Table II. Variation of the Hammett Equation[a] ρ Value with Solvent, at 50.0 °C[b]

solvent[c]	ρ^d	r^e
EtOH	-1.73 ± 0.21	-0.971
80% EtOH	-1.92 ± 0.33	-0.947
60% EtOH	-2.32 ± 0.29	-0.971
MeOH	-1.97 ± 0.23	-0.974
97% TFE[f]	-4.95 ± 0.75	-0.957
80% TFE	-3.71 ± 0.58	-0.955
50% TFE	-3.65 ± 0.52	-0.962
CH_3CO_2H	-2.83 ± 0.49	-0.945
HCO_2H	-5.12 ± 0.77	-0.958
95% Me_2CO	-1.32 ± 0.19	-0.961
60T-40E[g]	-2.74 ± 0.33	-0.972

[a] $\log (k/k_0) = \rho\sigma$. [b] Using log k values for the unsubstituted compound and the five derivatives (see Table I) with electron-withdrawing groups; the σ values used are from ref 10. [c] On volume–volume basis (at 25.0 °C) with other component water, except for TFE–H_2O mixtures, which are on a weight–weight basis. [d] With associated standard errors. [e] Correlation coefficient. [f] 2,2,2-Trifluoroethanol. [g] TFE–ethanol.

The magnitude of the l and m values and the nature of their variation with substrate plus the nature of the variation of the ρ value with solvent suggest a S_N2 mechanism,[13-16] with variable transition-state structure, for the solvolyses of all but one of the esters. For the p-methyl derivative, the sharply lower l value (similar to values previously observed in solvolyses of the *tert*-butyldimethylsulfonium ion[17] and *tert*-butyl chloride[18] and ascribed[19] to nucleophilic solvation of a developing carbocation) and the large increase in the m value (to a value of close to unity) suggest a large superimposed component from an ionization (S_N1) process. The positive deviation from the Hammett plots supports this concept.

Supplementary Material Available: Table S1, containing the logarithmic values of the specific rates of sovolysis of the seven benzyl tosylates listed in Table I in the 11 solvents listed in Table II (1 page). Ordering information is given on any current masthead page.

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(13) Shiner, V. J., Jr.; Rapp, M. W.; Pinnick, H. R., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 232.

(14) Harris, J. M.; Shafer, S. G.; Moffatt, J. R.; Becker, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 3295.

(15) Kevill, D. N.; Rissmann, T. J. *J. Chem. Res.* (*S*) **1986**, 252.

(16) Maskill, H. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1241.

(17) Kevill, D. N.; Kamil, W. A.; Anderson, S. W. *Tetrahedron Lett.* **1982**, *23*, 4635.

(18) Bentley, T. W.; Carter, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 5741.

(19) Kevill, D. N.; Anderson, S. W.; Fujimoto, E. K. In *Nucleophilicity*; Harris, J. M., McManus, S. P., Eds.; Advances in Chemistry Series, No. 215, American Chemical Society: Washington, DC, 1987; pp 270–274.

Oxygenation of Alkenylsilanes in the Presence of Thiophenol. Direct and Regiospecific Conversion to α-Phenylthio Carbonyl Compounds

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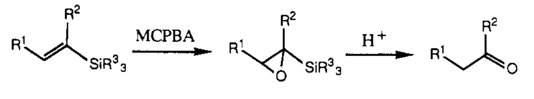
Received August 10, 1989

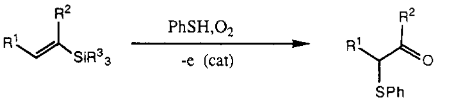
Summary: Electroinitiated oxygenation of alkenylsilanes was found to proceed smoothly in the presence of thiophenol to give the corresponding α-phenylthio carbonyl compounds regiospecifically.

Sir: Alkenylsilanes have been utilized as remarkably versatile intermediates in a variety of organic syntheses.[1] For example, alkenylsilanes are efficient precursors of carbonyl compounds which can be unmasked by epoxidation followed by acid catalyzed rearrangement (eq 1).[2]



(1)

Herein we report the direct transformation of alkenylsilanes into the carbonyl compounds having an activating group at the α-position. The electroinitiated oxygenation[3] of alkenylsilanes in the presence of thiophenol[4] took place smoothly to give the corresponding α-phenylthio carbonyl compounds as shown in eq 2. It is worth noting that the present reaction involves the cleavage of the carbon–silicon bond with triplet molecular oxygen.[5]



(2)

A typical procedure is as follows: 2-(Trimethylsilyl)-1-decene (0.50 mmol) and thiophenol (2.0 mmol) were dissolved in 0.2 M $Et_4NOTs/AcOH$ (5.0 mL), and oxygen gas was bubbled through the solution at room temperature. Constant electric current (20 mA) was passed using a carbon rod anode and a platinum plate cathode for 1 min. The electrolysis was repeated several times with an interval of 0.5 h until the most of the alkenylsilane was consumed (0.30 F/mol based upon the alkenylsilane) (method B). Workup with aqueous $NaHCO_3$ followed by flash chromatography afforded 1-(phenylthio)-2-decanone in 73% yield. The reaction also took place without electrochemical initiation (method A), but much longer reaction time was required for the completion, and the yields of the products were somewhat lower. Table I summarizes the results

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(1) For example, (a) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983; Chapter 7. (b) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (c) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988.

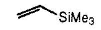
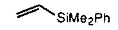
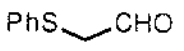
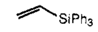
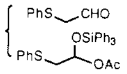
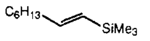
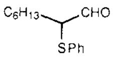
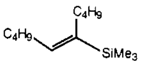
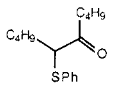
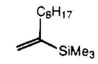
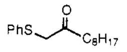
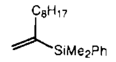
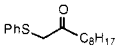
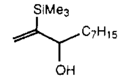
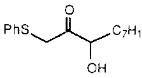
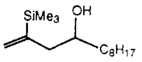
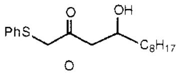
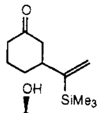
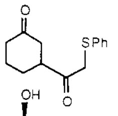
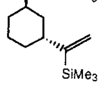
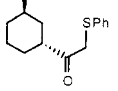
(2) (a) Stork, G.; Colvin, E. *J. Am. Chem. Soc.* **1971**, *93*, 2080. (b) Stork, G.; Jung, M. E. *Ibid.* **1974**, *96*, 3682.

(3) (a) Yoshida, J.; Sakaguchi, K.; Isoe, S. *Tetrahedron Lett.* **1987**, *28*, 667. (b) Yoshida, J.; Nakatani, S.; Sakaguchi, K.; Isoe, S. *J. Org. Chem.* **1989**, *54*, 3383. See also (c) Tang, R.; Yue, H. J.; Wolf, J. F.; Mares, F. *J. Am. Chem. Soc.* **1978**, *100*, 5248. (d) Clennan, E. L.; Simmons, W.; Almgren, C. W. *Ibid.* **1981**, *103*, 2098.

(4) Yoshida, J.; Nakatani, S.; Isoe, S. *J. Chem. Soc., Chem. Commun.* **1988**, 1468.

(5) (a) Efficient cleavage of carbon-silicon bonds in alkoxy- and fluorosilanes catalyzed by tetraacetylriboflavin in the presence of *N*-benzyl-1,4-dihydronicotinamide has been reported. Tamao, K.; Hayashi, T.; Ito, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 795. (b) Photosensitized oxygenation of alkenylsilanes has been reported, but in this case the carbon–silicon bond is not cleaved: Fristad, W. E.; Bailey, T. R.; Paquette, L. A.; Gleiter, R.; Böhm, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4420. See also ref 14b.

Table I. Oxygenation of Alkenylsilanes in the Presence of Thiophenol[a]

alkenylsilane	method[b]	electricity, F/mol	time, h	product	yield,[c] %
	A	-	45		24
	A B	- 0.16	25 2		35 68
	A	-	21		42 52
	A	-	95		24
	A B	- 1.12	13 days 32		33 13
	A B	- 0.30	31 6		68 73
	A B	- 0.49	38 5		71 76
	A B	- 0.38	24 4		43 89
	A B	- 0.21	30 2.5		91 93
	B	0.33	4		64
 [d]	B	0.33	4		80

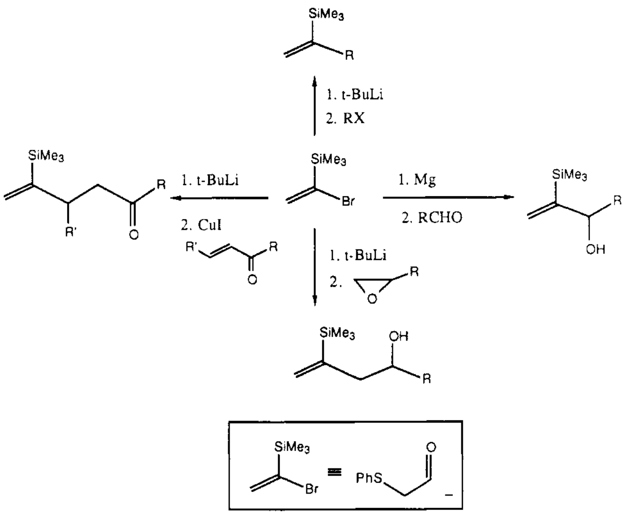
[a] The reactions were normally carried out with 0.3–0.5 mmol of alkenylsilanes and 2–4 equiv of thiophenol. [b] Method A: in AcOH without electrochemical initiation. Method B: in Et$_4$NOTs/AcOH with electrochemical initiation. [c] Isolated yields. [d] Trans/cis = 92:8.

obtained with several alkenylsilanes.

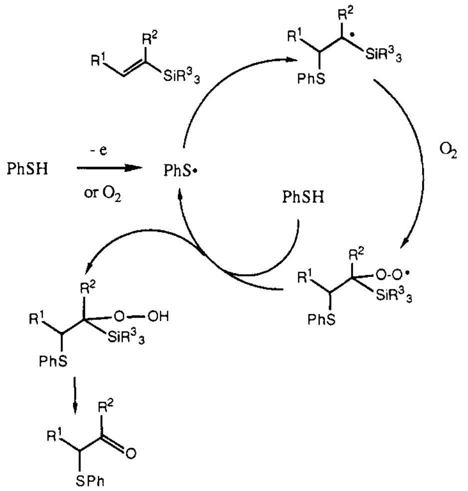
Although vinylphenyldimethylsilane and vinyltrimethylsilane gave phenylthioacetaldehyde, the oxygenation of vinyltriphenylsilane resulted in the formation of the silyl acetal together with the desired carbonyl compound as shown in Table I. However, the former product was readily hydrolyzed to the latter in hot H$_2$O/THF/AcOH.[6]

Although α-alkyl-substituted vinyltrimethylsilanes underwent smooth oxygenation to give the corresponding α-phenylthio ketones in good yields, reactivity of β-alkyl-substituted and α,β-dialkyl-substituted vinyltrimethylsilanes was low. Therefore, from a synthetic point of view, the present reaction is applicable only to α-alkyl-substituted vinylsilanes. However, since various types of α-alkyl-substituted vinylsilanes are easily accessible from 1-bromo-1-(trimethylsilyl)ethylene (Scheme I),[7] the present reaction provides a useful tool for organic synthesis, and 1-bromo-1-(trimethylsilyl)ethylene can be utilized as a synthon of phenylthioacetyl anion.

Scheme I



Scheme II



α-Phenylthio carbonyl compounds[8] obtained with the present reaction are versatile intermediate in organic synthesis.[9] For example, the carbon flanked by both a carbonyl group and a phenylthio group can be alkylated regioselectively without affecting the other α-position.[10] Conversion to α,β-unsaturated carbonyl compounds can be accomplished regioselectively by the oxidation of sulfur followed by elimination.[11] Without the phenylthio group, however, it is generally difficult to achieve these transformations with high regioselectivity. Therefore the present reaction greatly expands the synthetic utility of alkenylsilanes. Compatibility of the present reaction with various functional groups including free the hydroxyl group and the carbonyl group is also noteworthy.

The following radical chain mechanism seems to be reasonable for the present oxygenation (Scheme II). The electrochemical oxidation of thiophenol or its reaction with molecular oxygen produces phenylthio radical.[12] The attack of phenylthio radical to the alkenylsilane gives the carbon radical adjacent to the silicon.[13] The reaction of

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(6) Nakai, H.; Hamanaka, N.; Miyake, H.; Hayashi, M. *Chem. Lett.* **1979**, 1499.

(7) (a) Gröbel, B.-T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 867. (b) Boeckman, R. K., Jr.; Bruza, K. J. *J. Org. Chem.* **1979**, *44*, 4781. (c) Boeckman, R. K., Jr.; Blum, D. M.; Ganem, B.; Halvey, N. *Org. Synth.* **1978**, *58*, 152.

(8) Other methods for regiospecific synthesis of α-phenylthio carbonyl compounds: (a) Blatcher, P.; Warren, S. *J. Chem. Soc., Chem. Commun.* **1976**, 1055. (b) Durman, J.; Elliott, J.; McElroy, A. B.; Warren, S. *Tetrahedron Lett.* **1983**, *24*, 3927. See also ref 4.

(9) (a) Seebach, D.; Teschner, M. *Chem. Ber.* **1976**, *109*, 1601. (b) Trost, B. M.; Hiroi, K.; Kurozumi, S. *J. Am. Chem. Soc.* **1975**, *97*, 438.

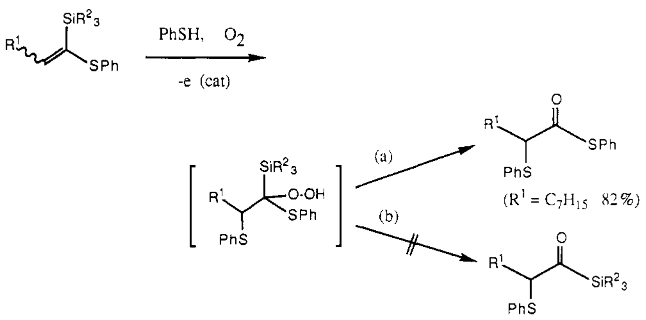
(10) Coates, R. M.; Pigott, H. D.; Ollinger, J. *Tetrahedron Lett.* **1974**, 3955. See also Trost, B. M.; Arndt, H. *J. Org. Chem.* **1973**, *38*, 3140.

(11) Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887.

(12) Oxidation potential of thiophenol is much less than those of alkenylsilanes.

(13) Addition of phenylthio radical to carbon–carbon unsaturated bond. See, for example: (a) Kharasch, M. S.; Nudenberg, W.; Mantell, G. J. *J. Org. Chem.* **1951**, *16*, 524. (b) Feldman, K. S.; Simpson, R. E.; Parvez, M. *J. Am. Chem. Soc.* **1986**, *108*, 1328. Radical addition to alkenylsilanes, see: (c) Sakurai, H.; Hosomi, A.; Kumada, M. *J. Org. Chem.* **1969**, *34*, 1764 and references cited therein.

Scheme III



the radical with molecular oxygen gives the hydroperoxy radical, which abstracts hydrogen from another molecule of thiophenol to regenerate the phenylthio radical. The resulting hydroperoxide may decompose to give the corresponding α-phenylthio carbonyl compounds.[14]

Previously we have reported the oxygenation of alkenyl sulfides in the presence of thiophenol[4] and proposed a mechanism involving the hydroperoxide intermediate substituted by a phenylthio group,[15] which decomposed to give the carbonyl compounds. 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, or (b) the carbon–sulfur bond cleavage to give the acylsilanes (Scheme III)? Thus the oxygenation of alkenylsilanes substituted by the phenylthio group at the α-carbon[16] was examined. The reaction took place smoothly, and the corresponding α-phenylthio thiolesters were obtained as a sole product in high yields. The acylsilanes were not detected at all. This result indicates that the cleavage of the carbon–silicon bond took place exclusively without affecting the carbon–sulfur bond. Although more data should be accumulated before elucidation of the detailed mechanism, the present reaction gives an important insight into the chemistry of hydroperoxides,[17] as well as provides a convenient method for the synthesis of thiolesters activated at the α-position.

Acknowledgment. Financial support of this project by Grant-in-Aid, Scientific Research on Priority Areas (Advance Molecular Conversions) (No. 63607526), the Ministry of Education, Science and Culture, Japan is gratefully acknowledged.

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[14] Various reactions involving decomposition of silyl-substituted peroxides reported in the literature seems to relate the present reaction. (a) Silyl-substituted hypochlorites: Kuwajima, I.; Abe, T.; Minami, N. *Chem. Lett.* **1976**, 993. (b) Silyl-substituted peroxymetals: Knochel, P.; Xiao, C.; Yeh, M. C. P. *Tetrahedron Lett.* **1988**, *29*, 6697. (c) Endoperoxides of silyl-substituted furans: Katsumura, S.; Hori, K.; Fujiwara, S.; Isoe, S. *Tetrahedron Lett.* **1985**, *26*, 4625. (d) intermediate in ozonolysis of alkenylsilanes: Büchi, G.; Wüest, H. *J. Am. Chem. Soc.* **1978**, *100*, 294.

[15] (a) Takata, T.; Hoshino, K.; Takeuchi, E.; Tamura, Y.; Ando, W. *Tetrahedron Lett.* **1984**, *25*, 4767. (b) Takata, T.; Tamura, Y.; Ando, W. *Tetrahedron* **1985**, *41*, 2133. (c) Takata, T.; Ando, W. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1275.

[16] 1-(Phenylthio)-1-(trimethylsilyl)alkenes were readily prepared by the reaction of aldehydes with the anion of (phenylthio)bis(trimethylsilyl)methane in THF/hexane.

[17] Patai, S., Ed. *The Chemistry of Peroxides*; Wiley: Chichester, 1983.

γ-Lithioalkoxides via Reductive Lithiation of Oxetanes by Aromatic Radical Anions

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Received August 28, 1989

Summary: Oxetanes are cleaved at 0 °C in tetrahydrofuran by lithium 4,4'-di-*tert*-butylbiphenylide, giving lithium γ-lithioalkoxides which can provide 2-substituted tetrahydrofurans by trapping with aldehydes and ketones followed by acid cyclization of the resulting 1,4-diols; the cuprates of these dianions undergo conjugate addition and nucleophilic substitution reactions.

Sir: While the reductive cleavage of phenyl thioethers by aromatic radical anions is an efficient and general method for production of organolithium compounds,[1] the same procedure applied to simple acyclic ethers has only rarely been used.[2,3] However, it has recently been found that the reductive lithiation of oxiranes at −78 or −95 °C is a useful method for generating β-lithioalkoxides, which react with various electrophiles in moderate to good yields.[4]

We now report that γ-lithioalkoxides (**2**) can be efficiently generated by reductive lithiation of readily available oxetanes **1**[5] using lithium 4,4'-di-*tert*-butylbiphenylide (LDBB).[6] The temperature required (∼0 °C) is substantially higher than that used for reductive cleavage of epoxides with the same reagent.[4b] Fortunately, the resulting γ-lithioalkoxides (**2**) do not undergo loss of lithium oxide as do β-lithioalkoxides[7] and are thus considerably more stable than the corresponding species derived from epoxides. The times required for the reductive cleavage range from 1 min to 4 h, depending on the substitution pattern; the reactivity order is **1d** > **1a** > **1b** >> **1c**. In unsymmetrical cases, the direction of opening is analogous to that observed in the reductive cleavage of epoxides.[4] Alkyl substituents at the 2-position lead to the least substituted carbanion (eq 1).[8] One explanation that has been put forth to explain this regiochemistry in the case of epoxides is that the greater stability of the more substituted alkoxide outweighs the lesser stability of the less

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[1] Cohen, T.; Bhupathy, M. *Acc. Chem. Res.* **1989**, *22*, 152.

[2] Review: Maercker, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 972.

[3] A notable exception is the preparation of allyllithiums by reductive lithiation of allyl phenyl ethers: Eisch, J. J.; Jacobs, A. M. *J. Org. Chem.* **1963**, *28*, 2145.

[4] (a) Bartmann, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 653. (b) Cohen, T.; Jeong, I.-H.; Mudryk, B.; Bhupathy, M.; Awad, M. A. A. *J. Org. Chem.*, in press.

[5] **2a** and **2b** are commercially available (Aldrich Co.). Other derivatives can easily be prepared. See, for example: (a) Okuma, K.; Tanaka, Y.; Kaji, S.; Ohta, H. *J. Org. Chem.* **1983**, *48*, 5133. (b) Picard, P.; Leclerq, D.; Bats, J. P.; Moulines, J. *Synthesis* **1981**, 550.

[6] Freeman, P.; Hutchinson, L. *J. Org. Chem.* **1980**, *45*, 1924.

[7] (a) Barluenga, J.; Flórez, J.; Yus, M. *J. Chem. Soc., Perkin Trans. 1* **1983**, 3019. (b) Barluenga, J.; Fernández-Simón, J. L.; Concellón, J. M.; Yus, M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 3339.

[8] Protonation of the reductive lithiation product of 2-octyloxetane provided 73% of 3-undecanol and 20% of 1-undecanol.