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ACTIVATION AND SYNTHETIC APPLICATIONS OF THIOSTANNANES. THIOALKOXYLATION OF ACETALS

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ABSTRACT: The Sn-S bonds in thiostannanes, $Bu_nSn(SPh)_{4-n}$, are activated towards acetals in the presence of $BF_3 \cdot OEt_2$. Acetals of various aldehydes and ketones are converted into the corresponding monothioacetals under mild conditions. Employment of α-enal acetals induces Michael addition to give synthetically useful γ-alkoxyally sulfides.

A tin-sulfur bond is thermodynamically most stable among various tin-hetero atom bonds in organotin comounds.[1] For instance, $Sn-NR_2$ and Sn-OR bonds are readily transformed into Sn-OR and Sn-SR bonds respectively by mixing with alcohols and thiols at room temperature, but no reverse reactions usually occur under analogous conditions. This is why thiostannanes have not enjoyed

$$Sn\text{-}NR_2 \underset{R_2NH}{\overset{ROH}{\rightleftharpoons}} Sn\text{-}OR \underset{ROH}{\overset{RSH}{\rightleftharpoons}} Sn\text{-}SR$$

synthetic applications so fruitfully as alkoxy- or aminostannanes.[2] Thiostannanes are easy to manipulate because of the stability towards heat, oxidation, and hydrolysis as well as of little odorous property. Accordingly, once an effective method for activating Sn-S bonds is developed, they are expected to serve as mild thioalkoxylation reagents. Most of precedent successful applications, though not so many, relied on reactions with alkyl or acyl halides with recourse to facile transformation of an Sn-S bond into an Sn-halogen bond.[3] More recently, Ogawa et al. disclosed thioglycosidation of 1-acetoxyglycosides as well as 1-halo derivatives through the combined use of thiostannanes and $SnCl_4$.[4] It has been reported that p-toluenesulfonic acid effected cleavage of $Bu_2Sn(SPr)_2$ with ethanol giving the corresponding ethoxide although the reaction proceeded very slowly to require about 200 hours of refluxing in an ethanol solvent for completion.[5] Now we have found that $BF_3 \cdot OEt_2$ (**2**) allows for this type of contra-thermodynamic reations with greater facility and mildness. Exposure of thiostannanes **1** to various acetals in the presence of **2** leads to alkoxystannanes; in the meanwhile monothioacetals are sole products when acetals other than α-enal acetals are employed whereas these acetals provide γ-alkoxyallyl sulfides.[6]

$Bu_nSn(SR)_{4-n}$
1a: n = 3, R = Ph
1b: n = 2, R = Ph
1c: n = 3, R = $PhCH_2$

Synthesis of Monothioacetals 3. Monothioacetals are synthetically useful reagents[7] and usually accessible through acid-promoted modification of acetals with thiols. This transacetalization method, however, suffers from low yields of **3** or contamination by dithioacetals **4** on some occasions.[8] Actually, we confirmed that treatment of benzaldehyde dimethyl acetal with 1.1 equiv of thiophenol in the presence of **2** (1.0 equiv) in toluene furnished the monothioacetal (62%), the dithioacetal (3%), and the unchanged acetal (33%) after 2 h. Diethylaluminum thiophenoxide accordingly was reported to serve well to this end.[8] Herein is described an organotin method (eq 1).

$$RR'C(OMe)_2 + \mathbf{1} \xrightarrow{\text{Lewis acid}} \underset{\mathbf{3}}{RR'C(OMe)(SPh)} + \underset{\mathbf{4}}{RR'C(SPh)_2} \qquad (1)$$

First, we have investigated the effect of Lewis acids in dichloromethane. As is evident from Table 1, only **2** was satisfactory. Contamination by **4** or low conversion resulted with other promotors including $SnCl_4$ which had been employed for 1-acetoxyglycosides.[5]

Table 1. Effect of Lewis Acids in the Reaction (1) Employing **1a** (1.3 equiv) in CH_2Cl_2.

acetal	Lewis acid[a]	conditions °C	conditions h	yield(%)[a] of **3**	yield(%)[a] of **4**	acetal unchanged(%)[b]
n-$C_8H_{17}CH(OMe)_2$	**2**	-20	0.5	83	4	13
	$AlCl_3$	-20	1	58	32	
	$ZnBr_2$	25	5	12	0	87
	$SnCl_4$	-20	2	39	25	36
cyclo-$C_6H_{11}CH(OMe)_2$	$TiCl_4$	-20	0.5	8	58	23
	BCl_3	-20	0.5	3	56	7

[a] One equivalent to an acetal.

[b] Based on GLC analysis.

Next, solvents were screened for the reaction between n-$C_8H_{17}CH(OMe)_2$ and **1a** (1.1 equiv) in the presence of **2** (1.0 equiv) at -20 °C. Table 2 indicates toluene to be the best: the yield of n-$C_8H_{17}CH(OMe)(SPh)$ (**3a**) was quantitative and no n-$C_8H_{17}CH(SPh)_2$ (**4a**) formed at all.

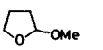
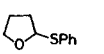
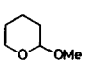
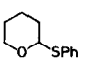
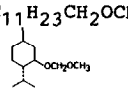
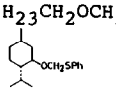
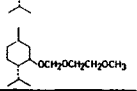
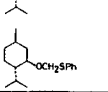
As a result, we chose **2** as a promotor and toluene as a solvent for the standard conditions. With these data in hand, we conducted various reactions to attest the generality of this method. The results are summarized in Table 3. Acetals of aliphatic aldehydes (entries 1-6), acyclic and cyclic ketones (entries 7,8),[9] an aromatic aldehyde (entries 9,10), and an α,β-acetylenic aldehdye (entry 11) are available. In the case where a dithioacetal is formed under standard conditions (entry 9), use of a mixed solvent (3:2 toluene-hexane) improves the selectivity for **3** (entry 10). This also holds for

Table 2. Solvent effect in the Reaction (1).

solvent	reactn time (h)	3a (%)	4a (%)	acetal unchanged(%)
toluene	1	100	0	
CH_2Cl_2[a]	0.5	83	4	13
ether	1	52	0	18
CH_3CN	2	31	0	69

[a] 1a (1.3 equiv) was employed; see Table 1.

Table 3. Synthesis of Monothioacetals 3.

entry	2	1[a]	reaction temp(°C)	time(h)	3	yield(%)[b]
1	n-$C_8H_{17}CH(OMe)_2$	1a(1.1)	-20	1	n-$C_8H_{17}CH(OMe)(SPh)$	100
2		1b(0.55)	-78	4		91(76)[c]
3		1c(1.1)	-40	4[d]	n-$C_8H_{17}CH(OMe)(SBn)$	78(80)[e]
4	n-$C_8H_{17}CH(OEt)_2$	1a(1.1)	-20	1	n-$C_8H_{17}CH(OEt)(SPh)$	100(85)
5	cyclo-$C_6H_{11}CH(OMe)_2$	1a(1.3)	-20	1	cyclo-$C_6H_{11}CH(OMe)(SPh)$	99(70)
6	n-$C_8H_{17}C(CH_3)_2CH(OMe)_2$	1a(1.1)	-20	1	n-$C_8H_{17}C(CH_3)_2CH(OMe)(SPh)$	100
7	n-$C_6H_{13}C(OMe)_2CH_3$	1a(1.1)	-78	1[d]	n-$C_6H_{13}C(OMe)(SPh)CH_3$	85[f]
8	$(CH_2)_5C(OMe)_2$	1a(1.1)	-78	1[g]	$(CH_2)_5C(OMe)(SPh)$	69[f]
9	$PhCH(OMe)_2$	1a(1.1)	-78	1	$PhCH(OMe)(SPh)$	87[h]
10		1a(1.1)	-78	1[d]		100
11	n-$C_6H_{13}C{\equiv}CCH(OMe)_2$	1b(0.6)	-50~-30	5	n-$C_6H_{13}C{\equiv}CCH(OMe)(SPh)$	96(73)
12		1a(1.1)	-78	2		100
13		1a(1.1)	-20	1		100(100)
14	n-$C_{11}H_{23}CH_2OCH_2OCH_3$	1a(1.1)	0	4	n-$C_{11}H_{23}CH_2OCH_2SPh$	69
15		1a(1.1)	0	4		80(64)
16		1a(1.1)	0	4		77

[a] The amount of employed 1 (equivalent to an acetal) is shown in the parentheses.

[b] Based on GLC unless otherwise noted. Isolated yields are given in the parentheses.

[c] GLC exhibited 4 in 6% yield.

[d] A mixture of toluene-hexane (3:2 in volume) was used as a solvent.

[e] GLC exhibited 4 in 8% yield.

[f] Based on NMR spectra.

[g] 2 (0.5 equiv) was used.

[h] GLC exhibited 4 in 2% yield.

entries 3 and 7, otherwise the yield of **4** increased. The thiophenoxides **1a** and **1b** work equally well, but the benzyl compound **1c** gives rise to somewhat lower selectivity and yield (entry 3). Practically, dibutyltin derivatives are preferable to the tributyltin counterparts since the amount of **1** required are halved and the dibutyltin oxide formed in aqueous workup are easily removed through filtration followed by column chromatogaphy.

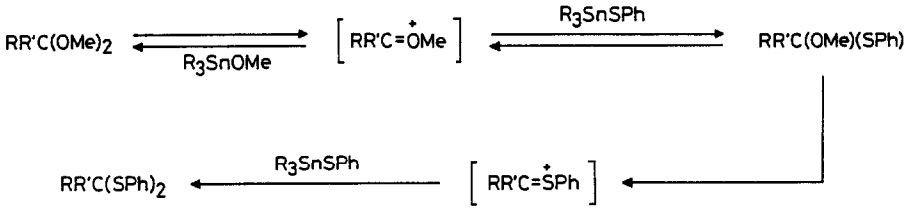
The reaction proceeds quantitatively with cyclic ethers having an α-alkoxy substituent. These results are of synthetic interest in relation to the recent studies which revealed conversion of 2-phenylthiotetrahydrofurans into 2,3-dihydrofurans.[10] Of further interest is exclusive cleavage of methoxymethyl (MOM) and (2-methoxyethoxy)methyl (MEM) ethers providing the phenylthiomethyl ethers (entries 14-16). No other products are detected. The only precedent example of this transformation has been reported by Morton et al. who utilized two-step procedure: reaction with dimethylboron bromide followed by treating the resulting bromomethyl ethers with thiols in the presence of diisopropylethylamine.[11]

In the hope of obtaining further insight into the reaction path, we investigated the reaction employing 2.2 equiv of **1a** (eq 2). GLC analysis

$$n\text{-}C_8H_{17}CH(OMe)_2 + \underset{\textbf{1a}}{Bu_3SnSPh} \xrightarrow{2(2.0\ \text{equiv})} \textbf{3a} + \textbf{4a} \qquad (2)$$

reaction time (h)	reaction temp (^{o}C)	yield (%) of **3a**	yield (%) of **4a**
12	-78	95	4
4	-20	0	100

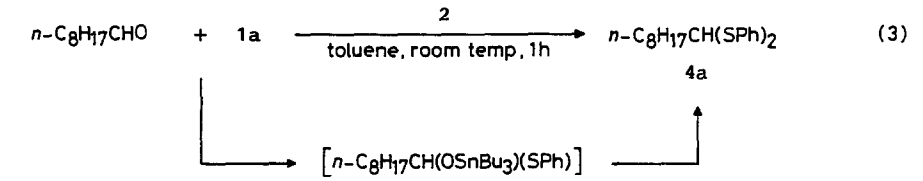
showed that at -78 ^{o}C after 12 h, the acetal was completely consumed to afford a quantitative yield of **3a** along with a small amount of **4a**. The reaction was no more forwarded to increase **4a**. When the reaction was conducted at -20 ^{o}C on the other hand, **4a** was produced in 100% yield after 4 h. The great gap in the reactivities of the acetal and the monothioacetal for the thioalkoxylation can be interpreted in terms of the increased facility with which an oxonium ion is generated from the acetal as compared with a thionium ion from the



monothioacetal. This, however, does not necessarily lead us to conclude that the high preference of the present reaction for monothioacetals is totally ascribed to the readiness of the cation formation. If this is true, the monothioacetal once formed might be reversed into the parent acetal on

interaction with the resulting alkoxystannane. Actually, treatment of Bu_3SnOMe with **3a** at -78 °C delivered, after 4 h, only 3% yield of the dimethylacetal along with **4a** (8%) and **3a** unchanged (87%). The appearance of the dimethylacetal and **4a** is attributed to the acid-promoted redistribution of **3a**. Apparently, activation of thiostannanes as well as acetals through coordination of **2** is responsible for the high selectivity.

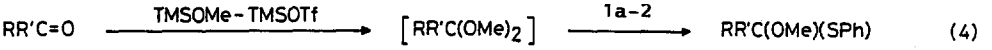
The reaction of unprotected aldehydes takes place quite differently. For example, exposure of nonanal to 1.1 equiv of **1a** furnished **4a** in 54% yield together with the unchanged aldehyde (39%) (eq 3).[12] Probably, **4a** was derived



(3)

from the proportionation of an intermediary O-stannylhemithioacetal, a result quite different from thiosilanes: ZnI_2-promoted reaction of (methylthio)-trimethylsilane with aldehydes provided O-silylhemithioacetals without any sign of redistribution.[13] Further worthy of note is that the present proportionation reaction is relatively slow so that employment of 2.2 equiv of **1a** afforded **4a** (85%) and the nonanal recovered (24%) after 1 h.

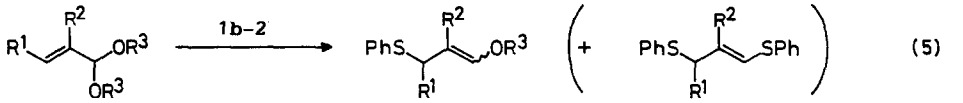
Failure of direct synthesis of monothioacetals from aldehydes or ketones was overcome with recourse to the Noyori's acetallization (eq 4). Initial treatment of carbonyls with TMSOMe-TMSOTf[14] and the subsequent addition of **1a-2** in situ provided monothioacetals quantitatively.



(4)

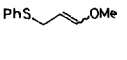
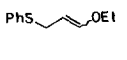
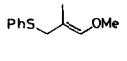
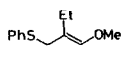
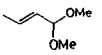
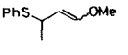
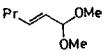
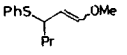
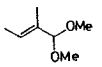
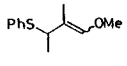
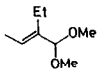
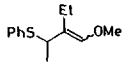
Synthesis of γ-Alkoxyallyl Sulfides 5. Synthetic utilities of **5** have been disclosed.[6b,15] Of special interest is the regiochemistry in the reaction between lithium salts of these compounds and electrophiles. In the presence of TMEDA, α-alkylation and γ-carbonylation take place[15] while all of electrophiles are incorporated at the α-position exclusively with t-BuLi-HMPA.[6b] The reaction products thus obtained were successfully applied to syntheses of α,β-unsaturated carbonyl compounds and trisubstituted furans. A few methods have appeared for preparation **5**. 3-Methoxy-1-phenylthio-2-propene was obtained from methoxyallene and thiophenol by Hoffmann.[16] Takei[17] and Julia[18] independently prerpared **5** by alkylation of 3-methoxy-1-phenylthio-1-propene. We devised a route to arrive at various types of **5** employing methoxy-(phenylthio)methane.[6b] Now, the thiostannane-mediated thioalkoxylation has provided us with a more general and simple method.

Treatment of α-enal acetals with **1b** together with **2** in toluene at -78 °C furnished **5** in good to excellent yields (eq 5). Table 4 summarizes the



(5)

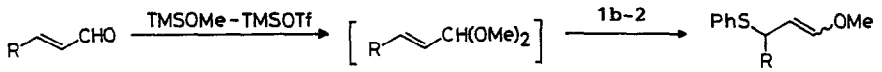
Table 4. Synthesis of γ-Alkoxyallyl Sulfides 5.

entry	$R^1CH=C(R^2)CH(OR^3)_2$	5	yield(%)[a]	E:Z
1			93	81:19
2			92	92:8
3			95	100:0
4			96	100:0
5			83(4)	90:10
6			78(8)	89:11
7			84(12)	73:27
8			70:(15)	63:37

[a] Yields of 6 are gvien in parentheses.

results. In the cases where R^1 = alkyl, γ-phenylthioallyl sulfides 6 formed as minor by-products, which were removed easily from 5 through column chromatography. The present method, however, proved not to be applicable to dimethyl acetals of 1-cyclopentene carbaldehyde and 2-cyclohexenone. In the former case, a mixture of the desired compound and a hemithio acetal (transacetallization product) was obtained while the latter compound resulted in complex produts which could not be identified.

The similar acid-promoted Michael addition has been reported for the reaction of (methythio)trimethylsilane with methacrolein to provide β-methlythioenol silyl ether.[13] One-pot transformation of α-enals into 5 based on the thiostannane method was achieved according to eq 6.



(6)

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EXPERIMENTAL

^{1}H NMR spectra were recorded at 100 MHz on a JEOL JNM-FX 100 spectrometer. Chemical shifts are given in ppm relative to tetramethylsilane as an internal standard. Mass spectra were obtained on a JEOL JMS-DX 303-HF mass spectrometer using electron impact ionization. Optical rotations were measured on a JASCO DIP-360 digital polarimeter using 10 cm cells. Column chromatography was performed on Kieselgel 60 (70-230 mesh) (E. Merck) and Aluminum Oxide 90 (E. Merck). Thin layer chromatography was performed on Merck Kieselgel 60 F_{254}. GLC was performed on Shimadzu GC-8A with 2% Silicone OV 17 on chromosorb W (3.2ϕ x 2000). Toluene, CH_2Cl_2, hexane, and CH_3CN were distilled from CaH_2. Ether was distilled from sodium-benzophenone ketyl prior to use.

Preparation of Monothioacetals 3; Typical Procedure. To a toluene solution of cyclohexanecarbaldehyde dimethyl acetal(79 mg, 0.5 mmol) and **1a** (259 mg, 0.65 mmol) was added $BF_3{\cdot}OEt_2$ (1.0 M toluene solution, 0.5 ml, 0.5 mmol) at -20 °C. The solution was stirred for 1 h. GLC analysis of the reaction mixture indicated formation of the corresponding monothioacetal in 99% yield relative to n-$C_{15}H_{32}$ as an internal standard. No dithioacetal was detected. Dry pyridine (0.24 ml) and 1 M NaOH solution (1 ml) were added to the reaction mixture, which, then, was diluted with ether. The organic layer was washed with 1 M NaOH solution and water. Drying (Na_2SO_4) and evaporation left a colorless oil, which was purified through column chromatography on silica gel (80:20 hexane-benzene) to give pure [methoxy(phenylthio)methyl]cyclohexane (165 mg, 70%) identical with an authentic specimen; δ_H ($CDCl_3$) 1.18 (5 H, m), 1.73 (6 H, m), 3.41 (3 H, s), 4.40 (1 H, d, J 6.6 Hz), 7.25 (3 H, m), 7.45 (2 H, m); m/z 236 (M^+); HRMS Found: M^+, 236.1253. $C_{14}H_{20}OS$ requires M^+, 236.1235.

Other monothioacetals were obtained as oils analogously and confirmed by comparison with authentic samples. Contamination by the corresponding dithioacetals was checked on the basis of GLC analysis.

1-Methoxy-1-phenylthiononane, b.p. 180 °C/0.1 mm; δ_H ($CDCl_3$) 0.87 (3 H, t, J 5.6 Hz), 1.25 (14 H, m), 3.46 (3 H, s), 4.62 (1 H, t, J 6.3 Hz), 7.35 (3 H, m), 7.42 (2 H, m); m/e 266 (M^+); HRMS Found: 266.1733 (M^+). $C_{16}H_{26}OS$ requires 266.1704 (M^+).

1-Benzylthio-1-methoxynonane; δ_H ($CDCl_3$) 0.87 (3 H, t, J 5.4 Hz), 1.24 (12 H, m), 1.75 (2 H, m), 3.32 (3 H, s), 3.73 (2 H, s), 4.37 (1 H, t, J 6.6 Hz), 7.28 (5 H, m); m/e 280 (M^+); HRMS Found: 280.1883 (M^+). $C_{17}H_{28}OS$ requires 280.1861 (M^+).

1-Ethoxy-1-phenylthiononane; δ_H ($CDCl_3$) 0.87 (3 H, t, J 5.4 Hz), 1.25 (17 H, m), 3.49 (1 H, m), 3.94 (1 H, m), 4.68 (1 H, t, J 6.3 Hz), 7.27 (3 H, m), 7.45 (2 H, m); m/e 280 (M^+); HRMS Found: 171.1743 (M^+ - C_6H_5S). $C_{11}H_{23}O$ requires 171.1749 (M^+ - C_6H_5S).

2,2-Dimethyl-1-methoxy-1-phenylthiodecane; δ_H ($CDCl_3$) 0.87 (3 H, t, J 6.1 Hz), 1.02 (3 H, s), 1.04 (3 H, s), 1.25 (14 H, m), 3.35 (3 H, s), 4.41 (1 H, s), 7.21 (3 H, m), 7.47 (2 H, m); m/e 308 (M^+).

2-Methoxy-2-phenylthiooctane; δ_H ($CDCl_3$) 0.88 (3 H, t, J 8.0 Hz), 1.25 (8 H, m), 1.39 (3 H, s), 1.68 (2 H, m), 3.46 (3 H, s), 7.27 (5 H, m); m/e 220 (M^+ - CH_3OH); HRMS Found: 220.1287 (M^+ -CH_3OH). $C_{14}H_{20}S$ requires 220.1286 (M^+ - CH_3OH).

1-Methoxy-1-phenylthiocyclohexane; δ_H ($CDCl_3$) 1.3-1.8 (10 H, m), 3.46 (3 H, s), 7.29 (5 H, m); m/e 190 (M^+ -CH_3OH); HRMS Found: 112.0905 (M^+ - C_6H_5SH). $C_7H_{12}O$ requires 112.0888 (M^+ - C_6H_5SH).

[Methoxy(phenylthio)methyl]benzene; δ_H ($CDCl_3$) 3.48 (3 H, s), 5.68 (1 H, s), 7.24 (10 H, m); m/e 199 ($M^+ - CH_3O$); HRMS Found: 199.0582 ($M^+ - CH_3O$). $C_{13}H_{11}S$ requires 199.0582 ($M^+ - CH_3O$).

2-Phenylthiotetrahydrofuran; δ_H ($CDCl_3$) 1.99 (3 H, m), 2.34 (1 H, m), 4.00 (2 H, m), 5.64 (1 H, dd, J 3.9 and 6.8 Hz), 7.27 (3 H, m), 7.48 (2 H, m); m/e 180 (M^+); HRMS Found: 180.0610 (M^+). $C_{10}H_{12}OS$ requires 180.0609 (M^+).

2-Phenylthiotetrahydropyran; δ_H ($CDCl_3$) 1.65 (6 H, m), 3.58 (1 H, m), 4.16 (1 H, m), 5.20 (1 H, dd, J 3.9 and 5.8 Hz), 7.26 (3 H, m), 7.44 (2 H, m); m/e 194 (M^+); HRMS Found: 194.0764 (M^+). $C_{11}H_{14}OS$ requires 194.0766 (M^+).

Lauryl phenylthiomethyl ether; δ_H ($CDCl_3$) 0.87 (3 H, t, J 5.9 Hz), 1.25 (20H, m), 3.59 (2 H, t, J 6.3 Hz), 4.98 (2 H, s), 7.22 (3 H, m), 7.43 (2 H, m); m/e 308 (M^+); HRMS Found: 308.2216 (M^+). $C_{19}H_{32}OS$ requires 308.2174 (M^+).

Menthyl phenylthiomethyl ether; $[\alpha]_D$ -199° (c 0.10, $CHCl_3$); δ_H ($CDCl_3$) 0.68 (3 H, d, J 6.8 Hz), 0.83 (3 H, d, J 7.1 Hz), 0.90 (3 H, d, J 6.6 Hz), 1.20-2.10 (9 H, m), 3.46 (1 H, dt, J 4.4 and 10.0 Hz), 4.98 (1 H, d, J 11.7 Hz), 5.16 (1 H, d, J 11.7 Hz), 7.21 (3 H, m), 7.47 (2 H, m); m/e 278 (M^+); HRMS Found: 278.1714 (M^+). $C_{17}H_{26}OS$ requires 278.1704 (M^+).

1-Methoxy-1-phenylthio-2-nonyne; ν_{max} (neat) 2215 cm^{-1}; δ_H ($CDCl_3$) 0.88 (3 H, t, J 5.6 Hz), 1.26 (8 H, m), 2.19 (2 H, m), 3.47 (3 H, s), 5.62 (1 H, t, J 2.2 Hz), 7.27 (3 H, m), 7.47 (2 H, m); m/e 262 (M^+); HRMS Found: 262.1400 (M^+). $C_{16}H_{22}OS$ requires 262.1391 (M^+).

One-pot Synthesis of 3 from Aldehydes; Typical Procedure. To a toluene solution (5 ml) of nonanal (142 mg, 1 mmol) were added methoxytrimethylsilane (0.33 ml, 2.4 mmol) and trimethylsilyl triflate (0.5 M CH_2Cl_2 solution, 0.4 ml, 0.2 mmol) at -78 °C. The solution was stirred for 2 h at this temperature. Then **1a** (439 mg, 1.1 mmol) and **2** (1.0 M toluene solution, 1 ml, 1 mmol) were added to this solution. The reaction mixture was kept under stirring at -78 °C. After 4 h, GLC analysis exhibited **3a** (72%) and **4a** (2%) relative to an internal standard, pentadecane.

Reaction of Benzaldehyde Dimethyl Acetal with Thiophenol in the Presence of $BF_3 \cdot OEt_2$. A toluene solution (5 ml) containing benzaldehyde dimethyl acetal (0.5 mmol), thiophenol (0.55 mmol), $BF_3 \cdot OEt_2$ (0.55 mmol), and hexadecane (100 μl) as an internal standard for GLC was stirred at -78 °C for 2 h. GLC analysis of the reaction mixture revealed foramation of the monothioacetal (62%), dithioacetal (3%), and dimethyl acetal unchanged (33%).

Preparation of γ-Alkoxyallyl sulfides 5, Typical Procedure. To a toluene solution (14 ml) of acrolein dimethyl acetal (204 mg, 2 mmol) and **2b** (496 mg, 1.1 mmol) was slowly added $BF_3 \cdot OEt_2$ (1 M toluene solution, 2 ml, 2 mmol) during the period of 5 min at -78 °C. The solution was stirred for 30 min at this temperature. Pyridine (0.48 ml) and 1 M NaOH solution were added. The reaction mixture was extracted with benzene (30 ml). The organic layer was washed with 1 M NaOH (10 ml) and brine (10 ml x 2). Drying (Na_2SO_4) and evaporation left an oil, which was purified through column chromatography on Aluminum oxide (activity II) (90:10-60:40 hexane-benzene) to give 1-methoxy-3-phenyl-1-propene (334 mg, 93%); δ_H (C_6D_6) 3.16 (3 H x 0.81, s), 3.38 (3 H x 0.19, s), 3.42 (2 H x 0.81, dd, J 1.0 and 7.6 Hz), 3.78 (2 H x 0.19, dd, J 1.0 and 6.8 Hz), 4.81 (1 H, m), 5.70 (1 H x 0.19, d, J 5.3 Hz), 6.36 (1 H x 0.81, d, J 12.6 Hz), 7.15 (3 H, m), 7.39 (2 H, m); m/e 180 (M^+); HRMS Found 180.0598 (M^+). $C_{10}H_{12}OS$ requires 180.0609 (M^+).

Other γ-alkoxylallyl sulfides were obtained as oils analogously.

1-Ethoxy-3-phenylthio-1-propene; δ_H (C_6D_6) 1.13 (3 H, t, J 6.8 Hz), 3.49 (2 H x 0.92, d, J 7.6 Hz), 3.49 (2 H, q, J 6.8 Hz), 3.88 (2 H x 0.08, d, J 7.1 Hz), 4.97 (1 H, dt, J 6.8 and 12.6 Hz), 5.88 (1 H x 0.08, d, J 7.3 Hz), 6.37 (1 H x 0.92, d, J 12.6 Hz), 7.1 (3 H, m), 7.47 (2 H, m); m/e 194 (M^+); HRMS Found 194.0766 (M^+). $C_{11}H_{14}OS$ requires 194.0766 (M^+).

(E)-1-Methoxy-2-methyl-3-phenylthio-1-propene; δ_H (C_6D_6) 1.87 (3 H, d, J 1.2 Hz), 3.10 (3 H, s), 3.33 (2 H, br s), 5.57 (1 H, br s), 7.08 (3 H, m), 7.37 (2 H, m); m/e 194 (M^+); HRMS Found 194.0750 (M^+). $C_{11}H_{14}OS$ requires 194.0766 (M^+).

(E)-2-Ethyl-1-methoxy-3-phenylthio-1-propene; δ_H (C_6D_6) 1.09 (3 H, t, J 7.6 Hz), 2.42 (2 H, q, J 7.6 Hz), 3.04 (3 H, s), 3.37 (2 H, d, J 1.0 Hz), 5.55 (1 H, br s), 7.05 (3 H, m), 7.35 (2 H, m); m/e 208 (M^+); HRMS Found 208.0899 (M^+). $C_{12}H_{16}OS$ requires 208.0922 (M^+).

1-Methoxy-3-phenylthio-1-butene; δ_H (C_6H_6) 1.32 (3 H x 0.9, d, J 6.8 Hz), 1.37 (3 H x 0.1, d, J 6.9 Hz), 3.07 (3 H x 0.9, s), 3.29 (3 H x 0.1, s), 3.61 (1 H, m), 4.42 (1 H x 0.1, dd, J 5.6 and 11.9 Hz), 4.69 (1 H x 0.9, dd, J 9.0 and 12.6 Hz), 5.51 (1 H x 0.1, d, J 5.6 Hz), 6.19 (1 H x 0.9, d, J 12.6 Hz), 7.10 (3 H, m), 7.39 (2 H, m); m/e 194 (M^+); HRMS Found 194.0777 (M^+). $C_{11}H_{14}OS$ requires 194.0766 (M^+).

1-Methoxy-3-phenylthio-1-hexene; δ_H (C_6H_6) 0.89 (3 H, t-like, J 6.3 Hz), 1.53 (4 H, m), 3.43 (3 H, s), 3.51 (1 H, m), 4.60 (1 H, dd, J 9.8 and 12.6 Hz), 5.57 (1 H x 0.11, d, J 5.7 Hz), 6.12 (1 H, d, J 12.6 Hz), 7.27 (5 H, m); m/e 222 (M^+); HRMS Found 222.0985 (M^+). $C_{13}H_{18}OS$ requires 222.1078 (M^+).

1-Methoxy-2-methyl-3-phenylthio-1-butene; δ_H (C_6H_6) 1.35 (3 H, d, J 7.1 Hz), 1.58 (3 H x 0.27, d, J 1.5 Hz), 1.86 (3 H x 0.73, d, J 1.2 Hz), 3.00 (3 H x 0.27, S), 3.04 (3 H x 0.73, s), 3.62 (1 H, q, J 7.1 Hz), 5.44 (1 H x 0.27, br s), 5.51 (1 H x 0.73, br s), 7.05 (3 H, m), 7.40 (2 H, m); m/e 208 (M^+); HRMS Found 208.0942 (M^+). $C_{12}H_{16}OS$ requires 208.0922 (M^+).

2-Ethyl-1-methoxy-3-phenylthio-1-butene; δ_H (C_6H_6) 0.99 (3 H x 0.37, t, J 7.3 Hz), 1.18 (3 H x 0.63, t, J 7.6 Hz), 1.38 (3 H x 0.63, d, J 7.1 Hz), 1.39 (3 H x 0.37, d, J 7.1 Hz), 2.37 (2 H, q, J 7.6 Hz), 3.08 (3 H, s), 3.66 (1 H, q, J 7.1 Hz), 5.54 (1 H x 0.37, br s), 5.58 (1 H x 0.37, br s), 7.11 (3 H, m), 7.43 (2 H, m); m/e 222 (M^+); HRMS Found 222.1117 (M^+). $C_{13}H_{18}OS$ requires 222.1078 (M^+).

One-pot Synthesis of **5** from α-Enals; Typical Procedure. To a toluene solution (3 ml) of trans-2-hexenal (98 mg, 1 mmol) and methoxytrimethylsilane (250 mg, 2.4 mmol) was added trimethylsilyl triflate (0.3 M toluene solution, 0.33 ml, 0.1 mmol) at -78 °C. The solution was stirred at -40 °C for 1.5 h and -20 °C for 30 min. Then, the solution was cooled again down to -78 °C, to which were added **2** (142 mg, 1 mmol) and **1b** (248 mg, 0.55mmol). After being stirred for 30 min at this temperature, the reaction mixture was treated with pyridine (0.24 ml) and 1N NaOH (1 ml) and extracted with benzene (15 ml). The organic layer was washed with 1N NaOH (7 ml) and brine (7ml x 2). The workup and purification as described above provided 1-methoxy-3-phenylthio-1-hexene (150 mg, 67%) and 1,3-bis(phenylthio)-1-hexene (2 mg, 0.6%).

Reaction of 1-Cyclopentene Carbaldehyde Dimethyl Acetal with **1b**. To a toluene solution (7 ml) of 1-cyclopentene carbaldehyde dimethyl acetal (142 mg, 1 mmol) and **1b** (248 mg, 0.55 mmol) was added **2** (1 M toluene solution, 1 ml, 1 mmol) at -78 °C. After being stirred for 30 min at this temperature, the reaction mixture was quenched with pyridine (0.48 ml) and 1N NaOH (1 ml), and then extracted with benzene (10 ml). The organic layer was washed with 1N NaOH (5 ml) and brine (5 ml x 2). Drying (Na_2SO_4) and evaporation left a crude oil which was subjected to column chromatography on ammonia-pretreated silaca gel

(9:1-6:4 hexane-benzene). The first fraction, a mixture of 1-(methoxymethylidene)-2-phenylthiocyclopentene and 1-[(methoxy)phenylthiomethyl]-1-cyclopentene (160 mg, 75%); δ_H (C_6D_6) 1.20-2.56 (6 H, m), 3.15 (1 H, m), 3.19 (3 H, s), 4.85 (1 H x 1/3, br s), 5.91 (1 H x 1/3, m), 6.29 (1 H x 1/3, m), 7.00 (3 H, m), 7.38 (2 H, m); m/e 220 (M^+); HRMS Found: 220.0866 (M^+). $C_{13}H_{16}OS$ requires 220.0922 (M^+). The second fraction, 2-phenylthio-1-(phenylthiomethylidene)cyclopentane (46 mg, 15%); δ_H (C_6D_6) 1.10-2.60 (6 H, m), 3.99 (1 H, m), 6.32 (1 H, m), 7.00-7.30 (10 H, m); m/e 298 (M^+); HRMS Found 298.0866 (M^+). $C_{18}H_{18}S_2$ requires 298.0850 (M^+).

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