THF. To this solution was added 0.73 mL of TMEDA (4.84 mmol). The solution was then treated with *sec*-BuLi in cyclohexane until an evident color change occurred. At this point a further 3.72 mL of *sec*-BuLi (1.30 M in cyclohexane, 4.84 mmol) was added dropwise at a rate to maintain a temperature of −70 °C (~10 min). After stirring for

Table I

carbonyl compound (36)	equiv of 35	deprotonation, %	yield, %
PhCHO	1.00	0	100
	1.00	0	100
	1.00	0	94
	1.00	7.2	92.6
	1.00	10.6	86.5
	1.00	21	60
	1.05	0	96

an additional 2.25 h at −78 °C, 0.48 mL of freshly distilled isobutyraldehyde (5.28 mmol) was added. After slowly being warmed to room temperature overnight, the reaction mixture was quenched with saturated aqueous NH_4Cl solution. The mixture was then extracted twice with pentane, and the combined organic layers were washed with H_2O and brine and subsequently dried over Na_2SO_4. Evaporation of the solvents in vacuo left an orange oil which was filtered through a plug of silica gel (10% ethyl acetate–hexane for elution). Evaporation of the solvents in vacuo left 0.883 g (96%) of the ketene *O,S*-acetal: NMR ($CDCl_3/Me_4Si$) δ 1.03 (6 H, d, J = 6.8 Hz, CH_3), 2.80 (1 H, complex m, CH), 3.53 (3 H, s, CH_3O), 5.25 (1 H, d, J = 9.1 Hz, vinyl), 7.26 (5 H, m, Ar CH); IR (film) cm^{-1} 3062, 3080 (Ar CH), 3040–2780 (CH envelope), 1630 (C=C), 1588 (Ar C=C). Anal. Calcd for $C_{12}H_{16}OS$: C, 69.19; H, 7.74. Found: C, 68.97; H, 8.00.

The following ketene *O,S*-acetals were prepared in a similar manner.

(*E*)-1-Methoxy-2-phenyl-1-(phenylthio)ethene (37a): NMR ($CDCl_3/Me_4Si$) δ 3.70 (3 H, s, CH_3O), 6.30 (1 H, s, vinyl), 7.3 (10 H, complex m, Ar CH); IR (film) cm^{-1} 3100–2820 (CH envelope), 1615 (C=C). Anal. Calcd for $C_{15}H_{14}OS$: C, 74.35; H, 5.82. Found: C, 74.24; H, 5.82.

1-Methoxy-4-phenyl-1-(phenylthio)-1,3-butadiene (37b): NMR ($CDCl_3/Me_4Si$) δ 3.68 (3 H, s, CH_3O), 6.02 (1 H, d, J = 6.4 Hz, vinyl), 6.13 (1 H, d, J = 6.4 Hz, vinyl), 6.51 (1 H, complex m, vinyl), 7.36 (10 H, m, Ar CH), IR (film) cm^{-1} 3125–2830 (CH envelope), 1590 (C=C). Anal. Calcd for $C_{17}H_{16}OS$: C, 76.08; H, 6.01. Found: C, 75.90; H, 6.16.

1-Methoxy-1-(phenylthio)-1,3-pentadiene (37c): NMR ($CDCl_3/Me_4Si$) δ 1.42 (3 H, d, J = 6.9 Hz, CH_3), 3.70 (3 H, s, OCH_3), 5.55 (1 H, d, J = 16 Hz, vinyl), 6.92 (2 H, m, vinyl), 7.34 (10 H, complex m, Ar CH); IR (film) cm^{-1} 3100–2820 (CH envelope), 1655 (C=C); high resolution mass spectrum calcd for $C_{12}H_{14}OS$ M^+ 206.0732, found M^+ 206.0762.

4-*tert*-Butyl-1-[methoxy(phenylthio)methylene]cyclohexane (37d): NMR ($CDCl_3/Me_4Si$) δ 0.87 (9 H, s, $C(CH_3)_3$), 1.23 (2 H, m, CH_2), 1.65 (1 H, m, CH), 1.91 (4 H, m, CH_2), 3.10 (2 H, m, CH_2), 3.53 (3 H, s, CH_3O), 7.30 (5 H, m, Ar CH); IR (film) cm^{-1} 3095, 3088 (Ar CH), 1640 (C=C), 1590 (Ar C=C). Anal. Calcd for $C_{18}H_{26}OS$: C, 74.43; H, 9.02. Found: C, 74.34; H, 8.97.

1-[Methoxy(phenylthio)methylene]-3,5,5-trimethylcyclohex-2-ene (37e): NMR ($CDCl_3/Me_4Si$) δ 0.92 (3 H, s, CH_3), 0.95 (3 H, s, CH_3), 1.85 (4 H, complex m, allylic CH_2), 2.28 (3 H, br s, allylic CH_3), 3.55 (3 H, s, CH_3O), 6.48 (1 H, s with fine splitting, vinyl), 7.25 (5 H, m, Ar CH); IR (film) cm^{-1} 3085, 3070 (Ar CH), 3040–2795 (CH envelope), 1590 (C=C). Anal. Calcd for $C_{17}H_{22}OS$: C, 74.40; H, 8.08. Found: C, 74.28; H, 7.87.

1-[Methoxy(phenylthio)methylene]-2-methyl-5-(propen-2-yl)cyclohex-2-ene (37f): NMR ($CDCl_3/Me_4Si$) δ 1.75 (3 H, br s, allylic CH_3), 1.90 (4 H, complex m, overlapping CH_2), 2.22 (3 H, br s, allylic CH_3), 2.43 (1 H, complex m, CH), 3.74 (3 H, s, CH_3O), 4.70 (1 H, m, vinyl), 7.28 (5 H, m, Ar CH); IR (film) cm^{-1} 3092 (Ar CH), 3050–2790 (CH envelope), 1670 (C=C). Anal. Calcd for $C_{18}H_{22}OS$: C, 75.48; H, 7.74. Found: C, 75.56; H, 7.66.

5-Phenyl 3-Methylbutanethioate (38) via Hydrolysis of 37g. A flame-dried, round-bottomed flask was charged with 0.035 g of the ketene *O,S*-acetal **37g** (0.166 mmol), 0.030 g of dry NaI (0.202 mmol), and 3.33 mL of dry CH_3CN. The reaction mixture was then treated with 0.025 mL of freshly distilled (CaH_2) chlorotrimethylsilane (0.200 mmol) and then stirred for 5 min. The solution was then filtered through a plug of activity III neutral alumina (acetonitrile for elution). After evaporation of the solvents in vacuo, 29 mg (90%) of the thio ester **38** was isolated: NMR ($CDCl_3/Me_4Si$) δ 1.01 (6 H, d, J = 6.5 Hz, CH_3), 2.05 (1 H, m, CH), 2.55 (2 H, d, J = 6.3 Hz, CH_2), 7.44 (5 H, m, Ar CH): IR (film) cm^{-1} 3080, 3060 (Ar CH), 3030–2800 (CH envelope), 1710 (C=O). Anal. Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26. Found: C, 67.88; H, 7.33.

2-Phenyl-1-(phenylthio)-1-[(trimethylsilyl)oxy]ethene (39). A round-bottomed flask fitted with a reflux condensor was flame-dried under nitrogen. The flask was then charged with 0.869 g of the ketene *O,S*-acetal **37a** (3.59 mmol) in 5 mL of dry CH_3CN. To this solution was added 1.02 mL of iodotrimethylsilane (7.18 mmol). The mixture was refluxed for 20 h and then cooled to room temperature. Dimethyl carbonate 0.605 mL (7.18 mmol) was added, and the mixture was stirred for an additional 2 h at 25 °C. The reaction mixture was then treated with 1.0 mL of triethylamine (7.17 mmol), and the solvents were removed in vacuo to leave a white suspension. This residue was triturated several times with dry hexane and centrifuged. The combined hexane extracts were concentrated to furnish 1.08 g of the silyl ether **39** (100%) as an oil which was determined to be 92.0% pure by GC analysis: NMR ($CDCl_3/Me_4Si$) δ 0.17 (9 H, s, $Si(CH_3)_3$), 6.13 (1 H, s, vinyl), 7.30 (10 H, m, Ar CH); IR (film) cm^{-1} 3080 (Ar CH), 3050–2800 (CH envelope). Anal. Calcd for $C_{17}H_{20}OSSi$: C, 67.95; H, 6.71. Found: C, 67.80; H, 6.59. The presence of 8% of the corresponding thio ester was also revealed.

1-(Phenylacetyl)pyrrolidine (42b). To an oven-dried, round-bottomed flask equipped with a magnetic stirring bar was added 0.147 g of the ketene *O,S*-acetal **37a** (0.60 mmol). The flask was flushed with N_2, and 2.43 mL of lithium thiomethoxide (1 M in HMPA, 2.43 mmol) was added. After being stirred at 25 °C for 30 min, 2.43 mL of AcOH (1 M in THF, 2.43 mmol) was added. After 2 min, 0.152 mL of pyrrolidine (1.82 mmol) was added, and the reaction mixture was then stirred at 60 °C for 36 h. The solution was poured into saturated aqueous NH_4Cl solution and extracted with pentane. The aqueous layer was extracted several times with a mixture of pentane–ether (1:1). The combined organic fractions were washed with saturated brine and dried over Na_2SO_4. After evaporation of the solvents in vacuo, the residue was filtered through a bed of silica gel (10% EtOAc–hexane for elution) which removed the nonpolar side products. Final elution with 5% MeOH in CH_2Cl_2 provided 0.109 g (95%) of the amide **42b**: NMR ($CDCl_3/Me_4Si$) δ 1.86 (8 H, complex m, CH_2), 3.45 (4 H, m, CH_2), 3.65 (2 H, s, CH_2), 7.27 (5 H, m, Ar CH); IR (film) cm^{-1} 2995–2900 (CH envelope), 1680 (C=O).

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Registry No. **12**, 5323-87-5; **15b**, 99706-73-7; **20**, 13865-50-4; **21b**, 6267-39-6; **22**, 99706-74-8; **24**, 50404-05-2; **25**, 99706-75-9; (*E*)-**26**, 99706-80-6; (*Z*)-**26**, 99706-81-7; (*E*)-**27**, 99706-78-2; (*Z*)-**27**, 99706-79-3; (*E*)-**28**, 99706-82-8; (*Z*)-**28**, 99706-83-9; **29**, 99706-77-1; **30a**, 99706-84-0; **32**, 99706-85-1; **33**, 93500-20-0; **34**, 88738-21-0; **35**, 87262-37-1; **36a**, 100-52-7; **36b**, 104-55-2; **36c**, 4170-30-3; **36d**, 98-53-3; **36e**, 78-59-1; **36f**, 99-49-0; **36g**, 78-84-2; (*E*)-**37a**, 88738-26-5; (*Z*)-**37a**, 88738-27-6; (*E*)-**37b**, 99706-86-2; (*Z*)-**37b**, 99706-88-4; (*E*)-**37c**, 99706-87-3; (*Z*)-**37c**, 99706-89-5; (*E*)-**37d**, 93500-45-9; (*E*)-**37e**, 93500-46-0; (*Z*)-**37e**, 93500-14-2; (*E*)-**37f**, 93500-47-1; (*Z*)-**37f**, 93500-15-3; (*E*)-**37g**, 93500-48-2; (*Z*)-**37g**, 93500-16-4; **38**, 93500-17-5; (*E*)-**39**, 93500-18-6; (*Z*)-**39**, 93500-19-7; **42b**, 3389-53-5; $BrCH_2COOBu$-*t*, 5292-43-3; methallyl iodide, 3756-30-7; dimethoxymethane, 109-87-5; thiophenol, 108-98-5; methyl acrylate, 96-33-3; methyl vinyl ketone, 78-94-4; 1,4-diiodobutane, 628-21-7; butyl iodide, 542-69-8; iodotrimethylsilane, 16029-98-4; pyrrolidine, 123-75-1.