Electroinitiated Oxygenation of Alkenyl Sulfides and Alkynes in the Presence of Thiophenol

Jun-ichi Yoshida,* Shogo Nakatani, and Sachihiko Isoe*

Institute of Organic Chemistry, Faculty of Science, Osaka City University, Sugimoto 3-3-138, Sumiyoshi, Osaka 558, Japan

Received March 4, 1993

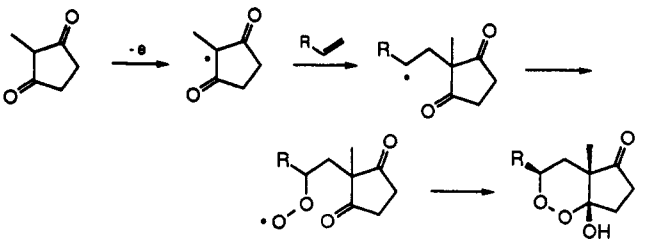
Electrolysis of alkenyl sulfides in the presence of thiophenol with bubbling of molecular oxygen gave the corresponding α-(phenylthio) carbonyl compounds with the consumption of a catalytic amount of electricity. An electroinitiated radical chain mechanism has been proposed. The reaction also took place without electrochemical initiation, but much (5–50 times) longer reaction time was required for the completion of the reaction. The potential utility of the present reaction in organic synthesis is demonstrated by the net 1,2-transposition of a phenylthio group and a carbonyl group. The electroinitiated oxygenation of ketene dithioacetals also proceeded smoothly to give the corresponding α-(phenylthio) thiol esters. It was also found that the electroinitiated oxygenation of alkynes in the presence of thiophenol gave α-(phenylthio) carbonyl compounds. A mechanism involving the initial formation of alkenyl sulfides has been proposed.

Introduction

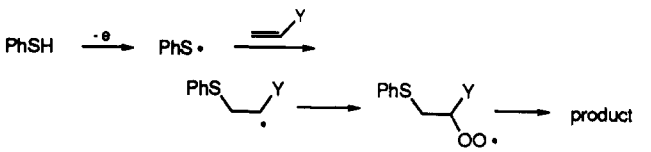
About 5 years ago we reported that the electrochemical reaction is quite effective for oxygenation reaction of 1,3-diketones with olefins.[1] The anodic oxidation of 1,3-diketones gives the corresponding carbon radical which adds to an olefin, and the resulting carbon radical reacts with molecular oxygen to give the peroxy radical which then cyclizes with the carbonyl group in an intramolecular fashion to afford the cyclic peroxide (Scheme I). In searching for other sources of the radical for this type of reaction, thiophenol was found to be quite effective in playing a similar role to 1,3-diketones in the electroinitiated oxygenation. Preliminary studies of our laboratory indicated that alkenyl sulfides were oxidized smoothly in the presence of thiophenol to give α-(phenylthio) carbonyl compounds and that the electrochemical oxidation was quite effective for the initiation of the reaction.[2] In this paper we report the full details of this study.

Electrochemical oxidation of thiophenol is reported to give the disulfide[3] or the sulfinate ester,[4] and these reactions may proceed by the initial formation of phenylthio radical. Therefore, if an appropriate olefin is present in the reaction medium, phenylthio radical should add to the olefin to generate the carbon radical[5] which reacts with molecular oxygen spontaneously (Scheme II). As a matter of fact, it has been reported that olefins are oxygenated in the presence of thiols to give β-hydroperoxy sulfides which decompose to the corresponding β-hydroxy sulfoxides.[6] Synthetic utility of this reaction is, however, rather limited because such reaction is essentially applicable only for activated olefins such as styrene derivatives. Beckwith and Wagner reported that peroxy radicals

Scheme I



Scheme II



generated by the addition of phenylthio radical to olefin followed by the reaction with oxygen are trapped by the carbon–carbon double bond situated at a suitable position in the molecule to form the corresponding cyclic peroxide.[7] Recently, Feldman et al. reported elegant oxygenation reactions of vinylcyclopropane derivatives in the presence of thiophenol or phenylselenol.[8] The addition of phenylthio or phenylseleno radical to the olefinic part of vinylcyclopropane followed by ring opening gives the allyl radical which reacts with molecular oxygen and recyclizes to liberate the phenylthio or phenylseleno radical. These studies demonstrated the potential utility of the oxygenation of olefins using thiols or selenols. Thus, we initiated a program aimed at new oxygenation reactions of olefins utilizing thiols.

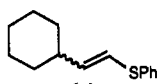
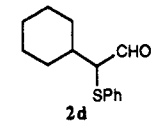
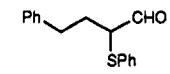
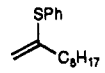
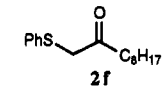
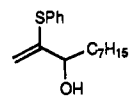
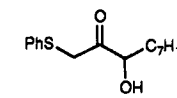
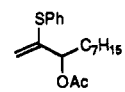
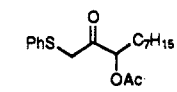
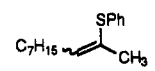
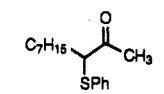
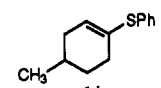
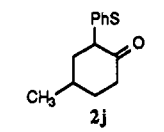
Results and Discussion

Electroinitiated Oxygenation of Alkenyl Sulfides. During the course of the preliminary investigation of

(1) (a) Yoshida, J.; Nakatani, S.; Sakaguchi, K.; Isoe, S. *J. Org. Chem.* **1989**, *54*, 3383. (b) Yoshida, J.; Sakaguchi, K.; Isoe, S. *Tetrahedron Lett.* **1987**, *28*, 667.
(2) Yoshida, J.; Nakatani, S.; Isoe, S. *J. Chem. Soc., Chem. Commun.* **1988**, 1468.
(3) Mango, F.; Bontempelli, G.; Pilloni, G. *J. Electroanal. Chem.* **1971**, *30*, 375.
(4) Nokami, J.; Fujita, Y.; Okawara, R. *Tetrahedron Lett.* **1979**, 3659.
(5) Griesbaum, K. *Angew. Chem.* **1970**, *82*, 276.
(6) (a) Kharasch, M. S.; Nudenberg, W.; Mantell, G. J. *J. Org. Chem.* **1951**, *16*, 524. (b) Oswald, A. A. *J. Org. Chem.* **1959**, *24*, 443.
(7) Beckwith, A. L. J.; Wagner, R. D. *J. Am. Chem. Soc.* **1979**, *101*, 7099.
(8) (a) Feldman, K. S.; Simpson, R. E.; Parvez, M. *J. Am. Chem. Soc.* **1986**, *108*, 1328. (b) Feldman, K. S.; Simpson, R. E. *J. Am. Chem. Soc.* **1989**, *111*, 4878.

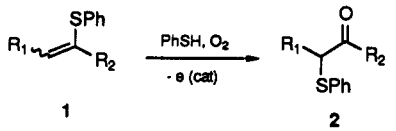
0022-3263/93/1958-4855$04.00/0

Table I. Oxygenation of Alkenyl Sulfides in the Presence of Thiophenol

alkenyl sulfide	method[a]	Solvent	Electricity (F/mol)	time (h)	product	yield[b] (%)
 1a	A	CH_3CN	0.05	2	 2a	77
	B	CH_3CN		41		52
	B	AcOH		48		45
 1b	A	CH_3CN	0.06	1	 2b	76
	B	CH_3CN		2		70
	B	AcOH		3		64
 1c	A	CH_3CN	0.012	2	 2c	91
	B	CH_3CN		23		71
	B	AcOH		10		74
 1d	A	CH_3CN	0.80	8	 2d	73
	A	AcOH	0.125	1.5		81
	B	CH_3CN		96		69
	B	AcOH		24		83
 1e	A	CH_3CN	0.25	2	 2e	63
	B	CH_3CN		31		54
	B	AcOH		8		85
 1f	A	CH_3CN	0.021	2	 2f	82
	B	CH_3CN		96		66
 1g	A	AcOH	0.17	3.5	 2g	71
	B	AcOH		19		91
 1h	A	CH_3CN	0.15	3	 2h	87
	B	CH_3CN		20		87
 1i	A	AcOH	0.300	3	 2i	70
 1j	A	AcOH	0.300	3	 2j	62
	B	AcOH		24		74

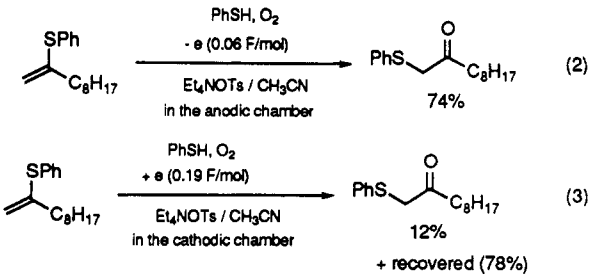
[a] Method A: the reactions were normally carried out with 0.5–1.0 mmol of alkenyl sulfide and 2–4 equiv of thiophenol in 5–10 mL of 0.2 Et_4NOTs/CH_3CN or AcOH. Method B: the reactions were normally carried out with 0.5–1.0 mmol of alkenyl sulfide and 2–4 equiv of thiophenol in 5–10 mL of CH_3CN or AcOH. [b] Isolated yields based on the alkenyl sulfide.

oxygenation reactions of various types of olefins in the presence of thiophenol we found alkenyl sulfides were quite effective as olefins. The electroinitiated oxygenation of alkenyl sulfides in the presence of thiophenol proceeded smoothly to give α-(phenylthio) carbonyl compounds (eq 1) (method A). The results are summarized in Table I.



1 2 (1)

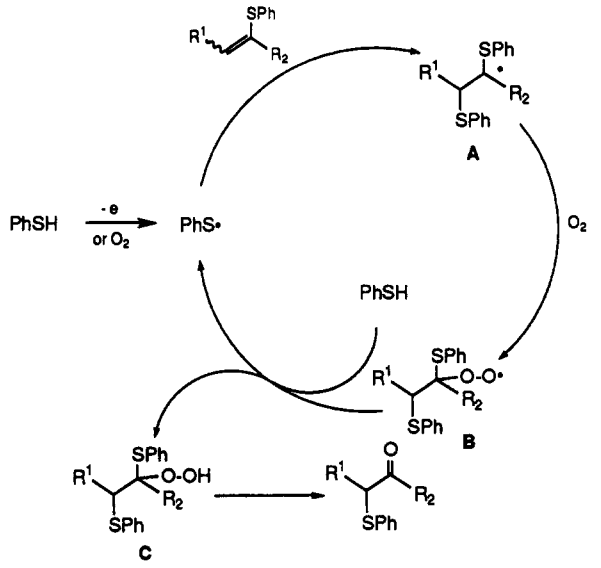
Only catalytic amount of electricity based upon the alkenyl sulfide was required for the completion of the reaction (0.01–0.8 F/mol). Acetic acid was also effective as solvent, and sometimes it was more effective than acetonitrile. In the absence of oxygen the reaction did not proceed appreciably. It is also noteworthy that the addition of a small amount of catechol as a radical scavenger markedly retarded the reaction. When a divided cell was used and the reaction was carried out in the anodic chamber, α-(phenylthio) ketone was obtained in comparable yield with that obtained with an undivided cell (eq 2). But when the reaction was carried out in the cathodic



chamber, most of the alkenyl sulfide was recovered unchanged (eq 3), indicating that electrochemical *oxidation* was responsible for the present reaction.

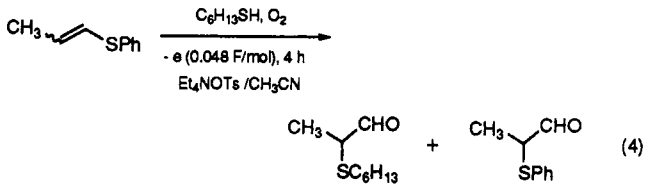
The present reaction also proceeded without electrochemical activation (method B), but much longer reaction time (5–50 times) was required for the completion of the

Scheme III



reaction (Table I). Presumably, phenylthio radical is produced by the autoxidation of thiophenol, but the efficiency of this process seems to be much lower than the electrochemical oxidation (*vide infra*).

The oxygenation of alkenyl sulfides with hexylmercaptan in place of thiophenol gave a mixture of 2-(hexylthio)propanal and 2-(phenylthio)propanal (eq 4). This

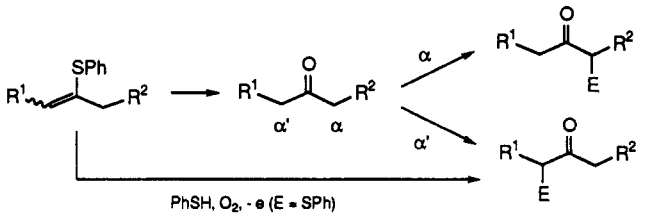


(4)

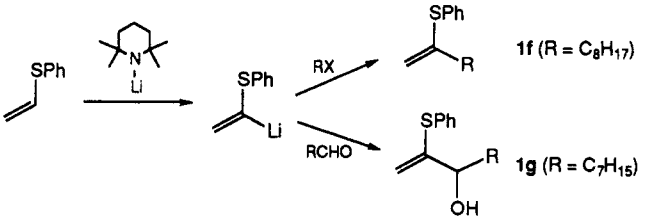
result indicates that phenylthio group released from the alkenyl sulfide was also used for the attack on another molecule of the alkenyl sulfide.

On the basis of these results, the following radical chain mechanism is proposed for the present reaction (Scheme III). One-electron oxidation of thiophenol on the surface of the anode produces the phenylthio radical.[9] Regioselective addition of this radical to alkenyl sulfide followed by the reaction of the resulting carbon radical **A** with molecular oxygen gives the peroxy radical **B**. Hydrogen abstraction from another molecule of thiophenol provides the hydroperoxide **C**,[10] regenerating the phenylthio radical which is used for the next cycle. Decomposition of this hydroperoxide **C** affords the corresponding α-(phenylthio) carbonyl compound as the final product. Although the detailed mechanism of this decomposition has not been clarified as yet, phenylthio group eliminated from **C** (presumably as PhSOH[11]) is converted into the phenylthio

Scheme IV



Scheme V



radical under the conditions at least in part and is used for the attack on another molecule of the alkenyl sulfide.

Alkenyl sulfides are versatile intermediates in organic synthesis.[12] For example, hydrolysis of alkenyl sulfides in the presence of mercuric ion gives the corresponding carbonyl compounds.[13] However, in the case of the resulting carbonyl compound being an unsymmetrical ketone where it is necessary to functionalize either the α- or the α'-position, there is the problem of regioselectivity (Scheme IV). Generally, regioselective activation of one of two α-positions of an unsymmetrical ketone is difficult. This problem, however, could be solved, since the present oxygenation reaction provides a regiospecific method for the conversion of alkenyl sulfides to carbonyl compounds having an activating group at the α-position; one can introduce various electrophiles selectively at the α carbon activated by a phenylthio group.[14] Oxidation of sulfur atom followed by elimination also provides a regiospecific access to α,β-unsaturated carbonyl compounds.[15]

Various methods for the synthesis of alkenyl sulfides have been reported. For instance, deprotonation of the olefinic proton of phenyl vinyl sulfide with lithium 2,2,6,6-tetramethylpiperidide followed by alkylation is a useful method for the preparation of α-substituted alkenyl sulfides such as **1f** and **1g** (Scheme V).[16] The reaction of the anion of (phenylthio)(trimethylsilyl)methane with carbonyl compounds also provides a convenient method for the synthesis of β-substituted alkenyl sulfides such as **1c**, **1d**, and **1e** (Scheme VI).[17]

(9) Although the oxidation potential of thiophenol (E_p = 1.59 V vs Ag/AgCl) is more than those of alkenyl sulfides (**1b**: E_p = 1.36 V vs Ag/AgCl), oxidation of thiophenol seems to have priority over those of alkenyl sulfides. See refs 3 and 4.

(10) (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.

(11) We do not have any evidence for the sulfenic acid intermediate. Sulfenic acids (RSOH) are generally unstable and are converted into various sulfur species depending on the reaction conditions. See, for example: Hogg, D. R. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon Press: New York, 1979; Vol. 3, Chapter 11.16.

(12) (a) Trost, B. M.; Lavoie, A. C. *J. Am. Chem. Soc.* **1983**, *105*, 5075. (b) Annunziata, R.; Cinquini, M.; Cozzi, F.; Cozzi, P. G.; Consolandi, E. *J. Org. Chem.* **1992**, *57*, 456. (c) Annunziata, R.; Cinquini, M.; Cozzi, F.; Cozzi, P. G.; Raimondi L. *J. Org. Chem.* **1992**, *57*, 3605. (d) Kudo, K.; Hashimoto Y.; Sukegawa, M.; Hasegawa, M.; Saigo, K. *J. Org. Chem.* **1993**, *58*, 579.

(13) (a) Corey, E. J.; Shulman, J. I. *J. Org. Chem.* **1970**, *35*, 777. (b) Mukaiyama, T.; Kamio, K.; Kobayashi, S.; Takei, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3723.

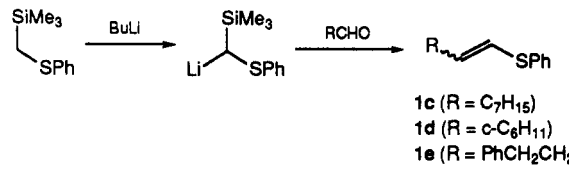
(14) Coates, R. M.; Pigott, H. D.; Olinger, J. *Tetrahedron Lett.* **1974**, 3955.

(15) (a) Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887. (b) Durman, J.; Elliott, J.; McElroy, A. B.; Warren, S. *Tertahedron Lett.* **1983**, *24*, 3927.

(16) (a) Oshima, K.; Shimoji, K.; Takahashi, H.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1973**, *95*, 2694. (b) Trost, B. M.; Lavoie, A. C. *Ibid.* **1983**, *105*, 5075. (c) Takeda, T.; Furukawa, H.; Fujimori, M.; Suzuki, K.; Fujiwara, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1863.

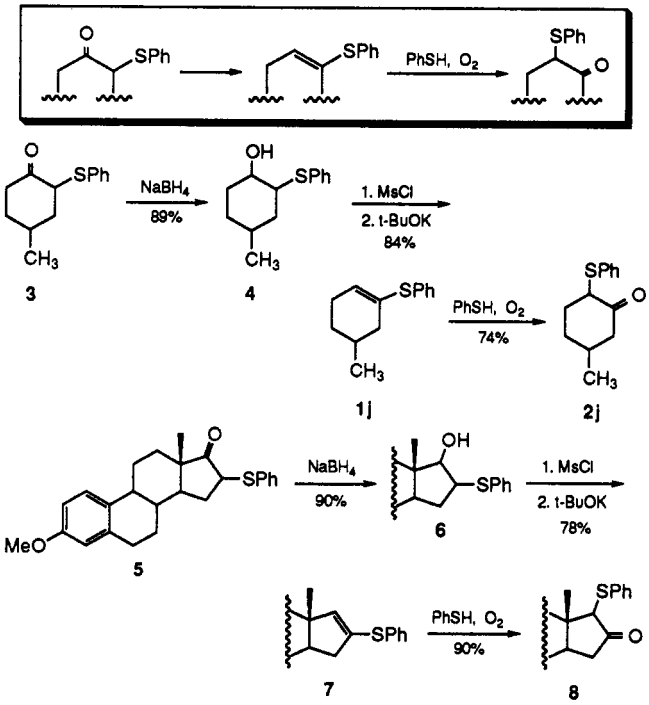
(17) (a) Carey, F. A.; Court, A. S. *J. Org. Chem.* **1972**, *37*, 939. (b) Ager, D. J. *Tetrahedron Lett.* **1981**, *22*, 2803.

Scheme VI



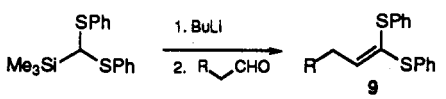
1c (R = C_7H_{15})
1d (R = c-C_6H_{11})
1e (R = $PhCH_2CH_2$)

Scheme VII



In order to demonstrate the synthetic utility of the present oxygenation reaction, the following net 1,2-transposition of phenylthio group and carbonyl group was investigated (Scheme VII).[18] For example, phenylthio ketone **3** derived from 4-methyl-1-cyclohexanone was reduced with $NaBH_4$ to give the corresponding alcohol **4**, which was converted to alkenyl sulfide **1j** by mesylation followed by elimination. Alkenyl sulfide **1j** was then oxygenated by the present reaction to obtain the 1,2-transposition product **2j**. An application of similar sequence to estrone methyl ether derivative **5** afforded the 1,2-transposition product **8** in high yield.

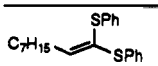
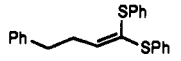
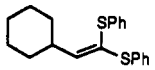
Electroinitiated Oxygenation of Ketene Dithioacetals. We also examined the oxygenation of olefins having two phenylthio groups (ketene dithioacetals)[19] in the presence of thiophenol. Ketene dithioacetals were readily synthesized by the reaction of aldehydes with bis(phenylthio)(trimethylsilyl)methane (eq 5).[20]



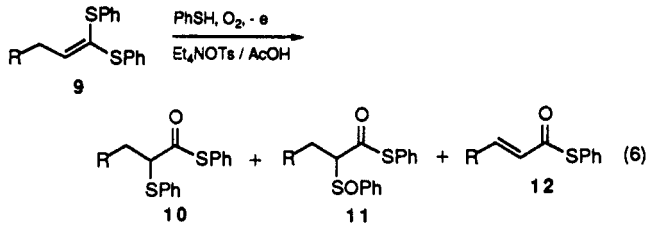
(5)

The electroinitiated oxygenation of ketene dithioacetals (**9**) in the presence of thiophenol proceeded smoothly to give the corresponding α-(phenylthio) thiol esters **10** as the major product[21] (eq 6, Table II).

Table II. Oxygenation of Ketene Dithioacetals in the Presence of Thiophenol[a]

ketene dithioacetal	method[b]	electricity (F/mol)	time (h)	yield (%)[c] 10	11	12
 9a	A	0.21	2	70		20
	B		81	61		20
 9b	A	0.17	2	58	24	8
	B		7	58	23	7
 9c	A	2.61	8	67	4	
	B		95[d]	40	8	

[a] The reactions were normally carried out with 0.3 mmol of ketene dithioacetal 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 ketene dithioacetal. [d] 47% of starting material was recovered.



(6)

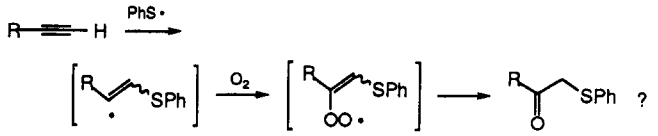
The sulfoxide **11** and the α,β-unsaturated thiol ester **12** were also obtained as byproducts. Although detailed mechanism for the formation of these byproducts has not yet been clarified, **11** and **12** did not seem to be produced from α-(phenylthio) thiol ester **10**, since a separate experiment revealed that α-(phenylthio) thiol ester **10** was not converted into **11** or **12** under the present oxygenation conditions.[15a]

Electroinitiated Oxygenation of Alkynes. In the previous section we have shown that phenylthio radical adds effectively to alkenyl sulfides in the electroinitiated oxygenation reaction.[22] Since alkynes are generally quite effective as radical acceptors,[23] we were interested in the electroinitiated oxygenation of alkynes in the presence of thiophenol. The phenylthio radical generated from thiophenol would add to alkynes. The alkenyl radical thus generated would react with molecular oxygen to give the hydroperoxide which would decompose to give the corresponding α-(phenylthio) ketone (Scheme VIII).

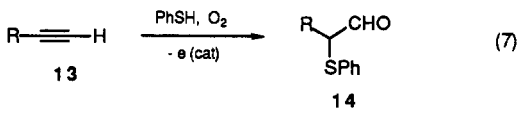
The electroinitiated oxygenation of alkynes proceeded smoothly. However, to our surprise, the corresponding α-(phenylthio) aldehydes were obtained (eq 7). The phenylthio group was introduced at the internal position,

(18) Trost, B. M.; Hiroi, K.; Kurozumi, S. *J. Am. Chem. Soc.* **1975**, *97*, 438.
(19) Seebach, D.; Kolb, M.; Grobel, B.-T. *Chem. Ber.* **1973**, *106*, 2277.
(20) Corey, E. J.; Seebach, D.; Freedmann, R. *J. Am. Chem. Soc.* **1967**, *89*, 434.
(21) Thiol esters: (a) Mukaiyama, T.; Araki, M.; Takei, H. *J. Am. Chem. Soc.* **1973**, *95*, 4763. (b) Gais, H.-J. *Angew. Chem.* **1977**, *89*, 251. (c) Effenberger, F.; Bessey, E. *Chem. Ber.* **1980**, *113*, 2100. α,β-Unsaturated thiol esters: (d) Lucast, D. H.; J. Wemple, J. *Tetrahedron Lett.* **1977**, 1103.
(22) For electroinitiated oxygenation, see ref 1 and: (a) Yoshida, J.; Nakatani, S.; Isoe, S. *Tetrahedron Lett.* **1990**, *31*, 2425. See also: (b) Tang, R.; Yue, H. J.; Wolf, J. F.; Mares, F. *J. Am. Chem. Soc.* **1978**, *100*, 5248. (c) Clennan, E. L.; Simmons, W.; Almgren, C. W. *J. Am. Chem. Soc.* **1981**, *103*, 2098.
(23) Generally both nucleophilic and electrophilic radicals react faster with alkenes than with alkynes. See: Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753.

Scheme VIII

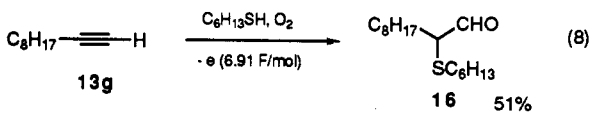


and the oxygen atom was introduced at the terminal position (Table III).



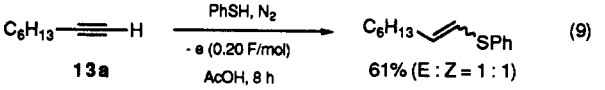
Methanol and benzene were also effective as solvent, but acetonitrile was not suitable because most of the 1-octyne was recovered unchanged. Various terminal alkynes containing free hydroxyl (**13c**), acetoxyl (**13d**), and benzyloxyl (**13e**) groups were oxidized without affecting such functionalities to give the corresponding α-(phenylthio) carbonyl compounds. But oxygenation of benzyl propargyl ether (**13b**) afforded the corresponding aldehyde **14b** in relatively low yield (23–44%). Although oxygenation of 4-butyn-1-ol (**13c**) in acetic acid gave a mixture of the hemiacetal **15** and the corresponding hemithioacetal, use of methanol as solvent suppressed the formation of the hemithioacetal. Internal alkynes such as 5-decyne (**13f**) were also oxidized smoothly in the presence of thiophenol to give the corresponding α-(phenylthio) ketones.

Alkyl thiols such as hexylmercaptan could also be used in place of thiophenol, but a large amount of electricity was required for the completion of the reaction and α-(hexylthio) aldehyde **16** was obtained only in 51% yield (eq 8).



The present reaction also proceeded without electrochemical activation (method B), but much longer reaction time was required for the completion of the reaction, and in some cases significant amounts of byproducts were obtained (Table III). The initiation with a radical initiator such as α,α'-azobis(isobutyronitrile) (AIBN) (method C) was also effective. However, the yields were lower than those for method A, and in some cases a significant amount of byproducts was produced probably because of higher reaction temperature (Table III).

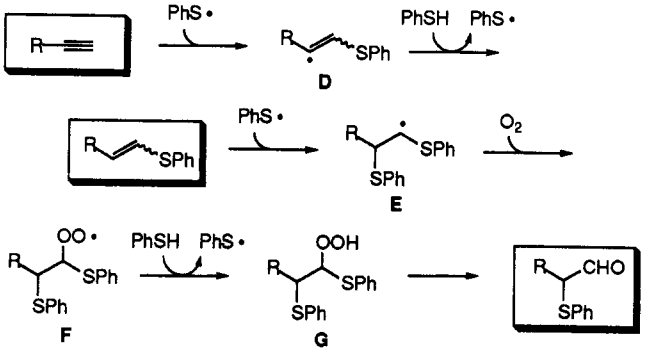
VPC monitoring of the reaction indicated that the alkenyl sulfide was formed initially and that the α-(phenylthio) aldehyde was produced gradually during the last half of the reaction period at the expense of the alkenyl sulfide. As a matter of fact, the alkenyl sulfide was formed as a major product when the reaction was carried out under an atmosphere of nitrogen (eq 9).[24] It is worth noting that



the alkenyl sulfide was obtained as a 1:1 mixture of *E* and *Z* isomers. Oshima et al. also reported a similar reaction of alkynes with thiols initiated by triethylborane to afford the alkenyl sulfides.[25]

On the basis of these results, the following radical chain mechanism seems to be reasonable (Scheme IX). The phenylthio radical, which is produced by electrochemical one-electron oxidation of thiophenol,[9] adds to the triple bond regioselectively to generate alkenyl radical **D**.[24] Since *E*–*Z* isomerization of alkenyl radical is very fast,[26] the isomerization of alkenyl radical **D** is also considered to be fast. Hydrogen abstraction from another thiophenol produces the alkenyl sulfide as a mixture of *E* and *Z* isomers and regenerates phenylthio radical. The alkenyl sulfide is then attacked by the phenylthio radical to generate alkyl radical **E** which reacts with molecular oxygen to give the peroxy radical **F**. Hydrogen abstraction from thiophenol produces the hydroperoxide **G**[10] which decomposes to give the (α-phenylthio) carbonyl compounds. It is interesting that alkenyl radical **D** prefers to abstract hydrogen rather than to react with molecular oxygen, whereas alkyl radical **E** prefers to react with molecular oxygen rather than to abstract hydrogen under the same conditions.[27] This phenomenon can be explained as follows: Generally, sp^2 carbon is more electronegative than sp^3 carbon. Therefore, the reactivity of the alkenyl radical to electrophilic molecular oxygen should be lower than that of the alkyl radical. On the contrary, the reactivity of the alkenyl radical to hydrogen donors should be greater than that of the alkyl radical. Thus, alkenyl radical **D** prefers to abstract hydrogen and alkyl radical **E** prefers to react with molecular oxygen.

Scheme IX



Several methods for the conversion of terminal alkynes to carbonyl compounds have been developed so far. For instance, hydroboration of terminal alkynes followed by oxidation gives the corresponding aldehydes.[28,29] Stork reported the conversion of terminal alkynes to aldehydes by a sequence of hydrosilylation, *m*-CPBA oxidation, and acid catalyzed hydrolysis.[30] Therefore, terminal alkynes are generally regarded as synthons of aldehydes.[31] The present oxygenation, however, provides a direct method for the conversion of alkynes to the carbonyl compounds

(24) (a) Mueller, W. H. *J. Org. Chem.* **1966**, *31*, 3075. (b) Griffiths, J.; Murphy, J. A. *Tetrahedron* **1992**, *48*, 5543.

(25) Ichinose, Y.; Wakamatsu, K.; Nozaki, K.; Birbaum, J.-L.; Oshima, K.; Utimoto, K. *Chem. Lett.* **1987**, 1647.

(26) Singer, L. A.; Kong, N. P. *J. Am. Chem. Soc.* **1966**, *88*, 5213.

(27) Griesbaum, K.; Oswald, A. A.; Hudson, B. E., Jr. *J. Am. Chem. Soc.* **1963**, *85*, 1969.

(28) Kretschmar, H. C.; Erman, W. F. *Tetrahedron Lett.* **1970**, 41.

(29) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1975**, *97*, 5249.

(30) Stork, G.; Colvin, E. *J. Am. Chem. Soc.* **1971**, *93*, 2080.

(31) Antonioletti, R.; D'Auria, M.; Piancatelli, G.; Scettri, A. *Tetrahedron Lett.* **1981**, *22*, 1041.

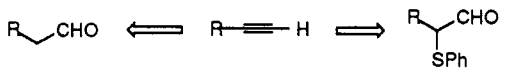
Table III. Oxygenation of Alkynes in the Presence of Thiophenol[a]

alkyne	solvent	method[b]	electricity F/mol (AIBN equiv)	time (h)	product	yield[c] (%)
C_6H_{13}—≡ **13a**	AcOH	A	0.35	7	C_6H_{13} CHO / SPh **14a**	80
		B		18		51
		C	(0.42)	1		73 (77:23)[d]
	MeOH	A	0.10	2		79 (92:8)[e]
		B		46		59 (25:75)[d]
		C	(2.92)	4		47
	C_6H_6	A	0.03	9		77
		B		98		52
		C	(1.24)	6		68 (74:26)[d]
	MeCN	A	0.30	6		trace
		B		50		0
		C	(1.12)	3		64 (80:20)[d]
BzlO≡ **13b**	AcOH	A	1.39	21	BzlO CHO / SPh **14b**	43
		B		69		32
		C	(0.41)	1		23
HO≡ **13c**	MeOH	A	0.77	9		44
	AcOH	A	0.50	10	SPh[f] / O / OH **15**	68 (35:65)[g]
		B		42		75 (11:89)[g]
	MeOH	A	0.40	8		62
		B		92		44
AcO≡ **13d**	AcOH	A	0.32	6.5	AcO CHO / SPh **14d**	72
BzlO≡ **13e**	AcOH	A	0.45	9	BzlO CHO / SPh **14e**	71
		B		25		63
		C	(0.84)	2		43
C_4H_9—≡—C_4H_9 **13f**	AcOH	A	1.24	25	C_4H_9 O C_4H_9 / SPh **14f**	67
		B		64		58
		C	(2.57)	5		55

[a] The reactions were normally carried out with 0.5 mmol of alkynes and 4–6 equiv of thiophenol. [b] Method A: initiated by electrolysis in 0.2 M Et_4NOTs/solvent. MethodB: initiated by oxygen (autoxidation). Method C: initiated by AIBN. [c] Isolated yields. [d] The corresponding dithioacetal was also formed. Ratio of the aldehyde to its dithioacetal is given in parentheses. [e] The corresponding dimethyl acetal was also formed. Ratio of the aldehyde to its dimethyl acetal is given in parentheses. [f] Trans:cis = 1:1. [g] The corresponding hemithioacetal (trans:cis = 1:1) was also formed. Ratio of the hemiacetal to hemithioacetal is given in parentheses.

having an activating group at the α-position which are versatile intermediates in organic synthesis (Scheme X).[14,15]

Scheme X



In conclusion, we have developed the electroinitiated oxygenation of alkenyl sulfides and alkynes in the presence of thiophenol and demonstrated potential utility of the present reaction in organic synthesis. Further investigation in this field will hopefully provide a new aspect to the chemistry of oxygenation reactions.

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 × 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.

General Procedure for the Electroinitiated Oxygenation of Alkenyl Sulfides in the Presence of Thiophenol (Method A). The reaction was carried out in an undivided cell equipped with carbon rod anode (i.d. = 6 mm) and platinum plate cathode (20 × 30 mm). Alkenyl sulfide (1.0 mmol) and thiophenol (2.0–4.0 mmol) were dissolved in 0.2 M Et_4NOTs/CH_3CN or Et_4NOTs/AcOH (10 mL), and oxygen gas was bubbled through the cell with magnetic stirring. The constant current electrolysis (20–50 mA, 1–5 min) was carried out at room temperature. After the reaction was initiated, the reaction mixture was stirred with bubbling of oxygen at this temperature. If the reaction was not complete, the electrolysis was repeated (0.5–1-h interval) until most of the alkenyl sulfide was consumed. The reaction mixture was then partitioned between ether and brine or aqueous $NaHCO_3$. The organic and aqueous phases were separated, and the aqueous phase was extracted with ether several times. The combined organic phase was dried over Na_2SO_4. Removal of the solvent under reduced pressure followed by flash chromatography on silica gel yielded the corresponding α-(phenylthio) carbonyl compound.

General Procedure for the Oxygenation of Alkenyl Sulfides in the Presence of Thiophenol (Method B). Alkenyl sulfide (1.0 mmol) and thiophenol (2.0–4.0 mmol) were dissolved in acetonitrile or acetic acid (10 mL), and oxygen gas was bubbled through the cell with magnetic stirring at room temperature. After the reaction was completed, the reaction mixture was partitioned between ether and brine or aqueous $NaHCO_3$. The organic and aqueous phases were separated, and the aqueous phase was extracted with ether several times. The combined organic phase was dried over Na_2SO_4. Removal of the solvent under reduced pressure followed by flash chromatography on silica gel yielded the corresponding α-(phenylthio) carbonyl compound.

(Phenylthio)acetaldehyde (2a): TLC R_f 0.29 (hexane/ethyl acetate (9:1)); VPC t_R 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.

2-(Phenylthio)propanal (2b): TLC R_f 0.36 (hexane/ethyl acetate (9:1)); VPC t_R 5.29 min (100–230 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 1.38 (d, J = 7.03 Hz, 3 H), 3.62 (dq, J_q = 7.03 Hz, J_d = 3.08 Hz, 1 H), 7.21–7.47 (m, 5 H), 9.44 (d, J = 3.30 Hz, 1 H); IR ($CHCl_3$) 3050 (m), 2990 (m), 2920 (m), 2870 (w), 2800 (m), 2700(m), 1710 (s), 1580 (m), 1480 (m), 1470 (m), 1435 (m), 1380 (m), 1300 (m), 1085 (m), 1065 (m), 1020 (m) cm^{-1}; low-resolution MS *m/e* (relative intensity) 166 (M, 32), 137 (100), 109 (49), 77 (11), 65 (15), 59 (17); high-resolution MS calcd for $C_9H_{10}OS$ 166.0450, found 166.0448.

2-(Phenylthio)nonanal (2c): TLC R_f 0.52 (hexane/ethyl acetate (9:1)); VPC t_R 5.78 min (100–230 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 0.81–1.83 (m, 15 H), 3.41–3.61 (m, 1 H), 7.12–7.46 (m, 5 H), 9.36 (d, J = 4.18 Hz, 1 H); IR ($CHCl_3$) 2920 (s), 2860 (m), 2720 (w), 1710 (s), 1585 (m), 1465 (m), 1440 (m), 1380 (w), 1305 (w), 1070 (w), 1025 (w) cm^{-1}; low-resolution MS *m/e* (relative intensity) 250 (M, 31), 232 (6), 221 (100), 148 (12), 147 (13), 123 (50), 110 (13), 109 (13); high-resolution MS calcd for $C_{15}H_{22}OS$ 250.1392, found 250.1409.

Cyclohexyl(phenylthio)acetaldehyde (2d): TLC R_f 0.48 (hexane/ethyl acetate (9:1)); VPC t_R 7.11 min (100–250 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 1.21–2.15 (m, 11 H), 3.34 (dd, J = 8.35 and 5.50 Hz, 1 H), 7.21–7.40 (m, 5 H), 9.32 (d, J = 5.49 Hz, 1 H); IR ($CHCl_3$) 2980 (w), 2920 (s), 2850 (m), 2700 (w), 1705 (s), 1580 (m), 1480 (m), 1445 (m), 1440 (m), 1170 (m), 1085 (m), 1060 (m), 1025 (m) cm^{-1}; low-resolution MS *m/e* (relative intensity) 234 (M, 26), 205 (71), 152 (9), 123 (76), 95 (100); high-resolution MS calcd for $C_{14}H_{18}OS$ 234.1077, found 234.1074.

4-Phenyl-2-(phenylthio)butanal (2e): TLC R_f 0.38 (hexane/ethyl acetate (9:1)); VPC t_R 8.38 min (100–250 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 1.80–2.37 (m, 2 H), 2.83 (t, J = 7.48 Hz, 2 H), 3.48 (dt, J_t = 7.47 Hz, J_d = 3.30 Hz, 1 H), 7.12–7.45 (m, 5 H), 9.43 (d, J = 3.30 Hz, 1 H); IR ($CHCl_3$) 3000 (m), 2910 (m), 2800 (m), 2700 (w), 1710 (s), 1600 (w), 1580 (m), 1470 (m), 1435 (m), 1080 (m), 1020 (m) cm^{-1}; low-resolution MS *m/e* (relative intensity) 256 (M, 30), 248 (22), 199 (14), 152 (26), 147 (34), 117 (92), 91 (100); high-resolution MS calcd for $C_{16}H_{16}OS$ 256.0921, found 256.0921.

1-(Phenylthio)-2-decanone (2f): TLC R_f 0.42 (hexane/ethyl acetate (9:1)); VPC t_R 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.

3-Hydroxy-1-(phenylthio)-2-decanone (2g): TLC R_f 0.18 (hexane/ethyl acetate (9:1)); VPC t_R 13.9 min (100–240 °C, 10 °C/min); mp 58–59 °C; ^1H 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 $C_{16}H_{24}O2S$ 280.1497, found 280.1515. Anal. Calcd for $C_{16}H_{24}O2S$: C, 68.53; H, 8.63. Found: C, 68.52; H, 8.66.

3-Acetoxy-1-(phenylthio)-2-decanone (2h): TLC R_f 0.27 (hexane/ethyl acetate (9:1)); ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.72 Hz, 3 H), 1.24–1.36 (m, 10 H), 1.66–1.79 (m, 2 H), 2.12 (s, 3 H), 3.80 (s, 2 H), 5.23 (dd, J = 7.94 and 4.27 Hz, 1 H), 7.20–7.38 (m, 5 H); IR ($CHCl_3$) 2910 (s), 2850 (m), 1735 (s), 1580 (w), 1480 (m), 1465 (m), 1440 (m), 1370 (m), 1230 (s), 1025 (m) cm^{-1}; low-resolution MS *m/e* (relative intensity) 322 (M, 86), 280 (9), 262 (56), 234 (29), 199 (15), 171 (19), 150 (51), 123 (100), 111 (83); high-resolution MS calcd for $C_{18}H_{26}O_3S$ 322.1602, found 322.1610. Anal. Calcd for $C_{18}H_{26}O_3S$: C, 67.04; H, 8.13. Found: C, 67.03; H, 8.19.

3-(Phenylthio)-2-decanone (2i): TLC R_f 0.31 (hexane/ethyl acetate (9:1)); VPC t_R 5.45 min (100–250 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 0.81–1.82 (m, 15 H), 2.12 (s, 3 H), 3.61 (t, J = 7.03 Hz, 1 H), 7.21–7.33 (m, 5 H); IR (neat) 2940 (s), 2860 (m), 1710 (s), 1585 (w), 1485 (w), 1470 (w), 1440 (w), 1360 (m), 1230 (w), 1160 (w), 1030 (w) cm^{-1}; low-resolution MS *m/e* (relative intensity) 264 (M, 21), 221 (100), 123 (48), 69 (52); high-resolution MS calcd for $C_{16}H_{24}OS$ 264.1548, found 264.1561. Anal. Calcd for $C_{16}H_{24}OS$ C, 72.68; H, 9.15. Found: C, 72.58; H, 9.20.

5-Methyl-2-(phenylthio)-1-cyclohexanone (2j). Compound **2j** was characterized as a mixture (3:2) of two stereoisomers. TLC R_f 0.31 and 0.36 (hexane/ethyl acetate (9:1)); VPC t_R 4.63 min (100–250 °C, 10 °C/min); ^1H NMR (400 MHz, $CDCl_3$) δ 1.02 (d, J = 6.35 Hz), 1.05 (d, J = 6.59 Hz) (total 3 H, 2:3), 1.35–2.35 (m), 2.68 (ddd, J = 12.94, 3.90, and 1.95 Hz), 2.79 (dd, J = 13.67 and 12.20 Hz) (total 7 H), 3.73 (ddd, J = 4.88, 3.17, and 1.46 Hz), 3.86 (ddd, J = 11.23, 5.86 and 1.22 Hz) (total 1 H), 7.23–7.41 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 207.88, 206.37, 133.91, 133.81, 132.30, 131.46, 129.05, 128.92, 127.47, 127.27, 57.33, 54.35, 49.04, 45.37, 34.68, 34.63, 33.16, 32.81, 31.54, 29.30, 21.98, 21.50; INEPTR ($CDCl_3$) δ 132.30 (+), 131.46 (+), 129.06 (+), 128.93 (+), 127.47 (+), 127.27 (+), 57.34 (+), 54.32 (+), 49.07 (−), 45.36 (−), 34.68 (+), 33.20 (−), 32.84 (−), 31.52 (−), 29.30 (−), 22.01 (+), 21.52 (+); IR ($CHCl_3$) 2990 (w), 2940 (m), 2910 (m), 2860 (w), 1700 (s), 1580 (w), 1475 (m), 1435 (m), 1185 (m), 1115 (w), 1085 (w) cm^{-1}; low-resolution MS *m/e* (relative intensity) 220 (M, 98), 192 (3), 176 (23), 149 (14), 136 (7), 135 (8), 110 (100); high-resolution MS calcd for $C_{13}H_{16}OS$ 220.0920, found 220.0920.

Electroinitiated Oxygenation of 1-(Phenylthio)-1-propene (1b) in the Presence of Hexylmercaptan. 1-(Phenylthio)-1-propene (150 mg, 1.0 mmol) and hexylmercaptan (1.4 mL, 9.9 mmol) were dissolved in 0.2 M Et_4NOTs/CH_3CN (10 mL), and oxygen gas was bubbled through the cell with magnetical stirring. The constant current electrolysis (20 mA, 1 min) was repeated four times with an interval of 1 h at room temperature. After the reaction was completed, the reaction mixture was partitioned between ether and brine. The organic and aqueous phases were separated, and the aqueous phase was extracted with ether three times. The combined organic phase was dried over Na_2SO_4. Removal of the solvent under reduced pressure followed by flash chromatography on silica gel (hexane/ethyl acetate (99:1–39:1)) gave 85 mg (0.48 mmol, 48%) of 2-(hexylthio)propanal and 56 mg (0.34 mmol, 34%) of 2-(phenylthio)propanal.

2-(Hexylthio)propanal: TLC R_f 0.55 (hexane/ethyl acetate (9:1)); VPC t_R 2.10 min (100–250 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 0.81–1.74 (m), 1.35 (d, J = 6.81 Hz) (total 14 H), 2.40 (t, J = 7.03 Hz, 2 H), 3.20 (dq, J_q = 7.03 Hz, Jd = 4.17 Hz, 1 H), 9.22 (d, J = 4.17 Hz, 1 H); IR ($CHCl_3$) 2910 (s), 2850 (m), 1705 (s), 1450 (m), 1375 (w), 1125 (w), 1020 (w) cm^{-1}; low-resolution MS *m/e* (relative intensity) 174 (M, 19), 145 (100), 117 (6), 116 (10), 83 (53), 75 (74); high-resolution MS calcd for $C_9H_{18}OS$ 174.1079, found 174.1091.

1-Hydroxy-4-methyl-2-(phenylthio)cyclohexane (4). To a solution of 4-methyl-2-(phenylthio)cyclohexan-1-one (**3**) (1.813 g, 8.23 mmol) in 10 mL of ethanol was added $NaBH_4$ (157 mg, 4.15 mmol) at room temperature. The mixture was stirred at this temperature for 1 h. The reaction mixture was concentrated under reduced pressure and diluted with ether. Aqueous NH_4Cl and 10% aqueous HCl were added, and the mixture was stirred at room temperature. The organic and aqueous phases were separated, and the aqueous phase was extracted with ether twice. The combined organic phase was dried over Na_2SO_4. Removal of the solvent under reduced pressure followed by bulb-to-bulb distillation (220 °C/1 mmHg) gave 1.621 g (7.29 mmol) of the title compound in 89% yield, which was characterized as a mixture of two stereoisomers. It was difficult to determine their ratio by NMR: TLC R_f 0.36, 0.38, and 0.50 (hexane/ethyl acetate (4:1)); VPC t_R 4.53 and 4.76 min (100–250 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 0.87 (d, J = 7.2 Hz), 0.92 (d, J = 5.72 Hz) (total 3 H), 1.11–3.43 (m, 8 H), 3.60–3.88 (m, 1 H), 7.17–7.51 (m, 5 H); IR ($CHCl_3$) 3620–3270 (br, m), 3050 (w), 3000 (w), 2850 (w), 1580 (m), 1475 (m), 1435 (m), 1375 (m), 1185 (m), 1045 (m) cm^{-1}; low-resolution MS *m/e* (relative intensity) 222 (M, 39), 204 (1), 163

(2), 135 (2), 123 (4), 110 (100), 95 (43), 94 (21); high-resolution MS calcd for $C_{13}H_{18}OS$ 222.1079, found 222.1081.

5-Methyl-1-(phenylthio)-1-cyclohexene (1j). To a solution of the 4-methyl-2-(phenylthio)cyclohexan-1-ol (1.621 g, 7.29 mmol) in 5 mL of pyridine was added methanesulfonyl chloride (1.50 mL, 19.4 mmol) at room temperature. The mixture was stirred at this temperature for 1 h. The reaction mixture was partitioned between ether and aqueous NH_4Cl. The organic and aqueous phases were separated, and the aqueous phase was extracted with ether several times. The combined phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude residue (2.574 g) was dissolved in 6.5 mL of dimethyl sulfoxide, and potassium *tert*-butoxide (2.358 g, 21.01 mmol) was added at 0 °C. The mixture was stirred at this temperature for 5 min and at room temperature for 1 h. The reaction mixture was partitioned between ether and aqueous NH_4Cl. The organic and aqueous phases were separated, and the aqueous phase was extracted with ether several times. The combined organic phase was dried over Na_2SO_4. Removal of the solvent under reduced pressure followed by flash chromatography on silica gel (hexane) gave 1.247 g (6.10 mmol) of the title compound in 84% yield: TLC R_f 0.81 (hexane/ethyl acetate (4:1)); VPC t_R 4.40 min (100–250 °C, 10 °C/min); ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.92 (d, J = 7.20 Hz, 3 H), 1.03–2.24 (m, 7 H), 5.95–6.14 (m, 1 H), 7.10–7.30 (m, 5 H); IR ($CHCl_3$) 3050 (w), 2900 (s), 1580 (m), 1470 (s), 1450 (m), 1415 (m), 1375 (w), 1340 (m), 1170 (w), 1135 (w), 1080 (m), 1060 (m), 1025 (m), 970 (m) cm^{-1}; low-resolution MS *m/e* (relative intensity) 204 (M, 100), 189 (7), 162 (7), 161 (8), 147 (11), 129 (11), 127 (6), 110 (18), 95 (92); high-resolution MS calcd for $C_{13}H_{16}S$ 204.0973, found 204.0974.

17-Hydroxy-3-methoxy-13-methyl-16-(phenylthio)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene (6). To a solution of the 3-methoxy-13-methyl-17-oxo-16-(phenylthio)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene (5) (523 mg, 1.33 mmol) in 10 mL of ethanol was added $NaBH_4$ (100 mg, 2.64 mmol) at room temperature. The mixture was stirred at this temperature for 4 h. After the solvent was removed under reduced pressure, the reaction mixture was partitioned between ether and aqueous NH_4Cl. The organic and aqueous phases were separated, and the aqueous phase was extracted with ether twice. The combined organic phase was dried over Na_2SO_4. Removal of the solvent under reduced pressure followed by flash chromatography on silica gel (hexane/ethyl acetate (9:1)) gave 404 mg (1.02 mmol, 77%) of the less polar alcohol and 67 mg (0.17 mmol, 13%) of the more polar alcohol.

The less polar alcohol (6a): TLC R_f 0.49 (hexane/ethyl acetate (4:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79 (s, 3 H), 1.19 (ddd, *J* = 12.81, 10.98, and 6.10 Hz, 1 H), 1.26–1.58 (m, 5 H), 1.86–1.91 (m, 1 H), 2.03 (dt, J_d = 12.81 Hz, J_t = 3.05 Hz, 1 H), 2.23 (dt, J_t = 10.99 Hz, J_d = 4.27 Hz, 1 H), 2.30–2.34 (m, 1 H), 2.49 (ddd, *J* = 12.82, 8.54, and 6.10 Hz, 1 H), 2.82–2.88 (m, 2 H), 3.77 (s, 3 H), 3.82 (d, *J* = 8.54 Hz, 1 H), 3.87 (q, *J* = 8.54 Hz, 1 H), 6.62–6.73 (m, 2 H), 7.17–7.41 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 157.57, 137.76, 137.57, 132.39, 129.18, 128.93, 126.32, 126.26, 113.84, 111.58, 80.11, 55.20, 50.99, 48.26, 43.90, 43.74, 38.31, 37.33, 34.22, 29.71, 27.42, 26.09, 11.95; INEPTR ($CDCl_3$) δ 129.14 (+), 128.93 (+), 126.33 (+), 113.84 (+), 111.56 (+), 80.11 (+), 55.23 (+), 50.96 (+), 48.23 (+), 43.90 (+), 38.29 (+), 37.33 (–), 34.21 (–), 29.73 (–), 27.42 (–), 26.09 (–), 11.95 (+); IR ($CHCl_3$) 3460 (br, m), 2920 (s), 1610 (m), 1580 (m), 1500 (s), 1480 (m), 1380 (w), 1250 (br, s), 1130 (m), 1075 (m), 1035 (m) cm^{-1}; low-resolution MS *m/e* (relative intensity) 394 (M, 100), 284 (11), 267 (5); high-resolution MS calcd for $C_{25}H_{30}O_2S$ 394.1964, found 394.1961.

The more polar alcohol (6b): TLC R_f 0.38 (hexane/ethyl acetate (4:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (s, 3 H), 1.25–1.50 (m, 4 H), 1.78–2.31 (m, 7 H), 2.80–2.84 (m, 2 H), 3.47 (ddd, *J* = 10.25, 7.57, and 2.93 Hz, 1 H), 3.63 (d, *J* = 7.56 Hz, 1 H), 3.76 (s, 3 H), 6.61 (m, 2 H), 7.17–7.41 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 157.46, 137.78, 136.52, 132.32, 130.03, 128.92, 126.29, 126.22, 113.81, 111.49, 87.19, 55.15, 50.98, 48.18, 44.03, 43.74, 38.24, 36.67, 33.96, 29.62, 27.10, 26.05, 11.72; INEPTR ($CDCl_3$) δ 130.00 (+), 128.93 (+), 126.27 (+), 126.23 (+), 113.80 (+), 111.49 (+), 87.16 (+), 55.15 (+), 50.95 (+), 48.18 (+), 43.74 (+), 38.24 (+), 36.67 (–), 33.96 (–), 29.64 (–), 27.10 (–), 26.05 (–), 11.73 (+); IR ($CHCl_3$) 3420 (br, s), 2920 (s), 1610 (m), 1580 (m), 1500 (s), 1235 (br, s), 1035 (m) cm^{-1}; low-resolution MS *m/e* (relative intensity) 394 (M, 100), 376 (7), 284 (16), 266 (16); high-resolution MS calcd for $C_{25}H_{30}O2S$ 394.1966, found 394.1983.

3-Methoxy-13-methyl-16-(phenylthio)-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthrene (7). To a solution of alcohol **6a** (384 mg, 0.97 mmol) in 1 mL of pyridine was added methanesulfonyl chloride (0.20 mL, 2.6 mmol) at room temperature. The mixture was stirred at this temperature for 1 h. The reaction mixture was partitioned between ether and aqueous NH_4Cl. The organic and aqueous phases were separated, and the aqueous phase was extracted with ether twice and with dichloromethane twice. The combined organic phase was dried over Na_2SO_4. Removal of the solvent under reduced pressure followed by flash chromatography on silica gel (hexane/ethyl acetate (9:1–3:1)) gave the corresponding methanesulfonate (473 mg). The methanesulfonate was dissolved in 3 mL of dimethyl sulfoxide, and potassium *tert*-butoxide (280 mg, 2.50 mmol) was added at room temperature. The mixture was stirred at this temperature for 5 h. The reaction mixture was partitioned between ether and aqueous NH_4Cl. The organic and aqueous phases were separated, and the aqueous phase was extracted with ether twice and with dichloromethane twice. The combined organic phase was dried over Na_2SO_4. Removal of the solvent under reduced pressure followed by flash chromatography on silica gel (hexane/ethyl acetate (19:1)) gave 287 mg (0.76 mmol) of the title compound in 78% yield: TLC R_f 0.68 (hexane/ethyl acetate (4:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (s, 3 H), 1.37–1.88 (m, 7 H), 2.16–2.34 (m, 4 H), 2.79–2.93 (m, 2 H), 3.77 (s, 3 H), 5.93 (d, J = 1.22 Hz, 1 H), 6.62–6.72 (m, 2 H), 7.17–7.39 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 157.52, 143.73, 137.86, 135.25, 134.51, 132.81, 131.03, 128.99, 126.90, 125.97, 113.87, 111.46, 55.62, 55.20, 46.95, 44.35, 37.24, 35.76, 35.68, 29.67, 27.86, 26.47, 16.99; INEPTR ($CDCl_3$) δ 143.77 (+), 131.02 (+), 128.99 (+), 126.90 (+), 125.98 (+), 113.85 (+), 111.45 (+), 55.60 (+), 55.21 (+), 44.35 (+), 37.23 (+), 35.76 (–), 35.67 (–), 29.67 (–), 27.86 (–), 26.47 (–), 16.99 (+); IR ($CHCl_3$) 2930 (s), 1610 (m), 1575 (m), 1500 (s), 1475 (m), 1460 (m), 1440 (m), 1370 (w), 1280 (m), 1250 (br, s), 1130 (w), 1090 (w), 1025 (m) cm^{-1}; low-resolution MS *m/e* (relative intensity) 376 (M, 42), 361 (100), 267 (14), 251 (7); high-resolution MS calcd for $C_{25}H_{28}OS$ 376.1860, found 376.1860.

Oxygenation of 3-Methoxy-13-methyl-16-(phenylthio)-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthrene (7) in the Presence of Thiophenol. The alkenyl sulfide **7** (75 mg, 0.20 mmol) and thiophenol (0.041 mL, 0.40 mmol) were dissolved in 10 mL of acetic acid, and oxygen gas was bubbled through the cell with magnetic stirring at room temperature for 19 h. The reaction mixture was partitioned between ether and aqueous $NaHCO_3$. The organic and aqueous phases were separated, and the aqueous phase was extracted with ether twice. The combined organic phase was dried over Na_2SO_4. Removal of the solvent under reduced pressure followed by flash chromatography on silica gel (hexane/ethyl acetate (9:1)) gave 71 mg (0.18 mmol) of the corresponding (α-phenylthio) ketone **8** in 90% yield.

3-Methoxy-13-methyl-16-oxo-17-(phenylthio)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene (8). Compound **8** was characterized as a mixture (2.3:1) of two stereoisomers: TLC R_f 0.25 (hexane/ethyl acetate (9:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (s), 1.02 (s) (total 3 H, 1:2.3), 1.44–2.59 (m, 11 H), 2.87–2.90 (m, 2 H), 3.37 (s), 3.79 (s) (total 1 H), 3.78 (s, 3 H), 6.64–6.75 (m, 2 H), 7.20–7.51 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 218.30, 211.25, 157.70, 137.66, 133.51, 132.24, 131.97, 131.19, 129.03, 127.59, 126.09, 113.87, 111.71, 64.39, 56.00, 55.21, 50.79, 46.32, 43.78, 43.34, 39.39, 39.05, 38.29, 38.18, 36.94, 33.03, 29.68, 28.09, 26.27, 26.05, 19.82, 18.15; INEPTR ($CDCl_3$) δ 137.66 (+), 132.24 (+), 129.05 (+), 127.60 (+), 126.10 (+), 113.87 (+), 111.71 (+), 64.39 (+), 56.00 (–), 55.24 (+), 50.77 (+), 46.31 (+), 43.78 (+), 43.34 (+), 39.07 (–), 38.28 (+), 38.16 (–), 36.95 (–), 33.03 (–), 29.70 (–), 28.11 (–), 26.27 (–), 26.05 (–), 19.83 (+), 18.17 (+); IR ($CHCl_3$) 2990 (m), 2910 (s), 2850 (m), 1730 (s), 1605 (m), 1580 (m), 1500 (s), 1480 (w), 1460 (m), 1450 (w), 1435 (m), 1380 (m), 1355 (w), 1335 (w), 1310 (m), 1280 (m), 1250 (s), 1230 (s), 1175 (m), 1160 (w), 1150 (w), 1130 (m), 1090 (m), 1030 (m) cm^{-1}; low-resolution MS *m/e* (relative intensity) 392 (M, 100), 294 (9), 293 (11), 292 (6), 227 (65), 173 (19), 147 (20); high-resolution MS calcd for $C_{25}H_{28}O_2S$ 392.1809, found 392.1806.

General Procedure for the Preparation of Ketene Dithioacetal. Bis(phenylthio)(trimethylsilyl)methane (1.50–1.93 mmol) was dissolved in 1.0–1.5 mL of tetrahydrofuran, and the solution was cooled to 0 °C. Butyllithium (1.6 M in hexane, 1.60–2.08 mmol) was added dropwise by syringe and stirred for 1 h at this temperature. At 0 °C, 1.73–2.23 mmol of aldehyde was added, and resulting reaction mixture was stirred at 0 °C for 1 h and at room temperature for an additional 1 h. The reaction mixture was poured into a separatory funnel containing ether and saturated aqueous NH_4Cl solution. The organic and aqueous phases were separated, and the aqueous phase was extracted with ether three times. The combined organic phase was dried over Na_2SO_4. Removal of the solvent under reduced pressure followed by flash chromatography on silica gel yielded the corresponding ketene dithioacetal.

1,1-Bis(phenylthio)-1-nonene (9a): TLC R_f 0.36 (hexane); VPC t_R 16.5 min (100–230 °C, 10 °C/min); ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.81–1.47 (m, 13 H), 2.43 (m, 2 H), 6.37 (t, J = 7.25 Hz, 1 H), 7.21 (s), 7.24 (s) (total 10 H); IR ($CHCl_3$) 3080 (w), 3020 (w), 2940 (s), 2880 (s), 1590 (m), 1480 (s), 1445 (m), 1385 (w), 1305 (w), 1180 (w), 1070 (w), 1030 (m) cm^{-1}; low-resolution MS m/e (relative intensity) 342 (M, 31), 257 (23), 233 (81), 179 (8), 149 (63), 147 (22), 135 (10), 123 (100); high-resolution MS calcd for $C_{21}H_{26}S_2$ 342.1475, found 342.1485.

4-Phenyl-1,1-bis(phenylthio)-1-butene (9b): TLC R_f 0.21 (hexane); VPC t_R 19.1 min (100–230 °C, 10 °C/min); ^{1}H NMR (90 MHz, $CDCl_3$) δ 2.66–2.73 (m, 4 H), 6.21–6.37 (m, 1 H), 7.13–7.30 (m, 15 H); IR ($CHCl_3$) 3050 (w), 2990 (w), 2910 (w), 1580 (m), 1475 (m), 1435 (m), 1255 (w), 1080 (m), 1020 (m) cm^{-1}; low-resolution MS m/e (relative intensity) 348 (M, 16), 257 (100), 179 (16), 161 (6), 147 (25), 129 (15), 128 (15), 123 (20), 91 (20); high-resolution MS calcd for $C_{22}H_{20}S_2$ 348.1005, found 348.0985.

2-Cyclohexyl-1,1-bis(phenylthio)ethene (9c): TLC R_f 0.26 (hexane); VPC t_R 15.9 min (100–230 °C, 10 °C/min); ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.20–1.76 (m, 10 H), 2.50–2.96 (m, 1 H), 6.24 (d, J = 9.23 Hz, 1 H), 7.20 (s, 10 H); IR ($CHCl_3$) 3060 (w), 3000 (w), 2920 (s), 2850 (s), 1580 (m), 1475 (s), 1435 (m), 1350 (w), 1300 (w), 1275 (w), 1140 (w), 1085 (w), 1035 (w), 1025 (m), 970 (m) cm^{-1}; low-resolution MS m/e (relative intensity) 326 (M, 100), 249 (16), 217 (90), 159 (40), 149 (39), 135 (27), 123 (34), 107 (83), 91 (29), 79 (63); high-resolution MS calcd for $C_{20}H_{22}S_2$ 326.1162, found 326.1162.

***S*-Phenyl 2-(phenylthio)nonanethioate (10a):** TLC R_f 0.31 (hexane/ethyl acetate (9:1)); VPC t_R 9.05 min (100–250 °C, 10 °C/min); ^{1}H 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 2-nonenethioate (12a):** TLC R_f 0.55 (hexane/ethyl acetate (9:1)); VPC t_R 11.7 min (100–240 °C, 10 °C/min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (m, 3 H), 1.26–1.56 (m, 8 H), 2.23 (dt, J_t = 7.08 Hz, J_d = 6.83 Hz, 2 H), 6.18 (d, J = 15.63 Hz, 1 H), 6.99 (dt, J_d = 15.38 Hz, J_t = 6.83 Hz, 1 H), 7.40–7.44 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 188.06, 147.04, 134.70, 129.31, 129.14, 127.81, 127.75, 32.35, 31.60, 28.87, 27.93, 22.55, 14.08; INEPTR ($CDCl_3$) δ 134.70 (+), 129.31 (+), 129.14 (+), 127.79 (+), 32.37 (–), 31.60 (–), 28.87 (–), 27.93 (–), 22.56 (–), 14.08 (+); IR ($CHCl_3$) 3010 (w), 2940 (s), 2860 (m), 1675 (s), 1630 (s), 1585 (w), 1480 (m), 1440 (m), 1285 (w), 1145 (m), 1025 (m), 970 (m) cm^{-1}; low-resolution MS m/e (relative intensity) 248 (M, 4), 218 (7), 139 (100), 109 (12); high-resolution MS calcd for $C_{15}H_{20}OS$ 248.1233, found 248.1233.

***S*-Phenyl 4-phenyl-2-(phenylthio)butanethioate (10b):** TLC R_f 0.43 (hexane/ethyl acetate (9:1)); VPC t_R 21.5 min (100–240 °C, 10 °C/min); ^{1}H 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 4-phenyl-2-(phenylsulfinyl)butanethioate (11b).** Compound **11b** was characterized as a mixture (3:2) of two diastereoisomers: TLC R_f 0.05 (hexane/ethyl acetate (9:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.20–2.28 (m), 2.47–2.54 (m) (total 2 H), 2.66–2.77 (m), 2.80–2.91 (m) (total 2 H), 3.72 (dd, J = 9.27 and 4.64 Hz), 3.81 (dd, J = 9.28 and 5.13 Hz) (total 1 H, 3:2), 7.14–7.66 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 192.46, 190.77, 141.77, 140.48, 139.79, 139.73, 134.17, 132.04, 131.86, 129.94, 129.81, 129.31, 129.25, 129.11, 128.61, 128.52, 126.51, 126.46, 126.35, 126.06, 125.28, 125.22, 78.30, 74.34, 33.04, 32.95, 29.01, 27.07; INEPTR ($CDCl_3$) δ 134.19 (+), 132.07 (+), 131.89 (+), 129.97 (+), 129.84 (+), 129.33 (+), 129.28 (+), 129.12 (+), 128.65 (+), 128.62 (+), 128.54 (+), 126.52 (+), 126.48 (+), 125.28 (+), 125.22 (+), 78.33 (+), 74.32 (+), 33.04 (–), 32.95 (–), 29.04 (–), 27.09 (–); IR ($CHCl_3$) 3070 (w), 3000 (m), 2930 (w), 1680 (s), 1585 (w), 1500 (w), 1480 (m), 1440 (s), 1085 (s), 1050 (s), 940 (s) cm^{-1}; low-resolution MS m/e (relative intensity) 380 (M, 2.7), 255 (13), 145 (100), 117 (63); high-resolution MS calcd for $C_{22}H_{20}O_2S_2$ 380.0905, found 380.0897.

***S*-Phenyl 4-phenyl-2-butenethioate (12b):** TLC R_f 0.50 (hexane/ethyl acetate (9:1)); VPC t_R 7.90 min (100–240 °C, 20 °C/min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56 (dd, J = 6.59 and 1.54 Hz, 2 H), 6.16 (dt, J_d = 15.62 Hz, J_t = 1.54 Hz, 1 H), 7.12 (dt, J_d = 15.63 Hz, J_t = 6.59 Hz, 1 H), 7.18–7.44 (m, 10 H); IR ($CHCl_3$) 2920 (w), 1680 (s), 1635 (m), 1480 (w), 1440 (w), 1260 (w), 1130 (w), 1020 (m), 980 (w) cm^{-1}; low-resolution MS m/e (relative intensity) 254 (M, 5.6), 145 (100), 117 (64), 91 (17); high-resolution MS calcd for $C_{16}H_{14}OS$ 254.0764, found 254.0761.

***S*-Phenyl 2-cyclohexyl-2-(phenylthio)ethanethioate (10c):** TLC R_f 0.50 (hexane/ethyl acetate (9:1)); VPC t_R 17.8 min (100–240 °C, 10 °C/min); ^{1}H 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.

***S*-Phenyl 2-cyclohexyl-2-(phenylsulfinyl)ethanethioate (11c).** This compound was characterized as a mixture (5:2) of two stereoisomers. TLC R_f 0.04 (hexane/ethyl acetate (9:1)); VPC t_R 10.9 min (100–240 °C, 10 °C/min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11–2.44 (m, 11 H), 3.30 (d, J = 10.01 Hz), 3.68 (d, J = 4.88 Hz) (total 1 H, 5:2), 6.99–7.71 (m, 10 H); IR ($CHCl_3$) 3010 (w), 2950 (s), 2860 (m), 1690 (s), 1585 (w), 1480 (w), 1445 (m), 1090 (m), 1055 (m), 995 (m) cm^{-1}; low-resolution MS m/e (relative intensity) 358 (M, 0.7), 342 (0.8), 249 (39), 205 (9), 123 (100); high-resolution MS calcd for $C_{20}H_{22}O_2S_2$ 358.1059, found 358.1053.

General Procedure for the Electroinitiated Oxygenation of Alkynes 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 × 30 mm). Alkyne (0.5–1.0 mmol) and thiophenol (2.0–4.0 mmol) were dissolved in 0.2 M Et_4NOTs/AcOH or Et_4NOTs/MeOH (5–10 mL), and oxygen gas was bubbled through the cell with magnetic stirring. The constant current electrolysis (20 mA, 1 min) was repeated several times with an interval of 30 min at room temperature. VPC monitoring of the reaction indicated that the alkenyl sulfide was formed initially and that the α-(phenylthio) carbonyl compounds was produced gradually during the last half of the reaction period at the expense of the alkenyl sulfide. After the reaction was completed, the reaction mixture was partitioned between ether and aqueous $NaHCO_3$ or brine. The organic and aqueous phases were separated, and the aqueous phase was extracted with ether several times. The combined organic phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. Flash chromatography on silica gel yielded the corresponding α-(phenylthio) carbonyl compound.

General Procedure for the Oxygenation of Alkynes in the Presence of Thiophenol (Method B). Alkyne (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 magnetic stirring at room temperature. After the reaction was complete, the reaction mixture was partitioned between ether and aqueous $NaHCO_3$ and brine. The organic and aqueous phases were separated, and the aqueous phase was extracted with ether several times. The combined phase was dried over Na_2SO_4, and the solvent was removed under reduced

pressure. Flash chromatography on silica gel yielded the corresponding α-(phenylthio) carbonyl compound.

General Procedure for the Oxygenation of Alkynes in the Presence of Thiophenol with AIBN (Method C). Alkyne (0.5–1.0 mmol), thiophenol (2.0–4.0 mmol), and α,α'-azobis(isobutyronitrile) were dissolved in 10 mL of acetic acid or methanol, and oxygen gas was bubbled through the glass tube with magnetic stirring. The reaction mixture was then heated to 50 °C with bubbling of oxygen. After the reaction was complete, the reaction mixture was partitioned between ether and aqueous $NaHCO_3$ and brine. The organic and aqueous phases were separated, and the aqueous phase was extracted with ether several times. The combined organic phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. Flash chromatography on silica gel yielded the corresponding α-(phenylthio) carbonyl compound.

2-(Phenylthio)octanal (14a): TLC R_f 0.46 (hexane/ethyl acetate (9:1)); VPC t_R 14.2 min (80–240 °C, 10 °C/min); ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.71 Hz, 3 H), 1.29–1.71 (m, 9 H), 1.76–1.86 (m, 1 H), 3.52 (dt, J_t = 7.32 Hz, J_d = 4.27 Hz, 1 H), 7.26–7.39 (m, 5 H), 9.36 (d, J = 4.28 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 195.35, 132.76, 132.03, 129.16, 128.10, 56.87, 31.52, 28.94, 27.90, 26.88, 22.53, 14.02; INEPTR ($CDCl_3$) δ 132.78 (+), 129.18 (+), 128.11 (+), 56.90 (+), 31.54 (–), 28.94 (–), 27.89 (–), 26.88 (–), 22.55 (–), 14.05 (+); IR ($CHCl_3$) 2920 (s), 2850 (m), 1710 (s), 1585 (m), 1485 (m), 1470 (m), 1440 (m), 1380 (w), 1070 (w), 1025 (w), 910 (w) cm^{-1}; low-resolution MS m/e (relative intensity) 236 (M, 37), 218 (3), 207 (100), 123 (64), 109 (20), 97 (16); high-resolution MS calcd for $C_{14}H_{20}OS$ 236.1236, found 236.1266. Anal. Calcd for $C_{14}H_{20}OS$: C, 67.12; H, 9.01. Found: C, 67.14; H, 9.07.

1,1-Dimethoxy-2-(phenylthio)octane (dimethyl acetal of 14a): TLC R_f 0.52 (hexane/ethyl acetate (9:1)); VPC t_R 15.4 min (80–240 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 0.79–1.90 (m, 13 H), 3.07–3.30 (m, 1 H), 3.35 (s, 3 H), 3.41 (s, 3 H), 4.30 (d, J = 5.05 Hz, 1 H), 7.19–7.42 (m, 5 H); IR ($CHCl_3$) 3060 (w), 2930 (s), 1585 (m), 1465 (m), 1375 (m), 1185 (m), 1110 (s), 1070 (s), 960 (m), 910 (w) cm^{-1}; low-resolution MS m/e (relative intensity) 282 (M, 3.7), 250 (2.4), 219 (0.4), 207 (0.5), 147 (1.7), 135 (1.1), 123 (2.4), 109 (2), 75 (100); high-resolution MS calcd for $C_{16}H_{26}O_2S$ 282.1654, found 282.1655. Anal. Calcd for $C_{16}H_{26}O_2S$: C, 68.04; H, 9.28. Found: C, 68.25; H, 9.21.

1,1,2-Tris(phenylthio)octane (dithioacetal of 14a): TLC R_f 0.46 (hexane/ethyl acetate (9:1)); ^1H NMR (90 MHz, $CDCl_3$) δ 0.80–2.36 (m, 13 H), 3.28–3.46 (m, 1 H), 4.50 (d, J = 2.63 Hz, 1 H), 6.92–7.46 (m, 15 H); IR ($CHCl_3$) 3050 (w), 2920 (s), 2850 (m), 1585 (m), 1480 (m), 1440 (m), 1090 (w), 1065 (w), 1025 (w) cm^{-1}; low-resolution MS m/e (relative intensity) 438 (M, 1.3), 329 (100), 251 (4), 231 (34), 218 (94), 219 (100), 149 (69), 135 (96), 123 (48), 110 (51), 85 (34); high-resolution MS calcd for $C_{26}H_{30}S_3$ 438.1510, found 438.1520. Anal. Calcd for $C_{26}H_{30}S_3$: C, 71.18; H, 6.89. Found: C, 71.36; H, 7.02.

3-(Benzyloxy)-2-(phenylthio)propanal (14b): TLC R_f 0.33 (hexane/ethyl acetate (9:1)); ^1H NMR (400 MHz, $CDCl_3$) δ 3.76–3.89 (m, 3 H), 4.55 (s, 2 H), 7.28–7.41 (m, 10 H), 9.54 (d, J = 3.06 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 194.27, 137.48, 133.25, 131.24, 129.25, 129.05, 128.51, 128.43, 127.94, 127.81, 73.56, 67.24, 56.19; INEPTR ($CDCl_3$) δ 199.47 (+), 133.28 (+), 129.27 (+), 129.05 (+), 128.52 (+), 127.95 (+), 127.82 (+), 73.69 (–), 67.24 (–), 56.19 (+); IR ($CHCl_3$) 2990 (m), 2850 (m), 1715 (s), 1580 (m), 1480 (m), 1450 (m), 1440 (m), 1360 (m), 1230 (br, w), 1095 (br, s), 1030 (w), 910 (w) cm^{-1}; low-resolution MS m/e (relative intensity) 272 (M, 5), 242 (11), 164 (11), 135 (32), 107 (25), 91 (100); high-resolution MS calcd for $C_{16}H_{16}O_2S$ 272.0871, found 272.0864.

2-Hydroxy-3-(phenylthio)tetrahydrofuran (15). This compound was characterized as a mixture (7:3) of two stereoisomers: TLC R_f 0.35 (hexane/ethyl acetate (2:1)); VPC t_R 10.4 min (80–240 °C, 10 °C/min); ^1H NMR (400 MHz, $CDCl_3$) δ 1.86–1.93 (m), 2.04–2.16 (m) (total 1 H), 2.33–2.44 (m), 2.49–2.57 (m) (total 1 H, 7:3), 1.80 (br), 3.33 (br) (total 1 H), 3.60–3.67 (m), 3.69–3.75 (m), 3.85–3.91 (m), 4.04–4.16 (m) (total 3 H), 5.40 (br, 1 H), 7.19–7.44 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 135.18, 134.80, 130.86, 130.22, 129.12, 129.06, 127.14, 126.68, 102.67, 96.84, 67.03, 66.20, 51.20, 51.11, 30.33, 30.17; INEPTR ($CDCl_3$) δ 130.84 (+), 130.19 (+), 129.12 (+), 129.08 (+), 127.14 (+), 126.68 (+), 102.66 (+), 67.03 (–), 66.23 (–), 51.15 (+), 51.08 (+), 30.31 (–), 30.17 (–); IR ($CHCl_3$) 3600 (w), 3400 (br, m), 2950 (m), 2900 (w), 1590 (m), 1485 (m), 1365 (w), 1300 (w), 1235 (br, w), 1180 (w), 1030 (br, s), 925 (br, m) cm^{-1}; low-resolution MS m/e (relative intensity) 196 (M, 94), 178 (51), 167 (32), 150 (50), 137 (76), 117(100), 109 (65); high-resolution MS calcd for $C_{10}H_{12}O_2S$ 196.0558, found 196.0548. Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.20; H, 6.16. Found: C, 61.19; H, 6.19.

2,3-Bis(phenylthio)tetrahydrofuran (Hemithioacetal of 15). This compound was characterized as a mixture (15:1) of two stereoisomers: TLC R_f 0.75 (hexane/ethyl acetate (2:1)); VPC t_R 20.0 min (80–240 °C, 10 °C/min); ^1H NMR (400 MHz, $CDCl_3$) δ 1.90–1.98 (m), 2.09–2.18 (m) (total 1 H), 2.47–2.54 (m, 1 H), 3.80–3.84 (m), 3.94–4.00 (m), 4.07–4.16 (m), 4.21–4.27 (m), 5.48 (d, J = 2.44 Hz), 5.75 (d, J = 6.11 Hz) (total 1 H, 15:1), 7.21–7.50 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 134.75, 134.23, 132.27, 132.13, 131.24, 131.02, 129.11, 128.92, 128.81, 127.40, 127.22, 127.08, 92.85, 91.79, 67.02, 65.89, 51.43, 50.29, 31.83; IR ($CHCl_3$) 2950 (m), 2890 (m), 2870 (m), 1585 (s), 1480 (s), 1440 (s), 1355 (w), 1305 (m), 1285 (m), 1175 (m), 1090 (s), 1045 (br, s), 920 (m) cm^{-1}; low-resolution MS m/e (relative intensity) 288 (M, 2), 218 (6), 179 (74), 161 (100), 128 (14), 109 (24); high-resolution MS calcd for $C_{16}H_{16}OS_2$ 288.0643, found 288.0628.

4-Acetoxy-2-(phenylthio)butanal (14d): TLC R_f 0.31 (hexane/ethyl acetate (4:1)); VPC t_R 13.6 min (80–240 °C, 10 °C/min); ^1H NMR (400 MHz, $CDCl_3$) δ 1.88–1.96 (m, 1 H), 2.03 (s, 3 H), 2.15–2.24 (m, 1 H), 3.65 (dt, J_t = 7.32 Hz, J_d = 3.05 Hz, 1 H), 4.21–4.32 (m, 2 H), 7.29–7.33 (m, 3 H), 7.39–7.42 (m, 2 H), 9.58 (d, J = 3.05 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 193.87, 170.69, 133.82, 130.68, 129.28, 128.71, 61.30, 53.98, 27.03, 20.77; INEPTR ($CDCl_3$) δ 133.86 (+), 129.28 (+), 128.74 (+), 61.30 (–), 53.97 (+), 26.98 (–), 20.80 (+); IR ($CHCl_3$) 2990 (m), 2950 (m), 2820 (m), 2710 (w), 1720 (br, s), 1585 (m), 1470 (m), 1420 (m), 1385 (m), 1365 (s), 1250 (br, s), 1040 (s) cm^{-1}; low-resolution MS m/e (relative intensity) 238 (M, 12), 196 (8), 178 (100), 149 (83), 116 (42), 109 (22); high-resolution MS calcd for $C_{12}H_{14}O_3S$ 238.0664, found 238.0660. Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.48; H, 5.92. Found: C, 60.24; H, 6.00.

4-(Benzyloxy)-2-(phenylthio)butanal (14e): TLC R_f 0.36 (hexane/ethyl acetate (9:1)); VPC t_R 17.2 min (100–240 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 1.70–2.38 (m, 2 H), 3.53–3.87 (m, 3 H), 4.48 (s, 2 H), 7.21–7.35 (m, 10 H), 9.46 (d, J = 3.08 Hz, 1 H); IR ($CHCl_3$) 3010 (m), 2870 (m), 1715 (s), 1585 (m), 1485 (m), 1455 (m), 1440 (m), 1365 (m), 1215 (br, w), 1100 (br, s), 1030 (m) cm^{-1}; low-resolution MS m/e (relative intensity) 286 (M, 13), 258 (11), 195 (10), 167 (9), 165 (13), 137 (18), 123 (12), 91 (100); high-resolution MS calcd for $C_{17}H_{18}O_2S$ 286.1028, found 286.1035. Anal. Calcd for $C_{17}H_{18}O_2S$: C, 68.89; H, 6.34. Found: C, 68.93; H, 6.06.

6-(Phenylthio)-5-decanone (14f): TLC R_f 0.51 (hexane/ethyl acetate (9:1)); VPC t_R 13.8 min (100–240 °C, 10 °C/min); ^1H NMR (400 MHz, $CDCl_3$) 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.

Electroinitiated Oxygenation of 1-Decyne in the Presence of Hexylmercaptan. 1-Decyne (69 mg, 0.50 mmol) and hexylmercaptan (0.085 mL, 0.60 mmol) was dissolved in 0.2 M Et_4NOTs/CH_3CN (5 mL), and oxygen gas was bubbled through the cell with magnetical stirring. The constant current electrolysis (20 mA, 1 min) was repeated 278 times with an interval of 5 min at room temperature, and hexylmercaptan (0.275 mL, 1.66 mmol) was added in two portions with an interval of 8 h. After 23 h, the reaction mixture was partitioned between ether and brine. The organic and aqueous phases were separated, and the aqueous phase was extracted with ether several times. The combined organic phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. Flash chromatography on silica gel gave 69 mg (0.25 mmol, 51%) of 2-(hexylthio)decanal (16).

2-(Hexylthio)decanal (16): TLC R_f 0.58 (hexane/ethyl acetate (9:1)); VPC t_R 14.2 min (100–240 °C, 10 °C/min); ^1H

NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.32 Hz, 6 H), 1.26–1.78 (m, 22 H), 2.36 (t, J = 7.33 Hz, 2 H), 3.07 (ddd, J = 8.55, 6.72, and 4.88 Hz, 1 H), 9.16 (d, J = 4.88 Hz, 1 H); IR (neat) 2930 (s), 2860 (s), 1715 (s), 1465 (m), 1380 (w) cm^{-1}; low-resolution MS m/e (relative intensity) 272 (M, 3), 243 (100), 159 (6), 131 (10); high-resolution MS calcd for $C_{16}H_{32}OS$ 272.2174, found 272.2202.

Reaction of 1-Octyne with Thiophenol under an Atmosphere of Nitrogen Initiated by Electrolysis. 1-Octyne (110 mg, 1.00 mmol) and thiophenol (0.113 mL, 1.10 mmol) were dissolved in 0.2 M Et_4NOTs/AcOH (10 mL), and nitrogen gas was bubbled through the cell with magnetic stirring. The constant current electrolysis (20 mA, 1 min) was repeated 16 times with an interval of 30 min at room temperature. After the reaction was complete, the reaction mixture was partitioned between ether and aqueous $NaHCO_3$. The organic and aqueous phases were separated, and the aqueous phase was extracted with ether several times. The combined organic phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. Flash chromatography on silica gel gave 134 mg (0.61 mmol, 61%) of 1-(phenylthio)-1-octene.

1-(Phenylthio)-1-octene. This compound was characterized as a mixture (1:1) of two stereoisomers: TLC R_f 0.75 (hexane/ethyl acetate (9:1)); VPC t_R 12.9 min (100–240 °C, 10 °C/min); ^1H NMR (400 MHz, $CDCl_3$) δ 0.87–0.91 (m, 3 H), 1.30–1.44 (m, 8 H), 2.16 (ddd, J = 14.65, 6.71, and 1.22 Hz), 2.25 (ddd, J = 14.65, 7.32, and 1.22 Hz) (total 2 H, 1:1), 5.82 (dt, J_d = 9.15 Hz, J_t = 6.71 Hz), 5.99 (dt, J_d = 14.65 Hz, J_t = 7.32 Hz) (total 1 H), 6.13 (dt, J_d = 14.65 Hz, J_t = 1.22 Hz), 6.18 (dt, J_d = 9.15 Hz, J_t = 1.22 Hz) (total 1 H), 7.19–7.35 (m, 5 H); IR ($CHCl_3$) 2920 (s), 2850 (m), 1585 (m), 1480 (s), 1440 (m), 1090 (m), 1025 (m), 950 (m) cm^{-1}; low-resolution MS m/e (relative intensity) 220 (M, 64), 149 (100), 134 (22), 115 (60), 110 (71); high-resolution MS calcd for $C_{14}H_{20}S$ 220.1286, found 220.1288.

Acknowledgment. We thank the Ministry of Education, Science and Culture, Japan, for a Gran-in-Aid for Scientific Research on Priority Areas (Advanced Molecular Conversions) (Nos. 62607520, 63607526) for financial support of this work.

Supplementary Material Available: ^1H NMR spectra of the products (38 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.