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Electro-Initiated Oxygenation of Alkenylsilanes in the Presence of Thiophenol.

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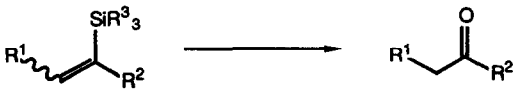
Abstract: Electrolysis of alkenylsilanes in the presence of thiophenol with bubbling of molecular oxygen gave the corresponding α-phenylthio carbonyl compounds with the consumption of a catalytic amount of electricity. An electro-initiated radical chain mechanism is proposed. The reaction also took place without electrochemical initiation, but much longer reaction time was required for the completion of the reaction. Since various types of alkenylsilanes are prepared by the alkylation of 1-bromo-1-(trimethylsilyl)ethene, 1-bromo-1-(trimethylsilyl)ethene can be utilized as a synthon of phenylthioacetyl anion. The oxygenation of 1-phenylthio-1-(trimethylsilyl)alkenes in the presence of thiophenol gave α-phenylthio thiolesters indicating that the carbon-silicon bond was cleaved exclusively without affecting the carbon-sulfur bond.

Alkenylsilanes are useful precursors of carbonyl compounds (Scheme I) which can be unmasked by epoxidation followed by acid-catalyzed rearrangement.[1] Recently, Tamao et al. reported that the oxygenation reaction of alkenylsilanes catalyzed by tetraacetylriboflavin in the presence of N-benzyl-1,4-dihydronicotinamide gave the corresponding carbonyl compounds.[2] Kato and Mukaiyama also reported the cobalt complex-catalyzed oxygenation of alkenylsilanes to the carbonyl compounds.[3]

Scheme I.

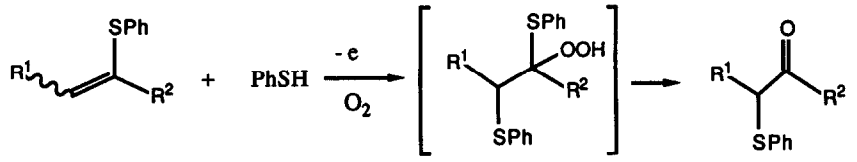


These reactions provide effective and useful methods for the conversion of alkenylsilanes into the carbonyl compounds. However, in the case of the resulting carbonyl compound being an unsymmetrical ketone where it is necessary to functionalize the α-position, there is the problem of regioselectivity. Generally regioselective activation of one of two α-position of an unsymmetrical ketone is difficult. But these two α-

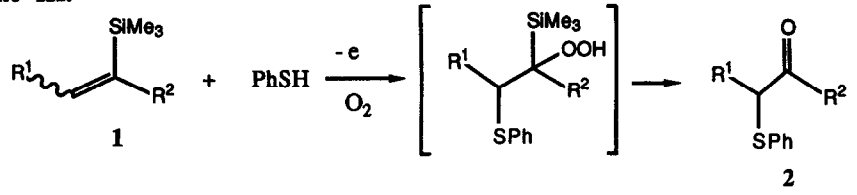
positions should be easily distinguished from one another in the original alkenysilanes, since one is associated with the olefinic carbon.

Recently we found that the electro-initiated oxygenation reaction of alkenyl sulfides gave the carbonyl compounds having phenylthio group at the α-position regiospecifically (Scheme II).[4] The phenylthio radical adds to the carbon-carbon double bond of alkenyl sulfides and the resulting radical reacts with molecular oxygen. The α-phenylthio substituted hydroperoxide intermediate thus obtained decomposes to give the corresponding α-phenylthio carbonyl compounds. This successful oxygenation of alkenyl sulfides prompted us to examine a similar reaction of alkenylsilanes. Preliminary investigation in our laboratory revealed that the oxygenation of alkenylsilanes in the presence of thiophenol also gave the corresponding α-phenylthio carbonyl compounds (Scheme III).[5] The reaction provides a direct and regiospecific route from alkenylsilanes to carbonyl compounds having an activating group at the α position. In this paper we wish to report the full details of the results.

Scheme II.



Scheme III.



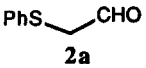
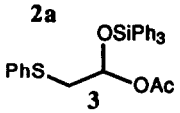
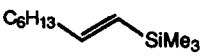
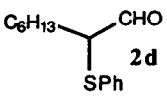
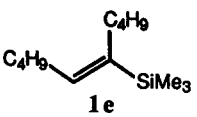
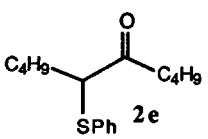
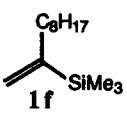
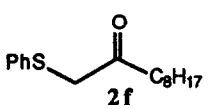
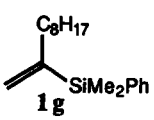
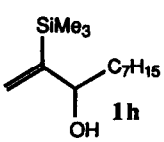
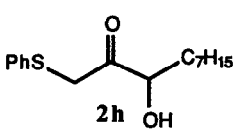
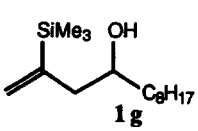
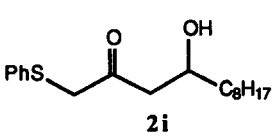
1 2

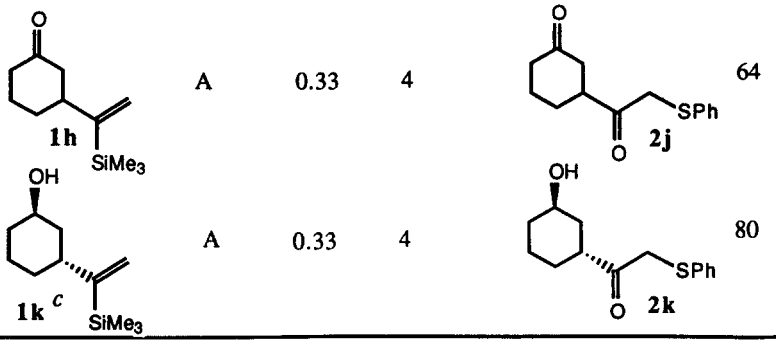
Results and Discussion

Electro-initiated oxygenation reactions of alkenylsilanes (**1**) were carried out as follows. An alkenylsilane and thiophenol were dissolved in 0.2 M Et_4NOTs / AcOH and oxygen gas was bubbled through the solution. Constant current electrolysis (1 min) was repeated with an interval of 30 min. After most of the alkenylsilane was consumed, aqueous work-up followed by flash chromatography gave the corresponding α-phenylthio carbonyl compound (**2**) (Method A, See Experimental Section).

As shown in Table I, phenylthiomethyl ketones can be obtained from the corresponding α-alkyl-substituted vinylsilanes (**1f** - **1k**) in good yields. However, reactivities of β-alkyl-substituted (**1d**) and α,β-dialkyl-substituted vinylsilanes (**1e**) are low. Therefore, from a synthetic point of view, the present reaction is applicable only to α-alkyl-substituted vinylsilanes. It is also noteworthy that hydroxyl and carbonyl groups are compatible with the present reaction. The electro-initiated oxygenation of alkenylsilanes having such functional groups gave the corresponding carbonyl compounds in high yields without protection of such functional groups.

Table I. Oxygenation of Alkenylsilanes in the Presence of Thiophenol Å

alkenylsilane	method [a]	electricity (F/mol)	time (h)	product	yield [b] (%)
 **1a**	A	0.16	2	 **2a**	68
	B		25	**2a**	35
 **1b**	B		45	**2a**	24
 **1c**	B		21	**2a**	42
				+  **3**	52
 **1d**	A	1.19	24	 **2d**	12
	B		95	**2d**	24
 **1e**	A	1.12	32	 **2e**	13
	B		13 days	**2e**	33
 **1f**	A	0.30	6	 **2f**	73
	B		31	**2f**	68
 **1g**	A	0.49	5	**2f**	76
	B		38	**2f**	71
 **1h**	A	0.38	4	 **2h**	89
	B		24	**2h**	43
 **1g**	A	0.21	2.5	 **2i**	93
	B		30	**2i**	91

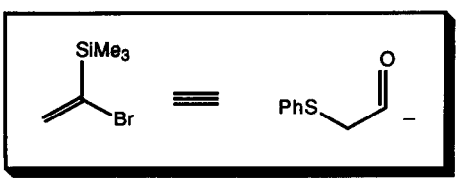


[a] Method A: The reactions were carried out with 0.3-0.5 mmol of alkenylsilane and 2-4 equiv of thiophenol in 0.2 M Et_4NOTs / AcOH with electrochemical initiation. Method B: The reactions were carried out with 0.3-1.0 mmol of alkenylsilane and 2-4 equiv of thiophenol in AcOH. [b]Isolated yields based on the alkenylsilane. [c]Trans / cis = 92:8

The present reaction also proceeded without electrochemical activation (Method B). Oxygen gas was bubbled through a solution of an alkenylsilane and thiophenol to obtain the corresponding α-phenylthio carbonyl compound. But much longer reaction time was required for the completion of the reaction, and in some cases significant amounts of by-products were obtained.

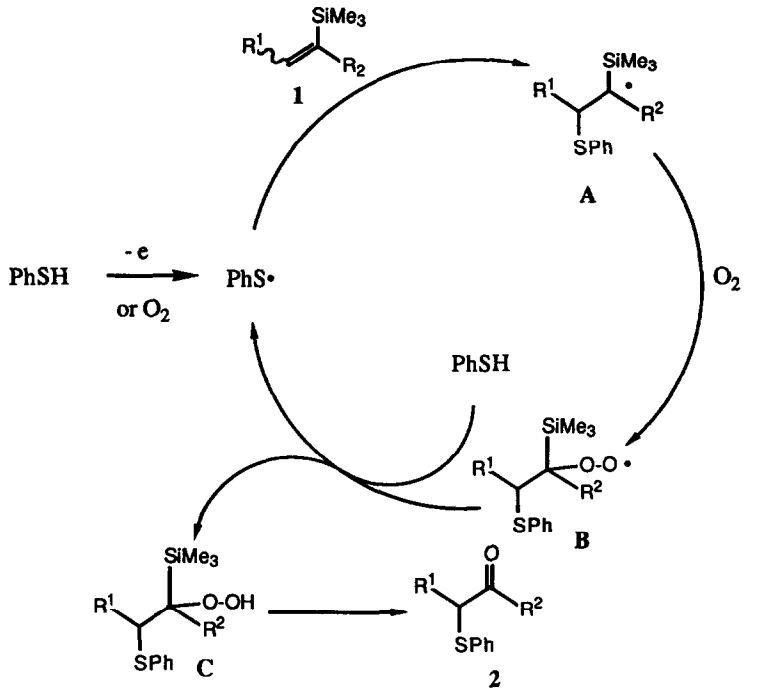
The present reaction provides a direct and regiospecific route from alkenylsilanes to α-Phenylthio carbonyl compounds which are versatile intermediates in organic synthesis[5,7] For example, the α-carbon bearing sulfur atom in α-phenylthio carbonyl compounds can be alkylated regioselectively.[6] α-Phenylthio carbonyl compounds are also converted into the corresponding α,β-unsaturated carbonyl compounds by oxidation of the sulfur atom followed by the elimination.[7]

Various α-substituted vinylsilanes are readily synthesized from 1-bromo-1-(trimethylsilyl)ethene.[8] 2-(Trimethylsilyl)alkenes are prepared by the alkylation of the vinyllithium reagent generated by the treatment of 1-bromo-1-(trimethylsilyl)ethene with t-butyllithium.[8a] The reaction of the vinyllithium reagent with 1-decene oxide gives 4-hydroxy-2-(trimethylsilyl)alkenes, which can be converted into β-hydroxyketones by the present oxygenation reaction.[8a] The copper-catalyzed conjugate addition of the vinyllithium reagent gives 5-oxo-2-(trimethylsilyl)alkenes,[8c] which are readily oxidized into 1,4-diketones in the presence of thiophenol. The Grignard reagent prepared from 1-bromo-1-(trimethylsilyl)ethene reacts with aldehydes to give the 3-hydroxyl-2-trimethylsilylalkenes,[8b] which can be oxidized into α-hydroxyketones. Therefore, 1-bromo-1-(trimethylsilyl)ethene can be utilized as a synthon of phenylthioacetyl anion by using the present oxygenation reaction.



We propose the following radical chain mechanism for the present oxygenation reaction (Scheme IV). Since the oxidation potential of thiophenol is much less positive than alkenysilanes, one-electron oxidation of thiophenol takes place on the surface of the anode to give phenylthio radical.[9] In the case of the oxygenation reaction without electrochemical initiation, thiophenol is oxidized by molecular oxygen to generate phenylthio

Scheme IV

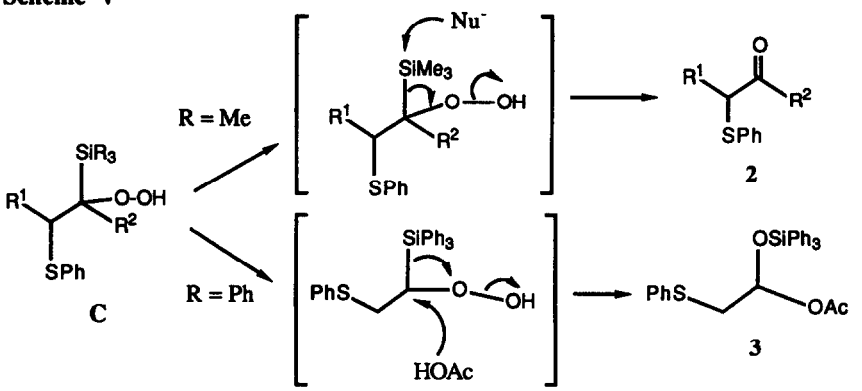


radical. Regioselective addition of phenylthio radical to the carbon-carbon double bond of the alkenylsilane[10,11] followed by the reaction of the resulting carbon radical **A** with molecular oxygen produces peroxy radical **B**. Hydrogen abstraction from thiophenol by radical **B** provides hydroperoxide **C**, regenerating phenylthio radical. Decomposition of hydroperoxide **C** gives the corresponding carbonyl compound **2**.

Although the detailed mechanism of the decomposition of the hydroperoxide intermediate **C** has not been clarified as yet, the following path seems to explain the formation of the α-phenylthio ketones (Scheme V, R = Me). The carbon-silicon bond is cleaved either by the external attack of an nucleophile or by the internal attack of the oxygen atom of the hydroperoxide. The oxygen-oxygen bond of the hydroperoxide moiety is simultaneously cleaved to give α-phenylthio carbonyl compound **2** as the final product.

Closely related mechanisms have been proposed for the decomposition of silyl-substituted hypochlorites,[12a] silyl-substituted peroxymetals,[12b] endoperoxides of silyl-substituted furans,[12c] and the intermediate in ozonolysis of alkenylsilanes.[12d]

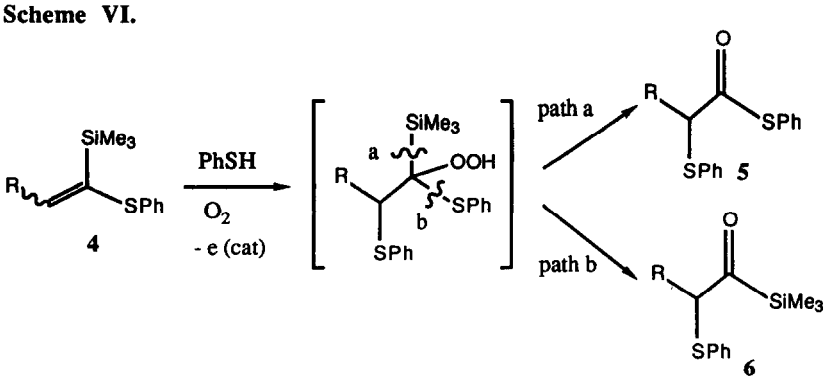
Scheme V



It is interesting that oxygenation of triphenylvinylsilane (**1c**) afforded the acetal **3** as a major product together with α-phenylthioacetaldehyde **2a** (Table I). The fact that the treatment of **2a** with triphenylsilanol in acetic acid did not give **3** indicates that **3** was not formed from **2a** under the conditions. It is also noteworthy that compound **3** was not converted to aldehyde **2a** under the present reaction condition, although hydrolysis of **3** in H_2O / THF / AcOH (3:1:1) gave **2a** in 94 % yield.[13] Therefore, the nucleophilic attack on the carbon competed the attack on the silicon because of the steric hindrance at the silicon substituted by three phenyl groups (Scheme V, R = Ph).

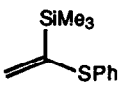
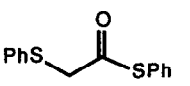
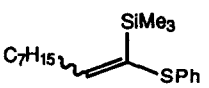
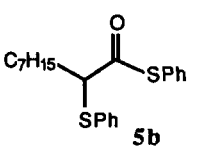
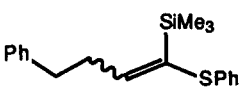
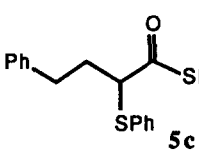
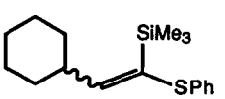
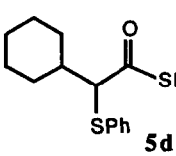
Previously we have reported that the oxygenation of alkenyl sulfides in the presence of thiophenol and proposed a mechanism involving the hydroperoxide intermediate substituted by a phenylthio group,[14] which decomposed to give α-phenylthio carbonyl compounds.[1] The following question then arises from a view point of decomposition mechanism of the hydroperoxide. If the hydroperoxide substituted by both a silyl group and a phenylthio group at the α-position is generated, which mode of decomposition would take place, (a) the carbon-silicon bond cleavage to give the thiolesters (**5**), or (b) the carbon-sulfur bond cleavage to give the acylsilanes (**6**) (Scheme VI)? Thus, the oxygenation of alkenylsilanes substituted by the phenylthio group at the α-carbon (1-phenylthio-1-(trimethylsilyl)alkenes) (**4**) was examined.

Scheme VI.



1-Phenylthio-1-(trimethylsilyl)alkenes (**4**) were easily prepared by the treatment of phenylthiobis-(trimethylsilyl)methane with buthyllithium followed by the reaction with aldehydes.[15] Oxygenation of 1-phenylthio-1-(trimethylsilyl)alkenes (**4**) took place smoothly, and the corresponding α-phenylthio thiol esters (**5**) were obtained as a sole product in high yields (Table II). The acylsilanes **6** were not detected at all. The results indicate that the cleavage of the carbon-silicon bond took place exclusively without affecting the carbon-sulfur bond. The high affinity of silicon to oxygen may play some role in the selective cleavage of the carbon-silicon bond. Although the detailed mechanism of the decomposition of the hydroperoxide has not been clearified as yet, the present reaction provides a convenient method for the synthesis of thiolesters activated at the α-position.

Table II. Oxygenation of 1-Phenylthio-1-(trimethylsilyl)alkenes in the Presence of Thiphenol.[a]

α-phenylthio-alkenylsilane	method[b]	electricity (F/mol)	time (h)	product	yield[c] (%)
 **4a**	A	0.04	0.5	 **5a**	99
	B	-	3		96
 **4b**	A	0.65	2.5	 **5b**	82
	B	-	81		96
 **4c**	A	0.49	6	 **5c**	91
	B	-	29		89
 **4d**	A	3.77	5.5	 **5d**	60
	B	-	67		32

[a]The reactions were normally carried out with 0.5 mmol of 1-phenylthio-1-(trimethylsilyl)alkene and 2-6 equiv of thiophenol. [b]Method A: in 0.2 M Et_4NOTs / AcOH. Method B: without electrochemical activation in AcOH. [c]Isolated yields based on the 1-phenylthio-1-(trimethylsilyl)alkene.

Experimental Section

General Comments. Glass-support precoated (Merk silica gel 60 F_{254}, 0.25 mm) plates were employed for analytical TLC. Vapor-phase chromatography (VPC) was performed on a Shimadzu gas chromatograph equipped with a 2 m x 3 mm column packed with Silicone OV-1 (2%) on Chromosorb WAW DMCS. Proton NMR spectra were determined on a Hitachi R-90H spectrometer (90 MHz) or a JEOL JNM-GX-400 spectrometer (400 MHz). Carbon NMR spectra were determined on a JEOL JNM-GX-400 spectrometer. Infrared (IR) spectra were determined on a JASCO A-102 diffraction grating spectrophotometer. Mass spectra were obtained on a JEOL JMS-AX500 spectrometer; the ionization potential was 70 eV.

Alkenylsilanes **1b** and **1c** were prepared by the reaction of vinylmagnesium bromide with chlorodimethylphenylsilane and chlorotriphenylsilane, respectively. Alkenylsilanes **1d** and **1e** were prepared by hydrosilylation of 1-octyne and 5-decyne, respectively with trichlorosilane followed by methylation. Alkenylsilanes **1f** and **1g** were prepared by the alkylation of the vinyllithium reagent generated by the treatment of 1-bromo-1-(trimethylsilyl)ethene and 1-bromo-1-(phenyldimethylsilyl)ethene, respectively with t-butyllithium.[8a] Alkenylsilane **1h** was prepared by the reaction of the Grignard reagent generated from 1-bromo-1-(trimethylsilyl)ethene with octanal.[8b] Alkenylsilane **1i** was prepared by the reaction of the lithium reagent generated from 1-bromo-1-(trimethylsilyl)ethene with 1-decene oxide.[8a] Alkenylsilane **1j** was prepared by the conjugate addition of the cuprate reagent generated from 1-bromo-1-(trimethylsilyl)ethene to cyclohexenone.[8c]

3-[1-(Trimethylsilyl)vinyl]-1-cyclohexanol (1k). To a 1.0 M THF solution of L-Selectride (2.00 mL, 2.00 mmol) was added a solution of 3-[1-(trimethylsilyl)vinyl]-1-cyclohexanone (**1j**) (197 mg, 1.00 mmol) in THF (1.0 mL) dropwise at -78 °C and the mixture was stirred for 1 h at this temperature. The cool reaction mixture was poured into aqueous NH_4Cl and extracted with ether three times. The combined ether layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane / ether 19:1-9:1) to obtain the title compound (109 mg, 0.55 mmol) in 55 % yield.

This compound was characterized as a mixture (92:8) of two stereoisomers. TLC Rf 0.49 and 0.37 (hexane / ethyl acetate 4:1); VPC tR 6.4 min (100-240°C, 10°C/min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.09 (s, 9 H), 1.13-1.78 (m, 8 H), 2.52-2.58 (m, 1 H), 3.57-3.64 (m), 4.14-4.16 (m) (total 1 H, 8:92), 5.35 (d, J = 2.44 Hz, 1 H), 5.58 (br, s, 1 H); ^{13}C NMR ($CDCl_3$) δ 157.11, 122.55, 67.03, 39.52, 36.30, 32.81, 32.59, 20.56, -0.89; INEPTR ($CDCl_3$) δ 122.55 (-), 67.05 (+), 39.51 (-), 36.28 (+), 32.81 (-), 32.57 (-), 20.56 (-), -0.88 (+); IR ($CHCl_3$) 3600 (w), 3450 (br, m), 2930 (s), 1445 (m), 1405 (m), 1250 (s), 1110 (m), 980 (s), 930 (m), 860 (s), 840 (s) cm^{-1}; low-resolution MS m/e (relative intensity) 198 (M, 0.6), 196 (0.5), 181 (16), 165 (6), 108 (34), 93 (55), 83 (100); high-resolution MS calcd for $C_{11}H_{22}OSi$ 198.1440, found 198.1450.

General Procedure for the Electro-initiated Oxygenation of Alkenylsilanes in the Presence of Thiophenol (Method A). The reaction was carried out in an undivided cell equipped with a carbon rod anode (i.d. = 6 mm) and a platinum plate cathode (20 x 30 mm). Alkenylsilane (0.3-1.0 mmol) and thiophenol (2.0-4.0 mmol) were dissolved in 0.2 M Et_4NOTs / AcOH (5-10 mL), and oxygen gas was bubbled through the cell with magnetical stirring. The constant current electrolysis (20 mA, 1 min) was repeated several times with an interval of 30 min at room temperature. After the reaction was completed, the reaction mixture was partitioned between ether and aqueous $NaHCO_3$. The aqueous and organic phases were separated, and the

aqueous phase was extracted with ether twice. The combined organic phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel to obtain the corresponding α-phenylthio carbonyl compound.

General Procedure for the Oxygenation of Alkenylsilanes in the Presence of Thiophenol (Method B). Alkenylsilane (0.5-1.0 mmol) and thiophenol (2.0-4.0 mmol) were dissolved in acetic acid or methanol (5-10 mL), and oxygen gas was bubbled through the cell with magnetical stirring at room temperature. After the reaction was completed, the reaction mixture was partitioned between ether and aqueous $NaHCO_3$. The aqueous and organic phases were separated, and the aqueous phase was extracted with ether twice. The combined organic phase was dried over Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel to obtain the corresponding α-phenylthio carbonyl compound.

Phenylthioacetaldehyde (2a).TLC Rf 0.29 (hexane / ethyl acetate 9:1); VPC tR 5.42 min (100-250°C, 10°C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 3.58 (d, J = 3.08 Hz, 2 H), 7.20-7.37 (m, 5 H), 9.53 (t, *J* = 3.08 Hz, 1 H); IR ($CHCl_3$) 3020 (m), 2960 (m), 2890 (m), 2790 (m), 2690 (w), 1710 (s), 1575 (m), 1470 (m), 1430 (m), 1380 (m), 1150 (m), 1080 (m), 1015 (m) cm^{-1}; low-resolution MS m/e (relative intensity) 152 (M, 72), 134 (9), 123 (100), 109 (16); high-resolution MS calcd for C_8H_8OS 152.0294, found 152.0293.

1-Acetoxy-1-(triphenylsilyloxy)-2-phenylthioethane (3).TLC Rf 0.77 (dichloromethane / hexane 4:1); ^1H NMR (400 MHz, $CDCl_3$) δ 1.63 (s, 3 H), 3.18 (dd, J = 14.16 and 5.13 Hz), 3.36 (dd, *J* = 14.16 and 5.12 Hz) (total 3 H), 6.26 (t, *J* = 5.12 Hz, 1 H), 7.15-7.62 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 169.40, 135.67, 135.53, 133.22, 130.29, 129.76, 128.87, 127.89, 126.30, 91.70, 39.90, 20.59; INEPTR (CDCl3) δ 135.53 (+), 130.30 (+), 129.75 (+), 128.89 (+), 127.91 (+), 126.30 (+), 91.70 (+), 39.87 (-), 20.62 (+); IR ($CHCl_3$) 3050 (m), 3000 (m), 1735 (s), 1590 (m), 1480 (m), 1430 (m), 1370 (m), 1245 (s), 1115 (s), 1050 (m), 1005 (s) cm^{-1}; low-resolution MS m/e (relative intensity) 470 (M, 2), 410 (100), 333 (9), 259 (78), 241 (76), 227 (52), 212 (22), 152 (14), 134 (10); high-resolution MS calcd for $C_{28}H_{26}O_3SSi$ 470.1373, found 470.1375.

2-Phenylthiooctanal (2d).TLC Rf 0.45 (hexane / ethyl acetate 9:1); ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.71 Hz, 3 H), 1.26-1.58 (m, 8 H), 1.62-1.71 (m, 1 H), 1.75-1.86 (m, 1 H), 3.51 (dt, *Jt* = 6.71 Hz, *Jd* = 4.27 Hz, 1 H), 7.22-7.49 (m, 5 H), 9.36 (d, *J* = 4.28 Hz, 1 H); IR ($CHCl_3$) 2920 (s), 2850 (m), 1710 (s), 1480 (m), 1440 (m), 1380 (w), 1300 (w), 1190 (m), 1065 (w), 1025 (w) cm^{-1}; low-resolution MS m/e (relative intensity) 236 (M, 49), 218 (20), 207 (100), 148 (17), 123 (36), 110 (6), 97 (16); high-resolution MS calcd for $C_{14}H_{20}OS$ 236.1235, found 236.1261.

1-Phenylthio-2-decanone (2f). TLC Rf 0.42 (hexane / ethyl acetate 9:1); VPC tR 6.59 min (100-230°C, 10°C/min); mp 49-50°C; ^1H NMR (90 MHz, $CDCl_3$) δ 0.88-1.60 (m, 15 H), 2.53 (t, *J* = 6.75 Hz, 2 H), 3.61 (s, 2 H), 7.10-7.34 (m, 5 H); IR ($CHCl_3$) 2950 (s), 2890 (m), 1715 (s), 1590 (m), 1490 (m), 1470 (m), 1445 (m), 1410 (m), 1375 (m), 1130 (w), 1075 (m), 1035 (m) cm^{-1}; low-resolution MS m/e (relative intensity) 265 (M+1, 10), 264 (M, 40), 141 (95), 124 (100), 123 (63), 109 (14), 71 (80), 57 (90); high-resolution MS calcd for $C_{16}H_{24}OS$ 264.1547, found 264.1552. Anal. Calcd for $C_{16}H_{24}OS$: C, 72.68; H, 9.15. Found C, 72.72; H, 9.19.

6-Phenylthio-5-decanone (2e). TLC Rf 0.51 (hexane / ethyl acetate 9:1); VPC tR 13.8 min (100-240°C, 10°C/min); ^1H NMR (400MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.32 Hz), 0.89 (t, *J* = 7.32 Hz) (total 6 H),

1.24-1.87 (m, 10 H), 2.56 (t, J = 7.32 Hz, 2 H), 3.62 (t, J = 7.33 Hz, 1 H), 7.25-7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 209.60, 133.46, 132.38, 129.02, 127.75, 57.08, 39.13, 30.22, 29.49, 26.05, 22.43, 22.33, 13.85; INEPTR ($CDCl_3$) δ 132.39 (+), 129.03 (+), 127.76 (+), 57.06 (+), 39.13 (-), 30.21 (-), 29.49 (-), 26.05 (-), 22.44 (-), 22.34 (-), 13.88 (+); IR ($CHCl_3$) 2970 (s), 2880 (m), 1715 (s), 1590 (w), 1470 (m), 1465 (m), 1035 (w) cm^{-1}; low-resolution MS m/e (relative intensity) 264 (M, 20), 179 (100), 123 (49), 109 (4); high-resolution MS calcd for $C_{16}H_{24}OS$ 264.1548, found 264.1552. Anal. Calcd for $C_{16}H_{24}OS$: C, 72.68; H, 9.15. Found: C, 72.53; H, 9.32.

3-Hydroxy-1-phenylthio-2-decanone (2h). TLC Rf 0.18 (hexane / ethyl acetate 9:1); VPC tR 13.9 min (100-240°C, 10°C/min); mp 58-59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.72 Hz, 3 H), 1.20-1.61 (m, 11 H), 1.76-1.84 (m, 1 H), 3.12 (br, d, J = 5.49 Hz, 1 H), 3.76 (d, J = 15.26 Hz, 1 H), 3.82 (d, J = 15.26 Hz, 1 H), 4.42-4.45 (m, 1 H), 7.23-7.38 (m, 5 H); IR ($CHCl_3$) 3500 (br, m), 2920 (s), 2850 (m), 1705 (s), 1585 (w), 1485 (m), 1470 (m), 1440 (m), 1395 (m), 1205 (br, m), 1070 (br, m) cm^{-1}; low-resolution MS m/e (relative intensity) 280 (M, 24), 153 (38), 135 (49), 127 (82), 123 (77), 110 (64), 57 (100); high-resolution MS calcd for $C_{16}H_{24}O_2S$ 280.1497, found 280.1515. Anal. Calcd for $C_{16}H_{24}O_2S$: C, 68.53; H, 8.63. Found: C, 68.52; H, 8.66.

4-Hydroxy-1-phenylthio-2-undecanone (2i). TLC Rf 0.32 (hexane / ethyl acetate 4:1); VPC tR 15.0 min (100-240°C, 10°C/min); mp 65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.84 Hz, 3 H), 1.26-1.50 (m, 14 H), 2.67 (dd, J = 17.34 and 8.79 Hz, 1 H), 2.77 (dd, J = 17.33 and 2.93 Hz), 2.77 (br, s) (total 2 H), 3.67 (d, J = 15.10 Hz), 3.68 (d, J = 15.10 Hz) (total 2 H), 3.95-4.03 (m, 1 H), 7.22-7.35 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 206.32, 134.45, 129.84, 129.16, 127.06, 67.91, 47.18, 44.60, 36.60, 31.83, 29.48, 29.20, 25.41, 22.62, 14.05; INEPTR ($CDCl_3$) δ 129.81 (+), 129.18 (+), 127.06 (+), 67.89 (+), 47.15 (-), 44.59 (-), 36.59 (-), 31.84 (-), 29.49 (-), 29.22 (-), 25.42 (-), 22.63 (-), 14.08 (+); IR ($CHCl_3$) 3530 (br, m), 2900 (s), 2840 (s), 1700 (s), 1580 (m), 1480 (m), 1460 (m), 1435 (m), 1400 (br, m), 1300 (w), 1220 (br, w), 1080 (br, m) cm^{-1}; low-resolution MS m/e (relative intensity) 290 (M, 37), 181 (13), 167 (100), 123 (62), 110 (8); high-resolution MS calcd for $C_{18}H_{26}OS$ 290.1705, found 290.1715. Anal. Calcd for $C_{18}H_{26}OS$: C, 70.08; H, 9.15. Found: C, 69.98; H, 9.17.

3-Phenylthioacetylcyclohexanone (2j). TLC Rf 0.26 (hexane / ethyl acetate 2:1); VPC tR 13.8 min (100-240°C, 10°C/min); mp 99-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26-1.74 (m, 2 H), 2.03 (m, 2 H), 2.25-2.38 (m, 3 H), 2.48 (dd, J = 14.40 and 11.48 Hz, 1 H), 3.22-3.30 (m, 1 H), 3.73 (s, 2 H), 7.22-7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 209.35, 204.96, 134.21, 129.92, 129.19, 127.19, 47.66, 42.69, 42.56, 40.81, 27.52, 24.75; INEPTR ($CDCl_3$) δ 129.89 (+), 129.21 (+), 127.19 (+), 47.65 (+), 42.69 (-), 42.57 (-), 40.82 (-), 27.54 (-), 24.78 (-); IR ($CHCl_3$) 2950 (m), 1710 (s), 1585 (w), 1485 (m), 1440 (m), 1350 (w), 1315 (w), 1265 (m), 1230 (br, m), 1110 (w), 1060 (w), 1030 (w), 980 (w) cm^{-1}; low-resolution MS m/e (relative intensity) 248 (M, 40), 139 (5), 123 (100), 109 (12), 97 (31); high-resolution MS calcd for $C_{14}H_{16}O_2S$ 248.0872, found 248.0878. Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.49. Found: C, 67.73; H, 6.51.

3-Phenylthioacetylcyclohexanol (2k). Compound **2k** was characterized as a mixture (9:1) of two stereoisomers. TLC Rf 0.32 and 0.26 (hexane / ethyl acetate 1:1); VPC tR 14.4 min (100-240°C, 10°C/min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22-1.81 (m, 8 H), 2.77 (tt, J = 11.29 and 3.32 Hz), 3.16 (tt, J = 10.68 and 3.97 Hz) (total 1 H), 3.74 (s), 3.76 (s) (total 2 H, 1:9), 4.09-4.14 (m, 1 H), 7.18-7.35 (m, 5 H); ^{13}C NMR

($CDCl_3$) δ 208.01, 135.02, 129.76, 129.05, 126.81, 65.81, 42.97, 42.75, 34.81, 32.50, 27.98, 19.55; IR ($CHCl_3$) 3600 (w), 3450 (br, m), 2910 (s), 1695 (s), 1580 (m), 1480 (m), 1435 (m), 1370 (w), 1285 (w), 1230 (br, m), 1125 (m), 1060 (w), 975 (m) cm^{-1}; low-resolution MS m/e (relative intensity) 250 (M, 10), 232 (2), 141 (8), 127 (28), 124 (20), 123 (20), 110 (12), 109 (10), 81 (100); high-resolution MS calcd for $C_{14}H_{18}O_2S$ 250.1026, found 250.1021.

1-Phenylthio-1-(trimethylsilyl)ethene (4a). To a solution of 2,2,6,6-tetramethylpiperidine (0.570 mL, 3.38 mmol) and N,N,N',N'-tetramethylethylenediamine (0.68 mL, 4.5 mmol) in THF (17 mL) was added a solution of n-BuLi / hexane (2.75 mL of a 1.6 M solution, 4.40 mmol) at -78 °C. The mixture was warmed to 0 °C and stirred for 30 min at this temperature. After the mixture was cooled to -78 °C, phenyl vinyl sulfide (0.523 mL, 4.00 mmol) was added and the mixture was warmed to 0°C for 20 min. Trimethylchlorosilane (0.76 mL, 6.0 mmol) was added at 0 °C and the mixture was warmed to room temperature. After 1 h, the reaction mixture was concentrated under reduced pressure. The residue was poured into a separatory funnel containing ether and saturated aqueous NH_4Cl. The aqueous and organic phases were separated and aqueous layer was extracted with ether three times. The combined organic phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane) to obtain the title compound (648 mg, 3.11 mmol) in 78 % yield: TLC Rf 0.43 (hexane); VPC tR 4.4 min (100-250°C, 20°C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 0.18 (s, 9 H), 5.20 (d, J = 0.63 Hz, 1 H), 5.40 (d, J = 0.63 Hz, 1 H), 7.19-7.47 (m, 5 H); IR ($CHCl_3$) 2950 (m), 1570 (m), 1475 (m), 1440 (m), 1395 (m), 1245 (s), 1085 (w), 1065 (w), 1020 (w), 840 (s) cm^{-1}; low-resolution MS m/e (relative intensity) 208 (M, 27), 193 (7), 167 (34), 151 (11), 134 (22), 118 (100); high-resolution MS calcd for $C_{11}H_{16}SSi$ 208.0741, found 208.0734.

General Procedure for Preparation of 1-Phenylthio-1-(trimethylsilyl)alkenes. Phenylthio-bis(trimethylsilyl)methane[16] (1.47-1.95 mmol) was dissolved in 1.0-1.5 mL of tetrahydrofuran, and the solution was cooled to 0 °C. 1.60-2.16 mmol of n-BuLi (1.6 M in hexane) was added dropwise by syringe, and stirred for 1 h at this temperature. At 0 °C, 1.73-2.24 mmol of aldehyde was added, and resulting reaction mixture was stirred at 0 °C for 1 h and stirred at room temperature for an additional 1 h. The reaction mixture was poured into a separatory funnel containing ether and saturated aqueous NH_4Cl. The aqueous and organic phases were separated and aqueous phase was extracted with ether three times. The organic phase was combined, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the 1-phenylthio-1-(trimethylsilyl)alkene.

1-Phenylthio-1-(trimethylsilyl)-1-nonene (4b). This compound was characterized as a mixture (2:1) of two stereoisomers. TLC Rf 0.65 and 0.54 (hexane); VPC tR 11.7 and 12.3 min (100-230°C, 10°C/min); ^1H NMR (400 MHz, $CDCl_3$) δ 0.07 (s), 0.18 (s) (total 9 H), 0.91 (t, J = 7.08 Hz), 0.93 (t, J = 7.31 Hz) (total 3 H), 2.30 (dt, Jt = 7.57 Hz, Jd = 7.32 Hz), 2.42 (dt, Jd = 7.57 Hz, Jt = 7.08 Hz) (total 2 H, 2:1), 6.55 (t, J = 7.81 Hz), 6.62 (t, J = 6.84 Hz) (total 1 H), 7.17-7.29 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 154.12, 153.44, 138.13, 138.02, 133.27, 131.88, 129.24 128.71, 128.52, 127.89, 125.72, 124.96, 32.89, 31.81, 30.97, 29.60, 29.32, 29.19, 29.13, 28.85, 22.65, 14.10, 0.45, -1.13; INEPTR ($CDCl_3$) δ 154.15 (+), 153.47 (+), 129.22 (+), 128.73 (+), 128.54 (+), 127.88 (+), 125.72 (+), 124.96 (+), 32.89 (-), 31.80 (-), 30.97 (-), 29.60 (-), 29.32 (-), 29.19 (-), 29.13 (-), 28.85 (-), 22.65 (-), 14.11 (+), 0.43 (+), -1.14 (+);

IR ($CHCl_3$) 2920 (s), 2850 (m), 1580 (m), 1475 (m), 1440 (w), 1245 (s), 1080 (w), 1025 (w), 835 (s) cm^{-1}; low-resolution MS m/e (relative intensity) 306 (M, 56), 222 (15), 182 (20), 167 (58), 73 (100); high-resolution MS calcd for $C_{18}H_{30}SSi$ 306.1836, found 306.1836.

4-Phenyl-1-phenylthio-1-(trimethylsilyl)-1-butene (4c). This compound was characterized as a mixture (3:2) of two stereoisomers. TLC Rf 0.42 and 0.34 (hexane); VPC tR 13.0 and 13.6 min (100-230°C, 10°C/min); ^1H NMR (400 MHz, $CDCl_3$) δ 0.05 (s), 0.15 (s) (total 9 H), 2.61 (q, J = 7.57 Hz), 2.74-2.78 (m) (total 4 H), 6.50 (t, J = 7.57 Hz), 6.60-6.67 (m) (total 2 H, 3:2), 7.14-7.33 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 151.63, 151.04, 141.45, 141.21, 137.72, 137.38, 134.68, 133.40, 129.87, 128.77, 128.57, 128.43, 128.33, 128.17, 126.07, 126.01, 125.92, 125.14, 35.84, 35.08, 34.73, 32.60, 0.36, -1.13; IR ($CHCl_3$) 2950 (m), 1580 (m), 1475 (m), 1440 (w), 1250 (m), 1090 (m), 840 (s) cm^{-1}; low-resolution MS m/e (relative intensity) 312 (M, 18), 221 (43), 167 (16), 151 (10), 73 (100); high-resolution MS calcd for $C_{19}H_{24}SSi$ 312.1367, found 312.1382.

2-Cyclohexyl-1-phenylthio-1-(trimethylsilyl)ethene (4d). This compound was characterized as a mixture (3:2) of two stereoisomers. TLC Rf 0.64 and 0.55 (hexane); VPC tR 11.3 and 11.9 min (100-230°C, 10°C/min); ^1H NMR (400 MHz, $CDCl_3$) δ 0.04 (s), 0.18 (s) (total 9 H), 1.16-1.32 (m, 5 H), 1.67-1.82 (m, 5 H), 2.38-2.48 (m), 2.87-2.96 (m) (total 1 H, 2:3), 6.42 (d, J = 8.30 Hz), 6.44 (d, J = 11.23 Hz) (total 1 H), 7.24-7.29 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 159.96, 158.68, 138.32, 138.17, 131.05, 129.95, 128.87, 128.68, 128.49, 128.20, 125.56, 125.05, 53.40, 42.06, 39.42, 32.73, 32.34, 25.98, 25.77, 25.61, 25.57, 0.57, -0.95; IR ($CHCl_3$) 2920 (s), 2850 (m), 1580 (m), 1480 (m), 1450 (m), 1250 (s), 1080 (w), 1025 (w), 970 (w), 930 (w), 840 (s) cm^{-1}; low-resolution MS m/e (relative intensity) 290 (M, 56), 182 (12), 167 (27), 99 (28), 73 (100); high-resolution MS calcd for $C_{17}H_{26}SSi$ 290.1522, found 290.1515.

S-Phenyl 2-Phenylthioethanethioate (5a). TLC Rf 0.24 (hexane / ethyl acetate 9:1); VPC tR 13.3 min (100-230°C, 10°C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 3.89 (s, 2 H), 7.24-7.51 (m, 10 H); IR ($CHCl_3$) 3050 (m), 3000 (m), 1690 (s), 1585 (m), 1480 (s), 1440 (s), 1380 (w), 1165 (m), 1020 (s) cm^{-1}; low-resolution MS m/e (relative intensity) 260 (M, 32), 150 (21), 123 (100), 109 (22); high-resolution MS calcd for $C_{14}H_{12}OS_2$ 260.0328, found 260.0326.

S-Phenyl 2-Phenylthiononanethioate (5b). TLC Rf 0.31 (hexane / ethyl acetate 9:1); VPC tR 9.05 min (100-250°C, 10°C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 0.81-2.08 (m, 17 H), 3.87 (t, J = 7.25 Hz, 1 H), 7.24-7.47 (m, 10 H); IR ($CHCl_3$) 3070 (w), 3000 (w), 2930 (s), 2860 (m), 1690 (s), 1585 (m), 1480 (m), 1440 (m), 1380 (w), 1330 (w), 1300 (w), 1260 (w), 1190 (w), 1070 (m), 1025 (m) cm^{-1}; low-resolution MS m/e (relative intensity) 358 (M, 8), 221 (100), 137 (4), 123 (39), 109 (14); high-resolution MS calcd for $C_{21}H_{26}OS_2$ 358.1424, found 358.1417.

S-Phenyl 4-Phenyl-2-phenylthiobutanethioate (5c). TLC Rf 0.43 (hexane / ethyl acetate 9:1); VPC tR 21.5 min (100-240°C, 10°C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 1.98-2.53 (m, 2 H), 2.84 (t, J = 7.91 Hz, 2 H), 3.84 (t, J = 7.25 Hz, 1 H), 7.01-7.49 (m, 15 H); IR ($CHCl_3$) 3050 (m), 3000 (m), 2920 (m), 1685 (s), 1580 (m), 1480 (s), 1440 (s), 1190 (w), 1065 (m), 1020 (m), 940 (m) cm^{-1}; low-resolution MS m/e (relative intensity) 364 (M, 8), 255 (28), 227 (8), 149 (8), 117 (100), 91 (58); high-resolution MS calcd for $C_{22}H_{20}OS_2$ 364.0954, found 364.0941.

S-Phenyl 2-Cyclohexyl-2-phenylthioethanethioate (5d). TLC Rf 0.50 (hexane / ethyl acetate 9:1); VPC tR 17.8 min (100-240°C, 10°C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 1.12-2.20 (m, 11 H), 3.70 (d, J

= 7.91 Hz, 1 H), 7.23-7.51 (m, 10 H); IR ($CHCl_3$) 3070 (w), 3010 (w), 2930 (s), 2850 (s), 1690 (s), 1585 (m), 1480 (s), 1440 (s), 1275 (w), 1180 (w), 1065 (m), 1025 (m), 995 (m) cm^{-1}; low-resolution MS m/e (relative intensity) 342 (M, 14), 205 (100), 123 (48), 109 (10), 95 (69); high-resolution MS calcd for $C_{20}H_{22}OS_2$ 342.1112, found 342.1113.

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References and Notes

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