Electrooxidative Inter- and Intramolecular Carbon−Carbon Bond Formation Using Organothio Groups as Electroauxiliaries

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Received April 1, 1998

The introduction of an organothio group to an α-carbon of ethers results in significant decrease of the oxidation potentials. Anodic oxidation of α-organothioethers gives rise to facile cleavage of the C−S bond and the introduction of carbon nucleophiles on the carbon. Allylsilanes, silyl enol ethers, and trimethylsilyl cyanide serve as effective carbon nucleophiles. The anodic oxidation of the α-organothioethers having a carbon−carbon double bond in an appropriate position using Bu_4NBF_4 as the supporting electrolyte leads to the effective cyclization and the introduction of the fluoride to one of the formal olefinic carbon. The present study demonstrates the effectiveness of organothio groups as electroauxiliaries in electrooxidative inter- and intramolecular carbon−carbon bond formation.

Introduction

The electrochemical reactions of organic compounds provide efficient method for the generation of reactive intermediates such as cations, radicals, and anions, and their utility has been recognized by synthetic chemists.[1] The electrochemical reactions are usually controlled by cell potentials, solvents, supporting electrolytes, electrode materials, and so on.[2] Although such external parameters of electrolysis are important in controlling the generation and the reaction of reactive intermediates, we have recently proposed that an internal control approach is also important. This approach utilizes an auxiliary that activates organic molecules toward electron transfer, controls the fate of thus generated reactive intermediates, and then biases the formation of desired products. We call such auxiliaries electroauxiliaries, and this concept opens a new aspect of electroorganic synthesis.[3]

We have already demonstrated that silicon,[4] germanium,[5] and tin[6] are efficient electroauxiliaries in anodic oxidation of heteroatom compounds[7] (Scheme 1). The introduction of a group 14 metal on the carbon adjacent to a heteroatom such as oxygen, nitrogen, and sulfur lowers the oxidation potential. This effect is attributed to the interaction between the carbon−metal σ orbital with the nonbonding p orbital of the heteroatom raising the HOMO level which in turn favors the electron transfer.[8] The electrochemical oxidation of heteroatom compounds having group 14 metal on the α-carbon results in selective cleavage of the carbon−metal bond and regioselective formation of the carbocation adjacent to the heteroatom. Utility of group 14 metals as electroauxiliaries has been recognized not only in electrochemical reactions[9] but also in chemical electron-transfer reactions.[10]

The concept of electroauxiliary is especially important in the electrooxidative carbon−carbon bond formation of heteroatom compounds. To achieve the carbon−carbon bond formation, we must use carbon nucleophiles which react with electrogenerated carbocations adjacent to the heteroatom. However, the oxidation potentials of carbon nucleophiles are often lower than those of the heteroatom compounds. In such cases, activation of the heteroatom compounds is essential for the reaction. Another problem is overoxidation. The oxidation potentials of the products are generally quite similar to those of the starting materials because the hydrogen atom in the starting material is replaced by the carbon atom in this transformation. Therefore, activation of the starting material is essential for preventing the overoxidation.

Although tin serves as an efficient electroauxiliary for the electrooxidative carbon−carbon bond formation,[6] the introduction of a stannyl group into an appropriate

(1) For example: (a) Fry, A. J. *Synthetic Organic Electrochemistry*; Wiley: New York, 1989. (b) Little, R. D., Weinberg, N. L., Eds. *Electroorganic Synthesis*; Dekker: New York, 1991. (c) Synthetic Applications of Anodic Oxidations. *Tetrahedron* **1991**, 47. (d) Lund, H., Baizer, M. M., Eds. *Organic Electrochemistry*; Dekker: New York, 1991. (e) Shono, T. *Electroorganic Chemistry as a New Tool in Organic Synthesis*; Springer-Verlag: Berlin, 1984, and references cited therein.

(2) For example: Goodridge, F.; King, C. J. H. In *Technique of Electroorganic Synthesis*, Part 1; Weinberg, N. L., Ed. Wiley: New York, 1974; p 7. See also ref 1a.

(3) Yoshida, J. *J. Synth. Org. Chem. Jpn.* **1995**, *53*, 53. (b) Yoshida, J.; Takada, K.; Ishichi, Y.; Isoe, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2361.

(4) (a) Yoshida, J.; Isoe, S. *Chem. Lett.* **1987**, 631. (b) Yoshida, J.; Isoe, S. *Tetrahedron Lett.* **1987**, *28*, 6621. (c) Yoshida, J.; Murata, T.; Isoe, S. *J. Organomet. Chem.* **1988**, *345*, C23. (d) Yoshida, J.; Matsunaga, S.; Murata, T.; Isoe, S. *Tetrahedron* **1991**, *47*, 615.

(5) Yoshida, J.; Morita, Y.; Itoh, M. Ishichi, Y.; Isoe, S. *Synlett* **1992**, 843.

(6) (a) Yoshida, J.; Ishichi, Y.; Isoe, S. *J. Am. Chem. Soc.* **1992**, *114*, 7594. (b) Yoshida, J.; Ishichi, Y.; Nishiwaki, K.; Shiozawa, S.; Isoe, S. *Tetrahedron Lett.* **1992**, *33*, 2599. (c) Yoshida, J.; Itoh, M.; Isoe, S.; *J. Chem. Soc., Chem. Commun.* **1993**, 547. (d) Yoshida, J.; Itoh, M.; Morita, Y.; Isoe, S. *J. Chem. Soc., Chem. Commun.* **1994**, 549. (e) Yoshida, J.; Takada, K.; Ishichi, Y.; Isoe, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2361.

(7) Anodic oxidation of heteroatom compounds. (a) Nitrogen: Stechkhan, E. In ref 1d. (b) Oxygen: Hammerich, O.; Svensmark, B. In ref 1d. (c) Sulfur: Svensmark, B.; Hammerich, O. In ref 1d.

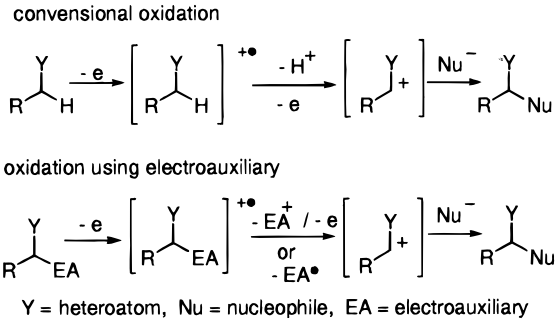
(8) Yoshida, J.; Maekawa, T.; Murata, T.; Matsunaga, S.; Isoe, S. *J. Am. Chem. Soc.* **1990**, *112*, 1962. See also: Yoshida, J. *Top. Curr. Chem.* **1994**, *170*, 40.

(9) Suda, K.; Hotoda, K.; Watanabe, J.; Shiozawa, K.; Takanami, T. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1283. (b) Suda, K.; Hotoda, K.; Iemura, F.; Takanami, T. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1553.

(10) (a) Fujii, T.; Hirao, T.; Ohshiro, Y. *Tetrahedron Lett.* **1993,** *34*, 5601. (b) Narasaka, K.; Arai, N.; Okauchi, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2995. (c) Yamaguchi, J.; Takagi, Y.; Nakayama, A.; Fujiwara, T.; Takeda, T. *Chem. Lett.* **1991**, 133.

S0022-3263(98)00601-X CCC: $15.00
Published on Web 08/05/1998

Scheme 1



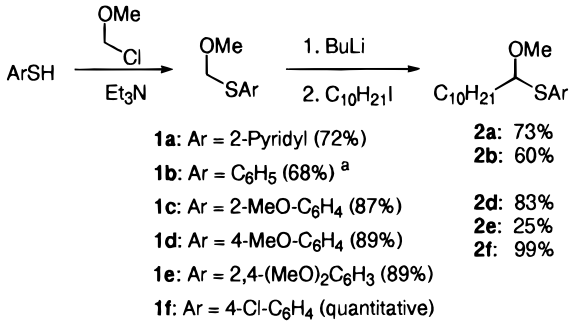
position of the starting materials is not always easy. This point would be sometimes the limitation of the use of tin as an electroauxiliary. The toxicity of tin is also disadvantageous. To overcome these problems and establish the generality of the concept of electroauxiliary, we searched for other types of electroauxiliaries and envisioned that organothio groups would serve effectively for the anodic oxidation of heteroatom compounds.

Several studies on electron-transfer reactions of α-organothio-substituted heteroatom compounds leading to cleavage of the C−S bond and generating carbocation intermediates have been reported.[11] Otera et al. reported that the anodic oxidation of α-organothio-substituted ethers in AcONa/AcOH resulted in the cleavage of C−S bond and the introduction of an acetoxy group.[11b,c] We also observed that the anodic oxidation of α-organothio-substituted ethers gave rise to the cleavage of the C−S bond and the introduction of a methoxy group to the carbon.[4a] It was also reported that the anodic oxidation of thioglycosides led to the cleavage of the C−S bond to achieve the effective glycosidation.[11d,e] Photoelectron transfer was also reported to be effective for the cleavage of the C−S bond.[11f] These studies suggest that organothio groups can be used as electroauxiliaries in the anodic oxidation of heteroatom compounds. Although the reactions of the carbocation intermediates with heteroatom nucleophiles such as alcohols have been studied extensively, little work has been carried out on the use of carbon nucleophiles to achieve carbon−carbon bond formation.[12] Recently we have reported preliminary results that the anodic oxidation of α-organothio-substituted ethers in the presence of carbon nucleophiles leads to inter- and intramolecular carbon−carbon bond formation, demonstrating the effectiveness of organothio groups as electroauxiliaries.[13] In this paper we report the full details of this study.

Results and Discussion

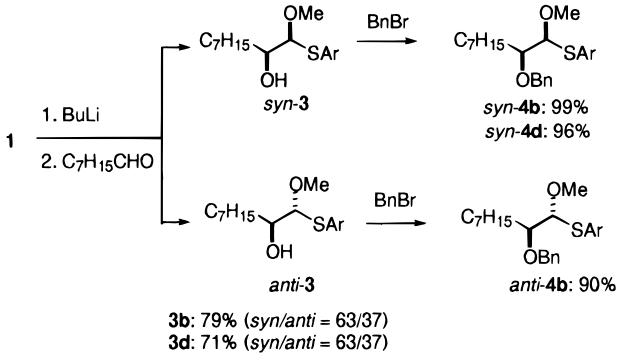
Synthesis of α-Organothio Ethers. Phenylthiomethyl methyl ether (**1b**) was prepared by the acid-catalyzed reaction of thiophenol with dimethoxymethane,[14] although this method cannot be applied for other arylthiomethyl methyl ethers. Other arylthiomethyl methyl ethers (**1a,c**−**f**) were prepared by the treatment of the corresponding arylthiols with chloromethyl methyl ether under basic conditions (Scheme 2). Deprotonation of thus obtained arylthiomethyl methyl ethers with butyllithium followed by the reaction with alkyl iodides gave the corresponding α-arylthioalkyl methyl ethers (**2**).[15] The reaction of the anion of **1** with aldehydes also proceeded smoothly to give β-hydroxy-α-arylthioalkyl methyl ethers (**3**) (Scheme 3).[16] The protection of the hydroxy group of **3** with benzyl bromide gave compound **4**. Arylthiobenzyl methyl ethers (**6**) were synthesized by the Lewis acid promoted acetal exchange reaction of the dimethylacetal (**5**) with the thiostannane (eq 1).[17]

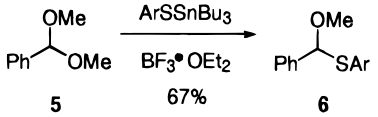
Scheme 2



[a] Prepared by the acid catalyzed reaction with dimethoxymethane.

Scheme 3





Oxidation Potentials. The oxidation potentials of α-organothioethers are much less positive than those of the corresponding simple aliphatic ethers (>2.3 V) (Table 1). However, the oxidation potentials of α-organothioethers are slightly more positive than those of the corresponding sulfides. For example, the oxidation potential of phenylthiomethyl methyl ether (**1b**) is 1.40 V, whereas that of phenylthiomethane is 1.24 V. This fact sharply contrasts to the effect of silicon and tin as an electroauxiliary for the oxidation of ethers. In cases of

(11) (a) Uneyama, K.; Torii, S. *Tetrahedron Lett.* **1971**, *4*, 329. (b) Mandai, T.; Irei, H.; Kawada, M.; Otera, J. *Tetrahedron Lett.* **1984**, *25*, 2371. (c) Mandai, T.; Yasunaga, H.; Kawada, M.; Otera, J. *Chem. Lett.* **1984**, 715. (d) Amatore, C.; Jutand, A.; Mallet, J. M.; Meyer, G.; Sinay, P. *J. Chem. Soc., Chem. Commun.* **1990**, 718. (e) Balavoine, G.; Gref, A.; Fischer, J.-C.; Lubineau, A. *Tetrahedron Lett.* **1990**, *31*, 5761. (f) Saito, I.; Takayama, M.; Sakurai, T. *J. Am. Chem. Soc.* **1994**, *116*, 2653, and references cited therein.

(12) Electrooxidative intramolecular coupling between benzylsulfides and aromatic rings has been reported. Kimura, M.; Ono, T.; Hayakawa, T.; Sawaki, Y. *The Abstract of 18th Symposium of Electroorganic Chemistry*; 1995, p 1.

(13) Yoshida, J.; Sugawara, M.; Kise, N. *Tetrahedron Lett.* **1996**, *37*, 3157.

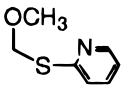
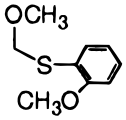
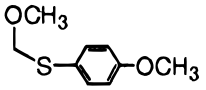
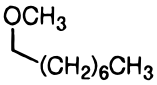
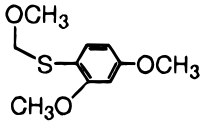
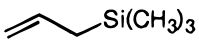
(14) Rawal, V. H.; Akiba, M.; Cava, M. P. *Synth. Commun.* **1984**, *14*, 1129.

(15) Otera, J.; Niibo, Y.; Nozaki, H. *J. Org. Chem.* **1989**, *54*, 5003.

(16) Sato, T.; Otera, J.; Nozaki, H. *J. Org. Chem.* **1990**, *55*, 6116.

(17) Sato, T.; Otera, J.; Nozaki, H. *Tetrahedron* **1989,** *45*, 1209.

Table 1. Oxidation Potentials of Organothio-Substituted Ethers and Related Compounds [a]

compd	E_d (V)	compd	E_d (V)
	1.78		
	1.40	CH_3SPh	1.24
	1.27		
	1.18		>2.3
	1.00		1.53

[a] The oxidation potentials (decomposition potentials, E_d) were determined with rotating disk electrode voltammetry using a glassy carbon working electrode in 0.1 M $LiClO_4/CH_3CN$. A Ag/AgCl electrode was used as a reference electrode.

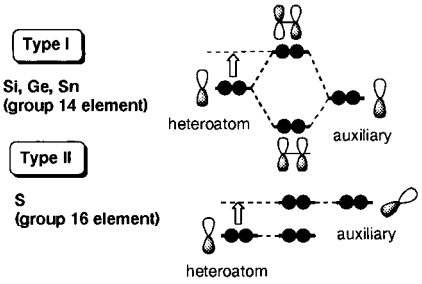


Figure 1. Principles of type I and type II electroauxiliaries.

silicon and tin, the oxidation potentials of silyl- and stannyl-substituted ethers are less positive than those of tetraalkylsilanes and -stannanes, respectively.[8] The carbon−metal σ bond interacts with the nonbonding p orbital of the oxygen to raise the HOMO level which in turn favors the electron transfer (Figure 1). In the case of sulfur, however, such interaction is absent. The electron transfer seems to take place mainly from the high-energy nonbonding p orbital of the sulfur atom, because the molecular orbital calculation indicates that the HOMO of the phenylthio-substituted ether is localized on the sulfur atom. Therefore, organothio groups serve as different types of electroauxiliaries from silicon and tin. Thus, we divide electroauxiliaries into two classes, type I (Si, Ge, Sn) and type II (S). Type I electroauxiliaries utilize the orbital interaction, whereas type II electroauxiliaries utilize high-energy nonbonding p orbitals.[18]

It is interesting that the oxidation potentials of α-organothioethers can be tuned by changing the nature of the substituent on the sulfur atom as shown in Table 1. The oxidation potentials of phenylthio-, (4-methoxyphenyl)thio-, and (2,4-dimethoxyphenyl)thio-substituted ethers are less positive than that of allyltrimethylsilane, suggesting that the allylsilane can be used as a nucleophile. The oxidation potential of the 2-pyridylthio-substituted ethers is more positive than that of allyltrimethylsilane, indicating that allyltrimethylsilane cannot be used as a nucleophile for the oxidation of these compounds.

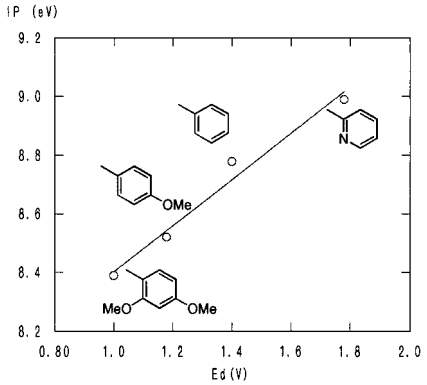
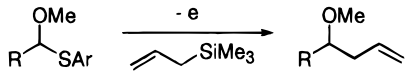


Figure 2. Correlation between the oxidation potentials (Ed) of (arylthio)methyl methyl ethers and the ionization potentials of the corresponding thiols obtained by PM3 calculations.

It is also noteworthy that there is a good correlation ($R = 0.987$) between the electrochemical oxidation potentials of α-organothioethers and the ionization potentials of the corresponding thiols obtained by PM3 calculations as shown in Figure 2. Therefore, it is easy to design α-organothioethers having specific oxidation potentials using molecular orbital calculations.

Intermolecular Carbon−Carbon Bond Formation. The intermolecular carbon−carbon bond formation with allylsilanes has been achieved using the phenylthio-, (4-methoxyphenyl)thio-, and (2,4-dimethoxyphenyl)thio groups as electroauxiliaries (eq 2). Preparative constant



(2)

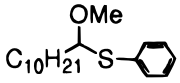
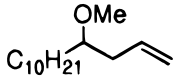
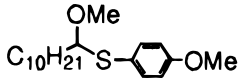
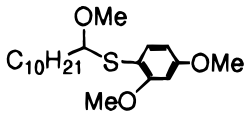
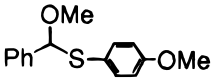
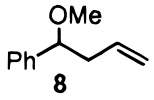
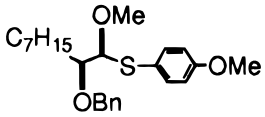
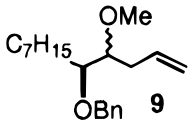
current electrolysis of α-arylthioethers in the presence of allyltrimethylsilane proceeded smoothly in an undivided cell equipped with a carbon rod anode and a platinum plate cathode in Bu_4NClO_4/CH_2Cl_2. To neutralize the acid that might be generated during the course of the electrolysis, the reaction was carried out in the presence of K_2CO_3 (powder). Molecular sieves was used to trap a trace amount of water in the reaction medium that might compete with the allylsilane as a nucleophile. Table 2 summarizes the results.

The yields of the allylated compounds depend on the nature of the substituent on the sulfur atom. The (4-methoxyphenyl)thio unit gave the best results among phenylthio, (4-methoxyphenyl)thio, and (2,4-dimethoxyphenyl)thio groups. As the supporting electrolyte, Bu_4NClO_4 gave the better yields than Bu_4NBF_4 and Bu_4NPF_6. It is also noteworthy that the anodic oxidation of diasteromerically pure *syn*-**4d** gave a 2:1 mixture of two diastereomers of the allylated product (**9**).[19] This result suggests a mechanism involving a carbocation intermediate which loses the orginal configuration.

(18) Tellurium can also be utilized as an electroauxiliary. We have already reported the electrochemical oxidation of telluroglycoside. See: Yamago, S.; Kokubo, K.; Yoshida, J. *Chem. Lett.* **1997**, 111.

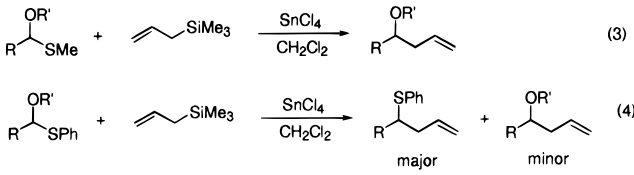
(19) The anodic oxidation of heteroatom compounds having a stannyl group as an electroauxiliary in the presence of allylsilanes leads to the formation of the corresponding allylated compunds. See ref 6c.

Table 2. Electrooxidative Intermolecular Carbon−Carbon Bond Formation Using Organothio Groups as Electroauxiliaries. Reaction with Allyltrimethylsilanes as a Carbon Nucleophile[a]

substrate		supporting electrolyte	electricity (F/mol)	product[b]	yield[c] (%)
	**2b**	Bu_4NClO_4	1.8		61(70)
	**2d**	Bu_4NClO_4 Bu_4NPF_6 Bu_4NPF_6	1.3 4.4 4.0	**7**	(81) (50) (50)
	**2e**	Bu_4NClO_4	1.6	**7**	(68)
	**6**	Bu_4NClO_4	2.1	 **8**	47
	***syn*-4d**	Bu_4NClO_4	2.1	 **9**	53 (2:1)

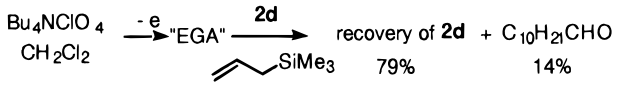
[a] The reactions were normally carried out with 0.5 mmol of α-organothio-substituted ether with 2 equiv of allyltrimethylsilane in 1.0 mL of 0.2 M solution of the supporting electrolyte in CH_2Cl_2 in an undivided cell equipped with a carbon rod anode and a platinum plate cathode under constant current conditions (10 mA) at room temperature. [b] The ratio of diastereomers was determined by ^{1}H NMR. [c] The isolated yields. The yields in parentheses were determined by ^{1}H NMR using an internal standard (1,1,2,2-tetrachloroethane).

Lewis acid-catalyzed reactions of α-organothio-substituted ethers with allylsilanes are well-known in the literature (eqs 3 and 4).[20] Therefore, an electrogenerated acid[21]-catalyzed (EGA-catalyzed) mechanism should also be considered as one of the possibilities. It has been reported that the acid-catalyzed reaction of *S*-phenyl compounds results in the formation of C−O cleavage compounds as the major product (eq 4), although the acid-catalyzed reaction of *S*-methyl compounds leads to the C−S cleavage (eq 3).

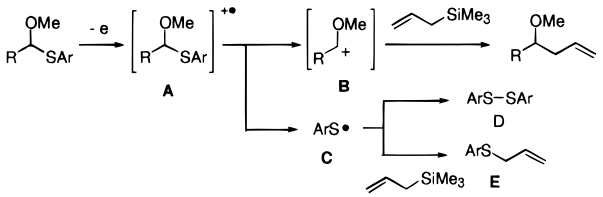


In the present electrochemical reaction, however, the C−S cleavage took place exclusively, even in the case of *S*-phenyl compounds. So, the electrogenerated acid-catalyzed reaction seems to be unlikely because of the following result. The electrolysis was carried out in the absence of the substrate (in Bu_4NClO_4/CH_2Cl_2) to generate the EGA. After the electricity was turned off, the α-organothioether and allyltrimethylsilane were added to the resulting solution. The α-organothioether was recovered unchanged together with a small amount of hydrolyzed aldehyde (Scheme 4). Therefore, EGA is not effective for the allylation even if it is formed during the course of the electrolysis. The fact that the reaction in the presence of K_2CO_3 gave better yields of the product than those in the absence of K_2CO_3 also argues against the mechanism involving EGA.

Scheme 4



Scheme 5



The fate of the organothio group was examined (Scheme 5). When the anodic oxidation of α-arylthio-substituted ethers was carried out in the presence of allyltrimethylsilane, the corresponding diaryl disulfide (**D**) and allyl aryl sulfide (**E**) were obtained. This result indicates that the cleavage of the C−S bond in the cation radical intermediate (**A**) leads to the formation of the arylthio radical (**C**) which dimerizes to give the diaryl disulfides (**D**). The allyl aryl sulfide (**E**) seemed to be formed by the addition of the arylthio radical to the allylsilane followed by the oxidation to the carbocation which underwent facile the β-silicon elimination. The formation of the arylthio radical (**C**) suggests that the cleavage of the C−S bond in the cation radical (**A**) leads to the formation of the carbocation (**B**), which reacts with allyltrimethylsilane to give the allylated product.

Silyl enol ethers were also effective as carbon nucleophiles. The anodic oxidation of the α-organothioether (**2d**) in the presence of 1.1 equiv of the silyl enol ether

(20) (a) Nishiyama, H.; Narimatsu, S.; Sakuta, K.; Itoh, K. *J. Chem. Soc., Chem. Commun*. **1982**, 459. See also: (b) Sato, T.; Okura, S.; Otera, J.; Nozaki, H. *Tetrahedron Lett*. **1987**, *28*, 6299. (c) Silveira, C. C.; Fiorin, G. L.; Braga, A. L. *Tetrahedron Lett*. **1996**, *37*, 6085, and ref 16. The Lewis acid promoted reactions of O, Se acetals with allylsilanes is also reported: (d) Hermans, B.; Hevesi, L. *J. Org. Chem*. **1995**, *60*, 6141.

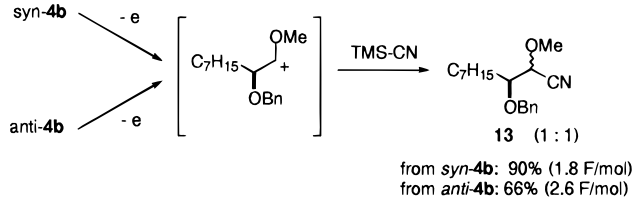
(21) For example: Torii, S.; Inokuchi, T.; Takagishi, S.; Horike, H.; Kuroda, H. Uneyama, K. *Bull. Chem. Soc. Jpn*. **1987**, *60*, 2173.

Table 3. Electrooxidative Intermolecular Carbon−Carbon Bond Formation Using Organothio Groups as Electroauxiliaries. Reaction with Trimethylsilyl Cyanide as a Carbon Nucleophile[a]

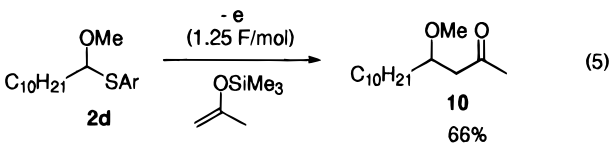
substrate	TMSCN (equiv)	F/mol	yield[b] (%) 11	12
2b	1.1	1.5	84(85)	(15)
	5.0	3.5	(66)	(17)
2d	1.1	1.0	65(72)	0
	5.0	1.0	(49)	(53)
2f	1.1	1.5	69(78)	0

[a] The reactions were normally carried out with 0.5 mmol of α-organothio-substituted ether with 1.1−5.0 equiv of trimethylsilyl cyanide in 1.0 mL of 0.2 M solution of Bu_4NClO_4 in CH_2Cl_2 in an undivided cell equipped a carbon rod anode and a platinum plate cathode under constant current conditions (10 mA) at room temperature. [b] The isolated yields. The yields in parentheses were determined by ^1H NMR using an internal standard (1,1,2,2-tetrachloroethane).

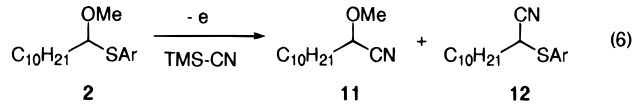
Scheme 6



derived from acetone resulted in the formation of the correspond coupling product (**10**) in moderate yield.



Trimethylsilyl cyanide (TMS−CN) was also found to be effective as a carbon nucleophile. The anodic oxidation of α-organothioethers in the presence of TMS−CN led to the cleavage of the C−S bond and the formation of the corresponding nitriles (**11**) (Table 3).[22] In this case the cleavage of the C−O bond leading to the formation of the nitrile (**12**) was also observed. The yield of **12** increased when an excess amount of TMS−CN was used. The mechanism of the formation **12** is not clear at present.



The anodic oxidation of diastereomerically pure *syn*-**4b** and *anti*-**4b** in the presence of TMS−CN gave a 1:1 mixture of two diastereomers (Scheme 6). This result also supports the mechanism involving the carbocation intermediate, because the stereochemistry of the starting material is lost in the carbocation intermediate.

Intramolecular Carbon−Carbon Bond Formation. The intramolecular carbon−carbon bond formation has also been achieved using organothio groups as electroauxiliaries. For example, the anodic oxidation of compound **14** having a carbon−carbon double bond, using Bu_4NBF_4 as the supporting electrolyte, gave rise to the cleavage of the C−S bond and the effective intramolecular C−C bond formation to one of the olefinic carbons and the introduction of fluoride to the other (Scheme 7). In this case the carbon−carbon double bond acted as a carbon nucleophile for the initially formed carbocation intermediate.[23]

Scheme 7

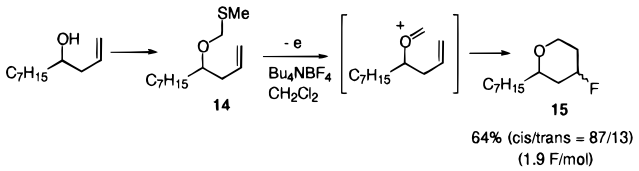
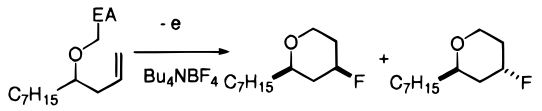


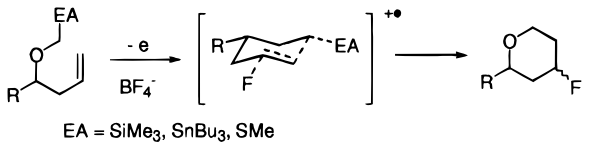
Table 4. Stereoselectivity of the Electrooxidative Cyclization Using Electroauxiliaries



EA	electricity (F/mol)	% yield	cis:trans
$SiMe_3$[a]	4.6	68	55:45
$SnBu_3$[a]	3.1	83	74:26
SMe	1.9	64	87:13

[a] Reference 6a.

Scheme 8



It is interesting that the stereoselectivity of the present reaction is higher than that using tin and silicon as electroauxiliaries (Table 4). The fact that stereoselectivity depends on the nature of the electroauxiliary suggests that the C−C bond formation and the C−F bond formation take place before the carbon−electroauxiliary bond is cleaved completely (Scheme 8). This mechanism sharply contrasts to the mechanism of the intermolecular reactions which involves the free carbocation. Presumably, in the case of intramolecular reaction, the attack of the carbon−carbon double bond might assist the cleavage of the carbon−electroauxiliary bond in the cation radical intermediate (Scheme 8).

One of the major advantages of the use of organothio groups as electroauxiliaries is that there are various methods for the synthesis of organothio-substituted substrates. The cyclic fluorine-containing compound **15** can also be synthesized by the anodic oxidation of **19** (Scheme 9). Compound **19** can be easily prepared by either anodic acetoxylation of sulfide **16**[24] followed by the Lewis acid-catalyzed reaction with homoallyl alcohol[25] or deprotonation of homoallyloxymethyl sulfide **18** followed by the alkylation.

The examples shown in Scheme 10 utilize compound **3** prepared by the addition of the sulfur stabilized

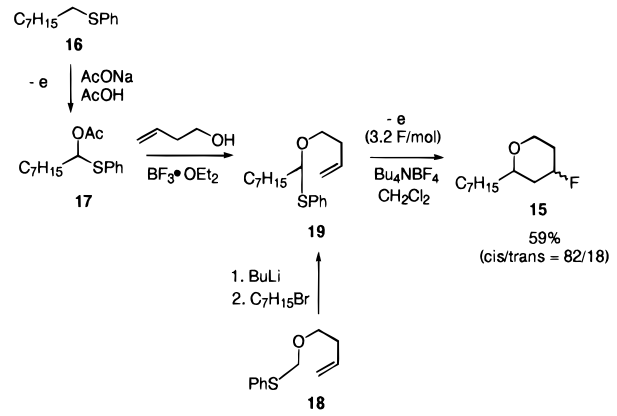
(22) The anodic oxidation of heteroatom compounds having a stannyl group as an electroauxiliary in the presence of TMS−CN leads to the formation of the corresponding nitriles and isonitriles. See ref 6d.

(23) The effective cyclization by the anodic oxidation α-stannyl ethers having a carbon−carbon double bond in an appropriate position has been achieved. See refs 6a,e.

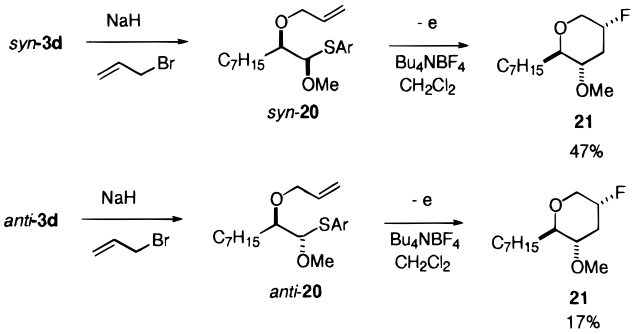
(24) Nokami, J.; Hatte, M.; Wakabayashi, S.; Okawara, R. *Tetrahedron Lett.* **1980**, *21*, 2557.

(25) Nokami, J.; Ryokume, K.; Inada, J. *Tetrahedron Lett.* **1995**, *36*, 6099.

Scheme 9



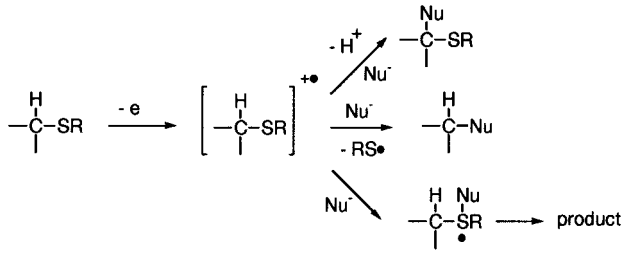
Scheme 10



carbanion to an aldehyde.[16] The allylation of the hydroxyl group of *syn*- and *anti*-**3d** gave *syn*- and *anti*-**20**, respectively. The electrochemical oxidation of *syn*-**20** gave rise to the facile formation of the cyclized fluorine-containing product (**21**) as a single diastereomer, although the aldehyde derived from the hydrolysis of **20** was also formed in ca. 20% yield. The anodic oxidation of *anti*-**20**, however, resulted in the formation of **21** in low yield together with a complex mixture. The present results indicate that the efficiency of the cyclization depends on the stereochemistry of the starting material, and this is consistent with the mechanism suggested for the electrooxidative cyclization of **14**. The partial carbon−carbon bond formation may take place before the cleavage of the C−S bond. Presumably anti starting material is conformationally less favorable for this process.

Mechanism of the Carbon−Sulfur Bond Cleavage. In the previous section of this paper we propose a mechanism involving the C−S bond cleavage in the cation radical intermediate leading to the organothio radical and the carbocation (Scheme 5). In the oxidative electron-transfer reactions of diorgano sulfides, there are three major modes of reaction pathways, as shown in Scheme 11.[26] The first one is the cleavage of the α-C−H bond followed by the introduction of nuleophiles on the carbon.[24] This mode is common for other heteroatom compounds such as amines and their derivatives.[27] The second type is the cleavage of the C−S bond followed by

Scheme 11



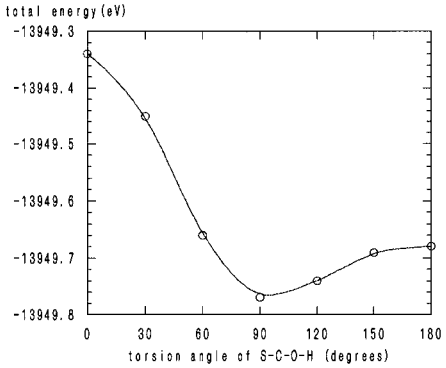


Figure 3. Variation of the total energy of the cation radical of $HSCH_2OH$ with the torsion angle of S−C−O−H (MP2/6-31G*).

the introduction of nucleophiles on the carbon.[11] The third type is the attack of nucleophiles on the sulfur atom.[28] Therefore, the questions of why and how the C−S bond is cleaved in the present reaction arise naturally. To get deeper insight into these questions, we carried out theoretical studies using ab initio molecular orbital calculations.

The electron-transfer driven reactions of organothio-substituted heteroatom compounds involves the initial transfer of one electron from the substrate molecule to form the cation radical species. Therefore, in the first place, we studied the structure of the cation radical. $HSCH_2OH$ was chosen as a model compounds, and the calculations were carried out at MP2/6-31G* level. The total energy of the cation radical varies with the torsion angle of S−C−O−H and becomes the minimum when the torsion angle is about 90° (Figure 3). This result suggests that there is some interaction between the C−S σ orbital and the p orbital of the oxygen, although its nature is not clear at present. As a matter of fact, the C−S bond becomes longest when the torsion angle is 90° (1.90 Å) (Figure 4), and this bond length is longer than that in the neutral molecule (1.82−1.84 Å) and that in the cation radical of CH_3SH (1.79 Å). This means that the C−S bond in the cation radical of $HSCH_2OH$ is weakened and is ready to be cleaved.

In the previous part, we have proposed that the C−S bond of the cation radical intermediate is cleaved to give the carbocation and the organothio radical, becasuse the products derived from the organothio radical were obtained. The ab initio calculations also suggest the cleavage of the C−S bond in the cation radical intermediate. Then, the question of why the cleavage of the C−S

(26) Reactivity patterns of cation radicals, for example: Schmittel, M.; Burghart, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2550, and references cited therein.

(27) The cleavage of the α-C−C bond, α-C−Si, and α-C−Sn bond is also reported. α-C−C: (a) Takemoto, Y.; Ohra, T.; Koike, H.; Furuse, S.; Iwata, C. *J. Org. Chem.* **1994**, *59*, 4727. (b) Takemoto, Y.; Ohra, T.; Furuse, S.; Koike, H.; Iwata, C. *J. Chem. Soc., Chem. Commun.* **1994**, 1529. α-C−Si: (c) Yoshida, J.; Isoe, S. *Chem. Lett.* **1987**, 631. α-C−Sn: Refs 6c,d.

(28) For example: (a) Nicholson, M. M. *J. Am. Chem. Soc.* **1954**, *76*, 2539. (b) Cottrell, P. T.; Mann, C. K. *J. Electrochem. Soc.* **1969**, *116*, 1499. See also: ref 11a. The α-C−H oxidation products are also formed via Pummerer rearrangement of the initially formed S-attack products. (c) Almdal, K.; Hammerich, O. *Sulfur Lett.* **1984**, *2*, 1.

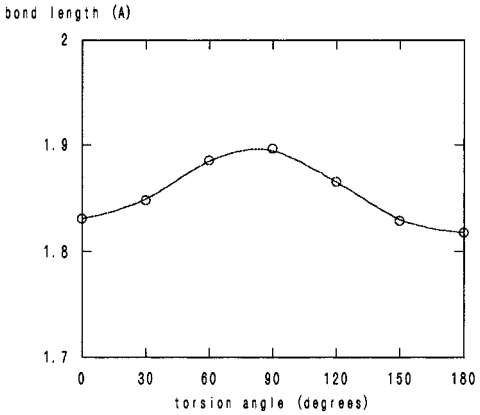


Figure 4. Variation of the length of C-S bond of the cation radical of $HSCH_2OH$ with the torsion angle of S−C−O−H (MP2/6-31G*).

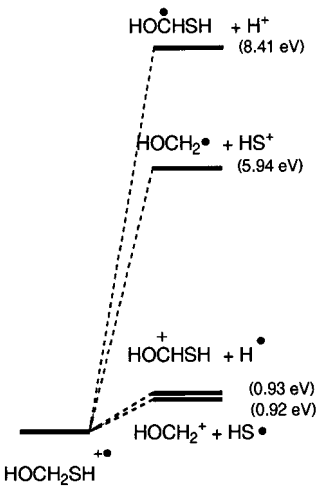


Figure 5. Energy diagram for the decomposition of the cation radical of $HOCH_2SH$ (MP2/6-31G*).

bond gives the carbocation and organothio radical comes out. To get an answer to this question, we calculated the energy changes for the bond cleavage.

The energy changes for the several modes of the decomposition of the cation radical of $HOCH_2SH$ were determined with the ab initio calculations (MP2/6-31G*). As shown in Figure 5, all modes of the decomposition are endothermic. The most energetically favorable mode is the cleavage of the C−S bond generating the carbocation and the sulfur radical. The C−H bond cleavage to generate the carbocation and hydrogen radical is comparable, although the formation of hydrogen radical seems to be unlikely. The cleavage of the C−H bond to generate the carbon radical and the cleavage of the C−S bond to generate the carbon radical and sulfur cation are much less favorable. The stabilization of the carbocation by the adjacent oxygen atom seems to play an important role and determines the mode of the decomposition of the cation radical. Although the kinetic factors seem to control the reaction mode, generalized Bell−Evans−Polany relationship (the more exothermic (or less endothermic) the reactions, the lower the barrier height is)[29] is in accordance with the experimental results.

We also examined the energy change for the cleavage of the C−S bond of the cation radical intermediate

(29) (a) Bell, R. P. *Proc. R. Soc. London, Ser. A* **1936**, *154*, 414. (b) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1936**, *32*, 1340.

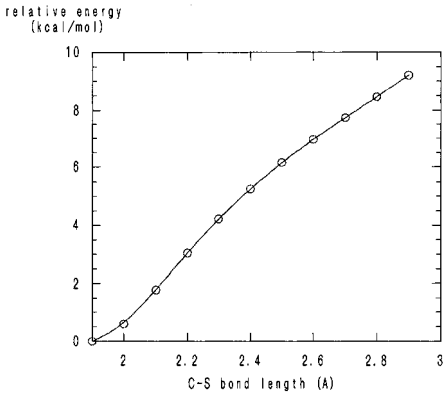


Figure 6. Change of total energy of $HSCH_2OH$ cation radical with the C−S bond length (MP2/6-31G*).

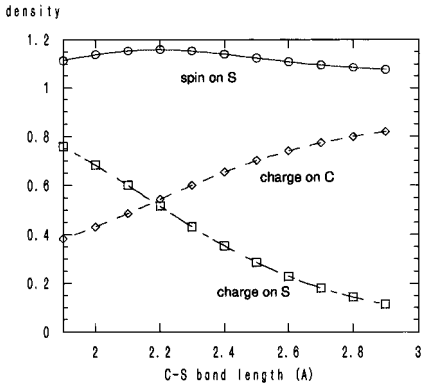


Figure 7. Changes of atomic spin density of S and atomic charge densities of O and S with the C−S bond length of the $HSCH_2OH$ cation radical (MP2/6-31G*). The atomic charge densities of hydrogens were summed into the heavy atom.)

(Figure 6). The cleavage of the C−S bond is endothermic in the absence of solvents and nucleophiles, and there is no transition state (TS). The spin density is localized on the sulfur atom in the cation radical, and this situation does not change appreciably during the course of the cleavage of the C−S bond, as shown in Figure 7. The atomic charges, however, change significantly with the cleavage of the C−S bond (Figure 7). With the increase of the C−S distance, the atomic charge on the sulfur decreases and the atomic charge on the carbon increases. These results indicate that the sulfur becomes the radical and the carbon becomes the cation with the cleavage of the C−S bond. This mode is consistent with the experimental results.

Conclusions

The research reported above exhibits the utility of organothio groups as electroauxiliaries in the electrooxidative inter- and intramolecular carbon−carbon bond formation of heteroatom compounds with various carbon nucleophiles. Easy access to α-organothio-substituted heteroatom compounds is advantageous from a synthetic point of view. The ab initio molecular orbitral calculations revealed that the carbon−sulfur bond is cleaved in the cation radical intermediate to generate the carbocation and the organothio radical. The present study also demonstrates the generality of the concept of electroauxiliary. The somewhat concerted nature observed for the intramolecular carbon−carbon bond formation suggests

the possibility of the control of stereochemistry using electroauxiliary. It is also hoped that exploitation of various types of electroauxiliaries based upon different principles will be developed in the future and that they will enable problems of chemo- and regioselectivity in electron-transfer driven reactions to be overcome satisfactorily.

Experimental Section

Materials. Dichloromethane was washed with saturated aqueous NaCl to remove a trace amount of alcohol, dried over P_2O_5, and distilled before use. The amount of water in dichloromethane was determined with the Karl Fischer Method (Hiranuma Aquacounter AQ-7).

Rotating Disk Electrode Voltammetry. Rotating disk electrode voltammetry was carried out with Hokuto HA-301 and Nikko Keisoku RRDE−1 using a glassy carbon working electrode, platinum wire counter electrode, and Ag/AgCl (saturated aqueous KCl) reference electrode in 0.1 M $LiClO_4$/CH_3CN at 1000 rpm. The sweep rate was 10 mV/s.

Molecular Orbital Calculations. The semiempirical molecular orbital calculations were carried out using the Spartan 3.1 program using a PM3 Hamiltonian with geometry optimization. Ab initio calculations were carried out with GAUSSIAN 94W[30] program at the MP2/6-31G* level (UHF) with geometry optimization. Mulliken population analysis was used for the analyses of spin and charge densities.

2-Pyridylthiomethyl Methyl Ether (1a). To a solution of 2-pyridinethiol (119.6 mg, 1.1 mmol) in tetrahydrofuran (THF) (2.0 mL) was added triethylamine (0.28 mL, 2.0 mmol) and chloromethyl methyl ether (0.12 mL, 1.5 mmol) at 0 °C. After being stirred at room temperature for 2 h, the reaction mixture was partitioned between saturated aqueous NH_4Cl and ether. The organic phase was washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified with preparative TLC (hexane/EtOAc, 1/5) to obtain the title compound (120.4 mg, 72%) as a yellow oil. TLC: R_f 0.74 (EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.42 (s, 3 H), 5.34 (s, 2 H), 7.01−7.16 (m, 1 H), 7.27−7.32 (m, 1 H), 7.50−7.55 (m, 1 H), 8.46−8.49 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.59, 73.65, 120.27, 122.93, 136.50, 149.72, 157.93. MS (EI, *m/e* (%)): 155 (M^+, 100), 140 (22), 124 (27), 112 (75), 78 (63), 69 (62). HRMS (EI). Calcd for C_7H_9OSN: 155.0405. Found: 155.0394.

Compounds **1c**−**f** were synthesized in a similar fashion.

Phenylthiomethyl Methyl Ether (1b). This compound was prepared according to the literature method.[14] In a flask equipped with Dean−Stark water trap containing 4 Å molecular sieves, was added thiophenol (5.0 mL, 49 mmol), *p*-toluenesulfonic acid monohydrate (170 mg, 0.90 mmol), dimethoxymethane (30.0 mL, 340 mmol), and dichloromethane (100 mL), and the mixture was refluxed for 48 h. After removal of the solvent and excess dimethoxymethane, the mixture was partitioned between ether (150 mL) and 15% aqueous NaOH (50 mL). The organic phase was separated and then washed with water and brine. After removal of the solvent, the residue was purified by distillation (110 °C, 8 mmHg) to obtain the title compound (4.64 g, 68%). TLC: R_f 0.64 (hexane/EtOAc, 5/ 1). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.43 (s, 3 H), 4.96 (s, 2 H), 7.2−7.4 (m, 3 H), 7.4−7.5 (m, 2 H).

(2-Methoxyphenylthio)methyl Methyl Ether (1c). The reaction of 2-methoxybenzenethiol (0.30 mL, 2.5 mmol), chloromethyl methyl ether (0.22 mL, 3.0 mmol), and triethylamine (0.34 mL, 3.5 mmol) in THF (5.0 mL) gave the title compound in 87% yield (396 mg). TLC R_f 0.22 (hexane/EtOAc, 20/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.42 (s, 3 H), 3.89 (s, 3 H), 4.98 (s, 2 H), 6.87 (dd, J = 8.1, 1.2 Hz, 1 H), 6.94 (td, J = 7.5, 1.2 Hz, 1 H), 7.21 (dd, J = 6.6, 1.2 Hz, 1 H), 7.53 (dd, J = 7.5, 1.2 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.82, 55.93, 75.93, 110.58, 121.24, 123.59, 127.95, 131.08, 157.49. Anal. Calcd for $C_9H_{12}O_2S$: C, 58.67; H, 6.56. Found: C, 58.68, H; 6.58.

(4-Methoxyphenylthio)methyl Methyl Ether (1d). The reaction of 4-methoxybenzenethiol (5.0 mL, 40.6 mmol) with chloromethyl methyl ether (3.7 mL, 40 mmol) and triethylamine (10 mL, 71 mmol) in THF (50 mL) followed by distillation (95−96 °C, 15 mmHg) gave the title compound (6.54 g, 89%). TLC R_f 0.25 (hexane/EtOAc, 20/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.43 (s, 3 H), 3.80 (s, 3 H), 4.85 (s, 2 H), 6.85 (d, J = 8.7 Hz, 2 H), 7.43 (d, J = 8.7 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.27, 55.90, 79.25, 114.68, 125.99, 133.75, 159.43. Anal. Calcd for $C_9H_{12}O_2S$: C, 58.67; H, 6.56. Found: C, 58.55, H; 6.51.

(2,4-Dimethoxyphenyl)thiomethyl Methyl Ether (1e). The reaction of 2,4-dimethoxybenzenethiol (361 mg, 2.1 mmol) with chloromethyl methyl ether (0.25 mL, 3.0 mmol) and triethylamine (0.50 mL, 3.6 mmol) in THF (2.0 mL) followed by flash chromatography (hexane/EtOAc, 10/1) gave the title compound (398.3 mg, 89%). TLC: R_f 0.22 (hexane/EtOAc, 10/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.41 (s, 3 H), 3.80 (s, 3 H), 3.86 (s, 3 H), 4.85 (s, 2 H), 6.45−6.48 (m, 2 H), 7.43 (d, J = 9.3 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.30, 55.72, 55.93, 99.07, 105.04, 113.46, 135.06, 159.72, 161.13. Anal. Calcd for $C_{10}H_{14}O_3S$: C, 56.05; H, 6.59. Found: C, 55.93, H; 6.62.

(4-Chlorophenyl)thiomethyl Methyl Ether (1f). The reaction of 4-chlorobenzenethiol (1.59 g, 11 mmol) with chloromethyl methyl ether (1.0 mL, 13 mmol) and triethylamine (2.2 mL, 16 mmol) in THF (15 mL) followed by distillation (100 °C, 15 mmHg) gave the title compound (1.70 g, 100%). TLC: R_f 0.29 (hexane/EtOAc, 10/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.43 (s, 3 H), 4.93 (s, 2 H), 7.24−7.28 (m, 2 H), 7.37−7.41 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.96, 77.81, 129.09, 131.61, 132.92, 134.51. Anal. Calcd for C_8H_9ClOS: C, 50.93; H, 4.81. Found: C, 50.91, H; 4.84.

1-(Phenylthio)decyl Methyl Ether (2b). To a solution of phenylthiomethyl methyl ether (788 mg, 5.1 mmol) in THF (9.0 mL) was added slowly butyllithium (1.60 M in hexane, 3.4 mL, 5.5 mmol) at −78 °C. After being stirred at −40 °C for 1.2 h, the mixture was cooled to −78 °C. 1-Bromodecane (1.6 mL, 7.6 mmol) was added, and the mixture was stirred at the same temperature for 6 h. The mixture was warmed to room temperature and stirred at this temperature for 12 h. The reaction mixture was partitioned between saturated aqueous NH_4Cl and ether. The organic phase was separated and dried over $MgSO_4$. After the solvent was removed, the residue was purified using flash chromatography (hexane/benzene, 20/1) to obtain the title compound (703 mg, 47%). TLC: R_f 0.29 (hexane/benzene, 10/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.3 Hz, 3 H), 1.25 (br, 14 H), 1.38−1.54 (m, 2 H), 1.61−1.82 (m, 2 H), 3.47 (s, 3 H), 4.63 (t, J = 6.6 Hz, 1 H), 7.20−7.36 (m, 3 H), 7.42−7.50 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.98, 22.56, 26.10, 29.03, 29.21, 29.38, 29.42, 29.47, 31.81, 35.55, 55.28, 91.00, 127.48, 128.77, 133.49, 133.61. MS (EI, *m/e* (%)): 294 (M^+, 18), 263 (11), 185 (100), 170 (82), 109 (79), 97 (82), 83 (82), 71 (100), 55 (70). HRMS (EI). Calcd for $C_{18}H_{30}OS$: 294.2017. Found: 294.2011.

1-((4-Methoxyphenyl)thio)decyl Methyl Ether (2d). To a solution of (4-methoxylphenylthio)methyl methyl ether (2.54 g, 13.8 mmol) in THF (15 mL) was slowly added butyllithium (1.59 M in hexane, 8.80 mL, 14.0 mmol) at −78 °C. The mixture was stirred at −50 °C for 4 h and cooled to −78 °C. 1-Iododecane (3.8 mL, 17.8 mmol) was added, and the mixture was stirred at the same temperature for 1.5 h. Saturated aqueous NH_4Cl was added, and the mixture was warmed to room temperature. The organic materials were extracted with ether, and the organic phase was washed with brine and dried over $MgSO_4$. After the solvent was removed, the residue was purified with flash chromatography (hexane/EtOAc, 50/1) to obtain the title compound (3.75 g, 83%). TLC: R_f 0.35 (hexane/

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EtOAc, 10/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.9 Hz, 3 H), 1.24 (br, 14 H), 1.36−1.48 (m, 2 H), 1.61−1.72 (m, 2 H), 3.47 (s, 3 H), 3.80 (s, 3 H), 4.45 (t, J = 6.3 Hz, 1 H), 6.81−6.87 (m, 2 H), 7.35−7.43 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.99, 22.57, 26.12, 29.07, 29.22, 29.42, 29.48, 31.81, 35.56, 55.23, 55.58, 91.30, 114.35, 123.14, 136.38, 159.78. HRMS (EI). Calcd for $C_{19}H_{32}O_2S$: 324.2123. Found: 324.2124. Anal. Calcd for $C_{19}H_{32}O_2S$: C, 70.32; H, 9.94. Found: C, 70.06, H; 9.78.

1-((2,4-Dimethoxyphenyl)thio)decyl Methyl Ether (2e). To a solution of (2,4-dimethoxyphenylthio)methyl methyl ether (258 mg, 1.2 mmol) and TMEDA (0.20 mL, 1.3 mmol) in THF (1.2 mL) was added butyllithium (1.59 M in hexane, 0.80 mL, 1.40 mmol) dropwise at −78 °C. The mixture was stirred at the same temperature for 3.5 h, and 1-iododecane (0.30 mL, 1.40 mmol) was added. The mixture was stirred at the same temperature for 4 h, and saturated aqueous NH_4Cl was added. The mixture was warmed to room temperature, and the organic materials were extracted with ether. The organic phase was separated and washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified via flash chromatography (hexane/EtOAc, 20/1) to obtain the title compound (108 mg, 25%). TLC: R_f 0.17 (hexane/AcOEt, 10/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.6 Hz, 3 H), 1.25 (br, 14 H), 1.38−1.52 (m, 2 H), 1.73 (dt, J = 8.4, 7.2 Hz, 2 H), 3.43 (s, 3 H), 3.81 (s, 3 H), 3.85 (s, 3 H), 4.57 (t, J = 6.3 Hz, 1 H), 6.42−6.50 (m, 2 H), 7.37−7.43 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.96, 22.54, 26.05, 29.17, 29.20, 29.43, 29.46 (2 carbons), 31.78, 35.79, 55.31, 55.40, 55.64, 90.81, 98.98, 104.90, 112.11, 137.65, 106.95. MS (EI, *m/e* (%)): 354 (M^+, 59), 270 (23), 185 (69), 170 (100), 141 (32), 111 (45), 97 (75), 83 (72), 71 (71). HRMS (EI). Calcd for $C_{20}H_{34}O_3S$: 354.2229. Found: 354.2221.

1-((4-Chlorophenyl)thio)decyl Methyl Ether (2f). To a solution of (4-chlorphenylthio) methyl methyl ether (308 mg, 2.0 mmol) in THF (4 mL) was added butyllithium (1.55 M in hexane, 1.3 mL, 2.0 mmol) at −78 °C. The mixture was stirred at −45 °C for 3 h and cooled to −78 °C. 1-Iododecane (0.48 mL, 2.2 mmol) was added, and the mixture was stirred at −78 °C for 20 min. Saturated aqueous NH_4Cl was added, the organic materials were extracted with ether, and the organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified via flash chromatography (hexane/EtOAc, 50/1) to obtain the title compound (650 mg, 99%). TLC: R_f 0.43 (hexane/EtOAc, 50/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.6 Hz, 3 H), 1.15−1.80 (m, 21 H), 3.46 (s, 3 H), 4.54 (t, J = 6.8 Hz, 1 H), 7.26 (d, J = 8.7 Hz, 2 H), 7.40 (d, J = 9.0 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.98, 22.56, 26.08, 29.00, 29.21, 29.36, 29.42, 29.47, 31.80, 35.40, 55.28, 90.42, 128.94, 131.84, 133.77, 134.90. Anal. Calcd for $C_{18}H_{29}ClOS$: C, 65.73; H, 8.89. Found: C, 65.64, H; 8.82.

1-Methoxy-1-(phenylthio)-2-hydroxynonane (3b). To a solution of (phenylthio)methyl methyl ether (766 mg, 5.0 mmol) in THF (6.0 mL) was added butyllithium (1.60 M in hexane, 3.4 mL, 5.5 mmol) at −78 °C. The mixture was stirred at −40 °C for 1 h and cooled to −78 °C. 1-Octanal (711 mg, 5.5 mmol) was added, and the mixture was stirred at −78 °C for 4 h. Saturated aqueous NH_4Cl was added, the organic materials were extracted with ether, and the organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified via flash chromatography (hexane/EtOAc, 20/1) to obtain the title compound (1.12 g, 79%) as a mixture of two diastereomers (syn/anti, 1.4/1). The diastereomers were separated by careful flash chromatography. The relative stereochemistry was determined by comparison of their ^{1}H NMR spectra, especially the coupling constant of the methine proton at 4.41 (syn) and 4.46 (anti) with those of analogous compounds reported in the literature.[16] The selectivity of the addition reaction is also consistent with the literature data.[16]

Compound *syn*-3b. TLC: R_f 0.20 (hexane/EtOAc, 10/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.6 Hz, 3 H), 1.27 (br, 8 H), 1.40−1.54 (m, 2 H), 1.80−1.90 (m, 2 H), 2.51 (br, 1 H), 3.54 (s, 3 H), 3.56−3.65 (m, 1 H), 4.41 (d, J = 7.2 Hz, 1 H), 7.20−7.30 (m, 3 H), 7.45−7.55 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.98, 22.53, 25.27, 29.09, 29.40, 31.70, 32.49, 56.72, 72.90, 95.04, 127.92, 129.01, 132.98, 133.81. Anal. Calcd for $C_{16}H_{26}O_2S$: C, 68.04; H, 9.28. Found: C, 67.90; H, 9.36.

Compound *anti*-3b. TLC: R_f 0.25 (hexane/EtOAc, 10/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, J = 4.8 Hz, 3 H), 1.26 (br, 8 H), 1.40−1.54 (m, 2 H), 1.62−1.80 (m, 2 H), 2.46 (br, 1 H), 3.51 (s, 3 H), 3.53−3.60 (m, 1 H), 4.46 (d, J = 6.6 Hz, 1 H), 7.20−7.30 (m, 3 H), 7.45−7.55 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.96, 22.51, 25.49, 29.10, 29.53, 31.68, 32.49, 56.93, 71.99, 97.30, 127.97, 129.08, 132.69, 133.84. MS (EI, *m/e* (%)): 282 (M^+, 10), 250 (3), 173 (100). HRMS (EI). Calcd for $C_{16}H_{26}O_2S$: 282.1654. Found 282.1647.

1-Methoxy-1-((4-methoxyphenyl)thio)-2-hydroxynonane (3d). To a solution of (4-methoxyphenylthio)methyl methyl ether (993 mg, 5.4 mmol) in THF (6.0 mL) was added butyllithium (1.36 M in hexane, 4.1 mL, 5.6 mmol) at −78 °C. The mixture was stirred at −50 °C for 3 h and cooled to −78 °C. 1-Octanal (0.86 mL, 5.5 mmol) was added, and the mixture was stirred at −78 °C for 20 min. Saturated aqueous NH_4Cl was added, the organic materials were extracted with ether, and the organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified via flash chromatography (hexane/EtOAc, 20/1) to obtain the title compound (1.28 g, 76%) as a mixture of two diastereomers (syn/anti, 1.4/1). The diastereomers were separated by careful flash chromatography. The relative stereochemistry was determined by comparison of their ^{1}H NMR spectra, especially the coupling constant of the methine proton at 4.25 (syn) and 4.30 (anti) with those of analogous compounds reported in the literature.[16] The selectivity of the addition reaction is also consistent with the literature data.[16]

Compound *syn*-3d. TLC: R_f 0.12 (hexane/EtOAc, 10/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.6 Hz, 3 H), 1.27 (br, 8 H), 1.40−1.54 (m, 2 H), 1.80−1.95 (m, 2 H), 2.49 (s, 1 H), 3.50−3.60 (m, 1 H), 3.55 (s, 3 H), 3.81 (s, 3 H), 4.25 (d, J = 7.5 Hz, 1 H), 6.85 (d, J = 8.7 Hz, 2 H), 7.41 (d, J = 8.7 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.99, 22.55, 25.29, 29.12, 29.47, 31.73, 32.43, 55.24, 56.75, 72.75, 94.95, 114.53, 122.60, 136.36, 159.96. MS (EI, *m/e* (%)): 312 (M^+, 12), 280 (4), 173 (24), 140 (100). HRMS (EI). Calcd for $C_{17}H_{28}O_3S$: 312.1759. Found: 312.1759.

Compound *anti*-3d. TLC: R_f 0.18 (hexane/EtOAc, 10/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, J = 4.8 Hz, 3 H), 1.26 (br, 8 H), 1.40−1.54 (m, 2 H), 1.62−1.80 (m, 2 H), 2.51 (s, 1 H), 3.40−3.52 (m, 1 H), 3.53 (s, 3 H), 3.80 (s, 3 H), 4.30 (d, J = 6.9 Hz, 1 H), 6.86 (d, J = 8.7 Hz, 2 H), 7.42 (d, J = 8.7 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.97, 22.52, 25.50, 29.12, 29.56, 31.70, 32.47, 55.24, 56.97, 71.46, 97.26, 114.64, 122.03, 136.45, 160.03. Anal. Calcd for $C_{17}H_{28}O_3S$: C, 65.35; H, 9.03. Found: C, 65.25; H, 9.26.

***syn*-1-Methoxy-1-(phenylthio)-2-(benzyloxy)nonane (4b)**. To a solution of *syn*-1-methoxy-1-(phenylthio)-2-nonaol (**3b**) (384.8 mg, 1.36 mmol) in THF (3 mL) was added NaH (60% w/w in oil, 76 mg, 1.9 mmol) at 0 °C. The mixture was stirred for 1 h. Benzyl bromide (0.17 mL, 1.4 mmol) was added and stirred for 2 days at room temperature. MeOH (0.5 mL) was added to destroy the excess NaH. Saturated aqueous NH_4Cl was added, the organic materials were extracted with ether, and the organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified via flash chromatography (hexane/EtOAc, 10/1) to obtain the title compound (503 mg, 99%). TLC: R_f 0.55 (hexane/EtOAc, 10/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.6 Hz, 3 H); 1.15−1.81 (m, 12 H), 3.50 (s, 3 H), 3.55 (m, 1 H), 4.52 (d, J = 11.7 Hz, 1 H), 4.69 (d, J = 6.0 Hz, 1 H), 4.71 (d, J = 12.3 Hz, 1 H), 7.28−7.36 (m, 3 H), 7.50−7.53 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.00, 22.54, 25.46, 29.12, 29.44, 31.32, 31.71, 56.75, 73.57, 81.36, 95.08, 127.48, 127.63, 128.16, 128.35, 128.95, 133.28, 134.69, 138.70. MS (EI, *m/e* (%)): 372 (M^+, 8), 263 (90), 153 (65). HRMS (EI). Calcd for $C_{23}H_{32}O_2S$: 372.2123. Found: 372.2138.

***anti*-1-Methoxy-1-(phenylthio)-2-(benzyloxy)nonane (4b).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.6 Hz, 3 H),

1.15−1.81 (m, 12 H), 3.44 (s, 3 H), 3.65 (m, 1 H), 4.55 (d, J = 11.4 Hz, 1 H), 4.69 (d, J = 11.7 Hz, 1 H), 4.70 (d, J = 3.9, 1 H), 7.26−7.48 (m, 10 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.99, 22.53, 25.41, 29.10, 29.45, 30.68, 31.71, 57.13, 72.70, 81.15, 95.81, 127.31, 127.65, 128.16, 128.36, 128.94, 129.03, 132.87, 135.53, 138.61. Anal. Calcd for $C_{23}H_{32}O_2S$: C, 74.15; H, 8.66. Found: C, 73.94, H; 8.82.

***syn*-1-Methoxy-1-((4-methoxyphenyl)thio)-2-(benzyloxy)nonane (4d).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.0 Hz, 3 H), 1.24 (br, 9 H), 1.35−1.50 (m, 1 H), 1.58−1.70 (m, 1 H), 1.75−1.90 (m, 1 H), 3.4−3.5 (m, 1 H), 3.50 (s, 3 H), 3.81 (s, 3 H), 4.48 (d, J = 11.1 Hz, 1 H), 4.53 (d, J = 6.0 Hz, 1 H), 4.69 (d, J = 11.1 Hz, 1 H), 6.84 (d, J = 8.7 Hz, 2 H), 7.20−7.38 (m, 5 H), 7.44 (d, J = 8.7 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.99, 22.54, 25.45, 29.13, 29.46, 31.34, 31.72, 55.25, 56.87, 73.54, 81.17, 95.55, 114.48, 124.49, 127.57, 128.15, 128.30, 135.94, 138.78, 159.69. Anal. Calcd for $C_{24}H_{34}O_3S$: C, 71.60; H, 8.51. Found: C, 71.34, H; 8.36.

((4-Methoxyphenyl)thio)benzyl Methyl Ether (6). To a solution of 4-methoxybenzenethiol (1.23 mL, 10.0 mmol) and triethylamine (1.60 mL, 11.5 mmol) in CCl_4 (70 mL) was added tributyltin chloride (2.70 mL, 10.0 mmol) at room temperature, and the mixture was stirred at the same temperature overnight. The removal of the solvent gave (4-methoxyphenylthio)-tributylstannane (5.00 g), and this material was used for the subsequent reaction without further purification.

To a solution of (4-methoxyphenylthio)tributylstannane (960 mg, 1.92 mmol) and benzaldehyde dimethyl acetal (0.30 mL, 2.0 mmol) in toluene/hexane (8/3, 11 mL) was added $BF_3{\cdot}OEt_2$ (0.25 mL, 2.0 mmol) at −78 °C. The mixture was stirred at the same temperature for 8 h. Pyridine (0.5 mL) was added, and the mixture was warmed to room temperature. A 2 N aqueous NaOH solution (2.0 mL) was added, and the organic materials were extracted with ether. The organic phase was separated and washed with 1 N aqueous NaOH, water, and brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified via flash chromatography (hexane/EtOAc, 30/1) to obtain the title compound (347 mg, 67%). TLC: R_f 0.45 (hexane/EtOAc, 10/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.54 (s, 3 H), 3.77 (s, 3 H), 5.59 (s, 1 H), 6.81−6.90 (m, 2 H), 7.15−7.25 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.17, 56.46, 91.57, 114.10, 122.71, 126.20, 127.72, 127.98, 136,73, 139.58, 159.97. Anal. Calcd for $C_{15}H_{16}O_2S$: C, 69.20; H, 6.19. Found: C, 69.08, H; 6.18.

Electrooxidative Intermolecular Carbon−Carbon Bond Formation. General Procedure. To an undivided cell equipped with a carbon rod electrode (i.d. = 4 mm), a platinum plate cathode (2 × 3 cm), and a magnetic stirring bar was placed dried molecular sieves 4 Å (ca. 160 mg). The supporting electrolyte (0.20 mmol), the substrate (0.50 mmol), the nucleophile (1.0−2.5 mmol), and dichloromethane (1.0 mL) were added. A constant current (10 mA) was passed under an atmosphere of nitrogen. After most of the substrate was consumed (determined by TLC), the current was turned off, and the reaction mixture was transferred to a flask. After removal of the solvent, the crude materials were passed through a short (5 cm) column of silica gel (ether elution) to remove the supporting electrolyte. The crude product thus obtained was purified with flash chromatography. Sometimes the sulfur containing byproducts contaminated the desired product. In such a case, the crude product was treated with a small amount of *m*-chloroperoxybenzoic acid at 0 °C for ca. 5 min to oxidize the sulfur-containing byproducts. The oxidized sulfur-containing byproducts were easily separable by flash chromatography.

4-Methoxy-1-tetradecene (7). GLC: R_t 9.65 min (OV-1 25 m, 100−250 °C, 10 °C/min). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.9 Hz, 3 H), 1.27 (br, 16 H), 1.4−1.5 (m, 2 H), 2.26 (t, J = 6.0 Hz, 2 H), 3.34 (s, 3 H), 5.0−5.15 (m, 2 H), 5.7−5.9 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.98, 22.57, 25.17, 29.24, 29.53, 29.69, 31.82, 33.29, 37.69, 56.47, 80.54, 116.76, 135.15. Anal. Calcd for $C_{15}H_{30}O$: C, 79.58; H, 13.36. Found: C, 79.68, H; 13.65.

1-Methoxy-1-phenyl-3-butene (8).[20e] ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.3−2.6 (m, 2 H), 3.22 (s, 3 H), 4.17 (t, 2 H), 2.26 (t, J = 6.0 Hz, 1 H), 5.0−5.15 (m, 2 H), 5.7−5.9 (m, 1 H), 7.1−7.6 (m, 5 H).

4-Methoxy-5-(benzyloxy)-1-dodecene (9). This compound was isolated and characterized as a mixture of two diastereomers (2:1); the ratio was determined by using ^{1}H NMR spectroscopy. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.9 Hz, 3 H), 1.27 (br, 10 H), 1.4−1.5 (m, 2 H), 2.1−2.4 (m, 2 H), 3.1−3.2 (m, 1 H), 3.41 (s) and 3.42 (s) (total 3 H), 4.60 (m, 2 H), 5.0−5.1 (m, 2 H), 5.75−5.9 (m, 1 H), 7.1−7.6 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.03, 22.60, 25.71, 25.89, 29.20, 29.69, 29.86, 30.34, 31.79, 34.40, 34.74, 58.10, 58.44, 72.23, 72.74, 79.86, 82.25, 82.80, 116.72, 127.64, 127.80, 128.10, 128.41, 135.76, 139.05. MS (EI, *m*/*e* (%)): 304 (M^+, 11), 219 (10), 197 (30), 154 (25). HRMS (EI). Calcd for $C_{20}H_{32}O_2$: 304.2402. Found: 304.2390.

4-Methoxytetradecan-2-one (10). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.9 Hz, 3 H), 1.27 (br, 16 H), 1.4−1.5 (m, 2 H), 2.18 (s, 3 H), 2.2−2.3 (m, 1 H), 2.6−2.7 (m, 1 H), 3.32 (s, 3 H), 3.60−3.72 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.99, 22.57, 24.97, 29.24, 29.49, 29.61, 31.01, 31.82, 33.73, 48.18, 56.85, 208.09. IR (neat): 1719 cm^{-1} (C=O). MS (EI, *m*/*e* (%)): 242 (M^+, 10), 227 (35), 210 (12), 185 (20). HRMS (EI). Calcd for $C_{15}H_{30}O_2$: 242.2245. Found: 242.2243.

1-Cyano-1-methoxyundecane (11). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.9 Hz, 3H), 1.27 (br, 16 H), 1.4−1.5 (m, 2 H), 1.7−1.8 (m, 2 H), 3.48 (s, 3 H), 4.04 (t, J = 6.6 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.53, 24.55, 28.86, 29.16, 29.21, 29.33, 29.42, 31.76, 33.23, 57.83, 70.68, 118.23. Anal. Calcd for $C_{13}H_{25}NO$: C, 73.88; H, 11.92; N, 6.63. Found: C, 74.15; H, 11.67; N, 6.62.

1-Cyano-1-((4-methoxyphenyl)thio)undecane (12). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 7.2 Hz, 3 H), 1.26 (br, 16 H), 1.4−1.5 (m, 2 H), 1.7−1.8 (m, 2 H), 3.56 (t, J = 7.5 Hz, 1 H), 3.83 (s, 3 H), 6.91 (d, J = 6.6 Hz, 2 H), 7.56 (d, J = 6.6 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.97, 22.54, 26.92, 28.68, 29.16, 29.34, 29.41, 31.77, 32.23, 37.79, 55.31, 114.99, 119.51, 120.97, 137.42, 161.21. Anal. Calcd for $C_{19}H_{29}NOS$: C, 71.42; H, 9.15. Found: C, 71.35; H, 9.44.

1-Cyano-1-methoxy-2-(benzyloxy)nonane (13). This compound was characterized as a mixture of two diatereomers (1:1), and the ratio was determined by using ^{1}H NMR spectroscopy. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 0.88 Hz, 3 H), 1.50−1.80 (m, 12 H), 3.51 (s) and 3.52 (s) (total 3 H), 3.58−3.70 (m, 1 H), 4.03 (d, J = 5.4 Hz) and 4.11 (d, J = 5.4 Hz) (total 1 H), 4.607 (d, J = 11.7 Hz) and 4.614 (d, J = 11.4 Hz) (total 1 H), 4.71 (d, J = 11.7 Hz) and 4.79 (d, J = 11.4 Hz) (total 1 H), 7.22−7.42 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.95, 22.50, 24.81, 25.12, 29.01, 29.30, 30.73, 31.09, 31.65, 58.46, 58.54, 73.51, 73.86, 74.31, 78.41, 78.49, 116.76, 117.05, 127.98, 128.03, 128.07, 128.18, 128.50, 128.53, 137.83. Anal. Calcd for $C_{18}H_{27}NO_2$: C, 74.70; H, 9.40; N, 4.84. Found: C, 74.42; H, 9.48, N, 4.55.

4-((Methylthio)methoxy)-1-undecene (14). To a solution of allylmagnesium bromide in THF (0.77 M, 60.0 mL, 46.2 mmol) was added dropwise to a solution of octanal (6.0 mL, 38.4 mmol) in THF (10 mL) at 0 °C. The mixture was refluxed for 0.5 h and cooled to room temperature. Saturated aqueous NH_4Cl (9.6 mL) was added, and solid materials were removed by filtration. The solvent was evaporated and the residue was purified by distillation (71−74 °C, 1.2 mmHg) to obtain 1-undecen-4-ol[6a] (4.98 g, 76%). TLC: R_f 0.25 (hexane/EtOAc,-10/1). GC: R_t 2.43 min (OV-1 25 m, capillary 100−150 °C, 10 °C/min). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.3 Hz, 3 H), 1.28 (br s, 11 H), 1.4−1.5 (m, 2 H), 2.05−2.10 (m, 1 H), 2.20−2.38 (m, 1 H), 3.64 (br, 1 H), 5.11−5.17 (m, 2 H), 5.76−5.95 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.95, 22.53, 23.23, 29.15, 30.00, 31.71, 39.08, 43.60, 73.45, 118.61, 133.92.

To a suspension of silver nitrate (930 mg, 5.5 mmol) and triethylamine (0.83 mL, 6.0 mmol) in benzene (25 mL) was added a solution of 1-undecen-4-ol (884 mg, 5.0 mmol) and chloromethyl methyl sulfide (0.50 mL, 6.0 mmol) in benzene (2.5 mL). The mixture was heated at 60 °C for 17 h. The reaction mixture was filtered, and the filtrate was washed with

3% aqueous H_3PO_4, saturated aqueous $NaHCO_3$, water and dried over Na_2SO_4. After removal of the solvent, the residue was purified by bulb-to-bulb distillation (120 °C, 2.0 mmHg) to obtain the title compound (307 mg, 28%). TLC: R_f 0.47 (hexane/AcOEt, 10/1). GC: R_t 12.04 min (OV-1 25 m, capillary, 80−200 °C, 10 °C/min). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.6 Hz, 3 H), 1.27 (br, 10 H), 1.43−1.53 (m, 2 H), 2.17 (s, 3 H), 2.28 (t, J = 6.0 Hz, 2 H), 3.69 (dt, J = 6.0, 6.0 Hz, 1 H), 4.65 (s, 2 H), 5.04−5.17 (m, 2 H), 5.76−5.89 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.97, 22.54, 25.18, 29.17, 29.57, 31,-73, 33.46, 37.97, 72.96, 75.86, 117.11, 134.89. MS (EI, *m/e* (%)): 230 (M^+, 9), 200 (50), 183 (53), 152 (100), 127 (71), 111 (62), 97 (80), 83 (82). HRMS (EI). Calcd for $C_{13}H_{26}OS$: 230.1704. Found: 230.1630.

1-(Allyloxy)-1-(phenylthio)decane (19) (Method A). In an undivided cell equipped with a platinum plate anode (1 × 2 cm) and a platinum plate cathode (2 × 3 cm) were placed octyl phenyl sulfide (**16**) (2.50 g, 11.2 mmol), sodium acetate (250 mg, 3.1 mmol), and acetic acid (2.5 mL). The electric current (100 mA) was passed at 60 °C under constant current conditions. After 2.7 F/mol of electricity was consumed, the reaction mixture was transferred to a flask, and acetic acid was removed under reduced pressure. The residue was partitioned between ether and saturated aqueous $NaHCO_3$. The organic phase was washed with saturated aqueous $NaHCO_3$ and brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified via flash chromatography (hexane/EtOAc, 20/1) to obtain 1-acetoxy-1-phenylthiooctane (1.86 g, 59%) (**17**).[24] TLC: R_f 0.32 (hexane/EtOAc, 10 /1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (t, J = 6.9 Hz, 3 H), 1.26 (bs, 8 H), 1.35−1.44 (m, 2 H), 1.64 (q, J = 6.9 Hz, 2 H), 2.04 (s, 3 H), 6.11 (t, J = 6.9 Hz, 2 H), 7.2−7.5 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.93, 21.04, 22.46, 25.65, 28.84, 28.94, 31.56, 34.49, 80.41, 128.29, 128.94, 131.76, 133.84, 170.05. IR (neat): 1748 cm^{-1} (C═O).

To a solution of **17** (913 mg, 3.1 mmol) and 3-buten-1-ol (0.28 mL, 3.3 mmol) in THF (10 mL) was added BF_3·OEt_2 (0.40 mL, 3.2 mmol) at room temperature, and the mixture was stirred at room temperature for 19 h. The reaction mixture was partitioned between ether and saturated aqueous $NaHCO_3$. The organic phase was washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. After removal of the solvent, the residue was purified via flash chromatography (hexane/EtOAc, 100/1) to obtain the title compound (429 mg, 43%). TLC: R_f 0.27 (hexane/EtOAc, 50/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.9 Hz, 3 H), 1.24 (br, 12 H), 1.35−1.50 (m, 2 H), 1.75 (ddddd, J = 6.9, 6.6, 6.6, 1.8, 1.4 Hz, 2 H), 2.35 (dt, J = 6.6, 1.2 Hz, 2 H), 3.49 (dt, J = 9.3, 6.6 Hz, 1 H), 3.93 (dt, J = 9.3, 6.6 Hz, 1 H), 4.71 (t, J = 6.6 Hz, 1 H), 5.04 (ddt, J = 10.2, 1.8, 1.4 Hz, 1 H), 5.09 (ddt, J = 17.4, 1.8, 1.8 Hz, 1 H), 5.82 (ddt, J = 17.4, 10.2, 6.9 Hz, 1 H), 7.22−7.35 (m, 3 H), 7.44−7.52 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.98, 22.56, 26.16, 26.32, 29.03, 29.18, 29.39, 29.89, 31.79, 33.76, 35.84, 67.21, 89.51, 111.92, 116.49, 127.43, 128.77, 133.60, 135.31. Anal. Calcd for $C_{18}H_{28}OS$: C, 73.92; H, 9.65. Found: C, 73.65; H, 9.63.

1-(Allyloxy)-1-(phenylthio)decane (19) (Method B). To a suspension of NaH (60% in oil, 1.24 g, 31 mmol, washed with dry hexane three times) was added 3-buten-1-ol (2.6 mL, 30.2 mmol) slowly at 0 °C, and the mixture was stirred at this temperature for 50 min. Chloromethyl phenyl sulfide (3.8 mL, 28.0 mmol) and tetrabutylammonium iodide (0.55 g, 1.5 mmol) was added to the mixture and was stirred at room temperature for 15.5 h. Methanol (1.0 mL) was added, and the reaction mixture was partitioned between ether and saturated aqueous NH_4Cl. The organic phase was separated, washed with brine, and dried over $MgSO_4$. After removal of the solvent, the residue was purified via flash chromatography (hexane/EtOAc, 5/1) to obtain 3-butenyl phenylthiomethyl ether (**18**) (2.66 g, 49%). TLC: R_f 0.22 (hexane/benzene, 5/1). GC: R_t 7.94 min (OV-1 2% 2 m, 100−230 °C, 10 °C/min). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (tddd, J = 6.6, 6.6, 1.5, 1.5 Hz, 2 H), 3.67 (t, J = 6.6 Hz, 2 H), 5.01 (s, 2 H), 5.02−5.14 (m, 2 H), 5.75−5.88 (m, 1 H), 7.16−7.32 (m, 3 H), 7.45−7.49 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 33.63, 67.71, 76.18, 116.61, 126.72, 128.95, 130.29, 135.10, 136.22. Anal. Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26. Found: C, 68.24; H, 7.40.

To a solution of 3-butenyl phenylthiomethyl ether (**18**) (200 mg, 1.03 mmol) in THF (2.0 mL) was added butyllithium (1.59 M in hexane, 0.78 mL, 1.14 mmol) at −78 °C. The mixture was stirred at −40 °C for 1 h and cooled to −78 °C. 1-Iodoheptane (0.20 mL, 1.22 mmol) was added and the mixture was stirred at −78 °C for 3 h and at room temperature overnight. The reaction mixture was partitioned between ether and saturated aqueous NH_4Cl. The organic phase was separated and washed with saturated aqueous NH_4Cl and dried over $MgSO_4$. After removal of the solvent, the crude product was purified via flash chromatography (hexane) to obtain the title compound (154 mg, 51%).

***syn*-1-Methoxy-1-((4-methoxyphenyl)thio)-2-(allyloxy)-nonane (*syn*-20).** To a suspension of NaH (60% in oil, 140 mg, 3.5 mmol, washed with dry hexane three times) in THF (4.5 mL) was added *syn*-**3d** (685 mg, 2.2 mmol) at 0 °C. The mixture was stirred at 0 °C for 1 h and allylbromide (0.45 mL, 4.4 mmol) was added. The mixture was stirred at room temperature overnight. MeOH (1.0 mL) and saturated aqueous NH_4Cl was added, and the organic materials were extracted with ether, washed with brine, and dried over $MgSO_4$. After removal of the solvent, the residue was purified via flash chromatography to obtain the title compound (693 mg, 90%). TLC: R_f 0.32 (hexane/EtOAc, 20/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.6 Hz, 3 H), 1.27−1.35 (br, 10 H), 1.50−1.70 (m, 1 H), 1.75−1.85 (m, 1 H), 3.36−3.42 (m, 1 H), 3.48 (s, 3 H), 3.81 (s, 3 H), 3.94−4.01 (m, 1 H), 4.11−4.19 (m, 1 H), 4.50 (d, J = 6.0 Hz, 1 H), 5.10−5.26 (m, 2 H), 5.84−5.97 (m, 1 H), 6.84 (d, J = 8.7 Hz, 2 H), 7.42 (d, J = 8.7 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.97, 22.53, 25.50, 29.13, 29.51, 31.27, 31.73, 55.24, 56.88, 72.55, 81.27, 95.55, 114,46, 116.78, 124.73, 135.37, 135.83, 159.65. Anal. Calcd for $C_{20}H_{32}O_3S$: C, 68.14; H, 9.15. Found: C, 67.85; H, 9.03.

***anti*-1-Methoxy-1-((4-methoxyphenyl)thio)-2-(allyloxy)nonane (*anti*-20).** The anti isomer was also synthesized in a similar fashion (80%). TLC: R_f 0.27 (hexane/EtOAc, 20/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 7.2 Hz, 3 H), 1.27−1.35 (m, 10 H), 1.55−1.70 (m, 2 H), 3.45 (s, 3 H), 3.49−3.54 (m, 1 H), 3.80 (s, 3 H), 3.97−4.03 (m, 1 H), 4.11−4.17 (m, 1 H), 4.53 (d, J = 3.9 Hz, 1 H), 5.12−5.28 (m, 2 H), 5.86−5.99 (m, 1 H), 6.84 (d, J = 8.7 Hz, 2 H), 7.44 (d, J = 8.7 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.00, 22.56, 25.49, 29.15, 29.57, 30.53, 31.76, 55.28, 57.26, 71.64, 81.23, 96.20, 114.59, 116.99, 125.55, 135.31, 135.72, 159.64. MS (EI, *m/e* (%)): 352 (M^+, 30), 213 (100), 183 (42), 139 (65). HRMS (EI). Calcd for $C_{20}H_{32}O_3S$: 352.2072. Found: 352.2065.

Electrooxidative Intramolecular Carbon−Carbon Bond Formation. General Procedure. In an undivided cell equipped with a carbon rod anode (i.d. = 1.5 mm) and platinum plate cathode (2 × 3 cm) were placed molecular sieves 4 Å (ca. 160 mg), the substrate (0.25 mmol), Bu_4NBF_4 (0.5 mmol), and dichloromethane (2.5 mL); the mixture was stirred at room temperature for 0.5 h. The constant current electrolysis (5 mA) was carried out at room temperature. After most of the starting material was consumed (determined by TLC), the reaction mixture was transferred to a flask, and the solvent was removed. The residue was passed through a short silica gel column (ca. 5 cm, ether elution) to remove the supporting electrolyte. After removal of the solvent, the crude product was purified via flash chromatography. Sometimes the sulfur-containing byproducts contaminated the desired product. In such a case, the crude product was treated with a small amount of *m*-chloroperoxybenzoic acid at 0 °C for ca. 5 min to oxidize the sulfur-containing byproducts. The oxidized sulfur containing byproducts were easily separable by flash chromatography.

***cis*-2-Heptyl-4-fluorotetrahydropyran (*cis*-15).**[6a] TLC: R_f 0.17 (hexane/EtOAc, 50/1). GC R_t 4.82 min (OV-1 25 m capillary, 150−230 °C, 5 °C/min). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.6 Hz, 3 H), 1.2−1.8 (m, 14 H), 1.98−2.20 (m, 2 H), 3.24 (m, 1 H), 3.37 (m,1 H), 4.04 (m,1 H), 4.64 (m, 1 H).

***trans*-2-Heptyl-4-fluorotetrahydropyran (*trans*-15).**[6a] TLC: R_f 0.15 (hexane/EtOAc, 50/1). GC R_t 4.82 min (OV-1 25 m capillary, 150−230 °C, 5 °C/min). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.6 Hz, 3 H), 1.1−2.0 (m, 16 H), 3.65 (m, 1 H), 3.72−3.85 (m, 1 H), 4.98 (m, 1 H).

2-Heptyl-3-methoxy-5-fluorotetrahydropyran (21). This compound was obtained as a single diastereomer. The stereochemistry was determined by decoupling and NOE experiments. TLC: R_f 0.54 (hexane/EtOAc, 10/1). GC R_t 4.13 min (OV-1 2%, 2 m, 200−230 °C, 10 °C/min). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.6 Hz, 3 H), 1.20−1.58 (m, 13 H), 2.71 (m, 1 H), 2.96 (m, 1 H), 3.02 (m, 1 H), 3.37 (s, 3 H), 4.07 (m, 1 H), 4.54 (m, J_{H-F} = 48.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.10, 22.66, 25.52, 29.27, 29.69, 31.75 (d, J = 1.5 Hz), 31.83, 35.56 (d, J = 16.8 Hz), 56.68, 69.07 (d, J = 27.5 Hz), 77.68 (d, J = 9.9 Hz), 80.41 (d, J = 1.5 Hz), 85.42 (d, J = 177.8 Hz). MS (EI, *m*/*e* (%)): 232 (M^+, 8), 155 (8), 139 (15), 133 (12). HRMS (EI). Calcd for $C_{13}H_{25}O_2F$: 232.1838. Found: 232.1847.

Acknowledgment. We thank Prof. Junzo Nokami, Okayama University of Science, for valuable suggestions on anodic acetoxylation of sulfides and the Lewis acid-catalyzed reaction of acetoxy sulfides with alcohols. We also thank Mr. Tadao Kobatake for the measurement of mass spectra and Mr. Haruo Fujita for the NOE experiments. This work was supported by Grant-in-Aid for Scientific Research (Grant 07455360 and Priority Area No. 283, “Innovative Synthetic Reactions”) from Monbusho.

JO980601X