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Direct and indirect electrochemical generation of alkoxycarbenium ion pools from thioacetals

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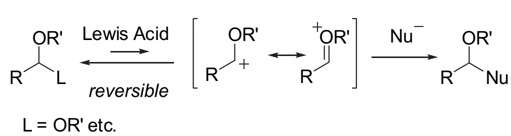
ABSTRACT

Thioacetals were found to be effective precursors to generate and accumulate alkoxycarbenium ions based on direct and indirect cation pool methods. Alkoxycarbenium ions thus generated reacted with carbon nucleophiles such as allylsilanes and enol silyl ethers to give C–C bond formation products in good yields.

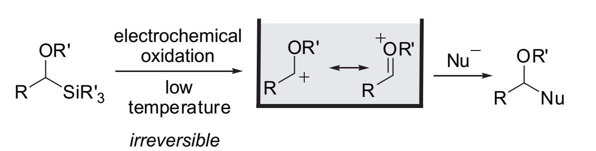
1. Introduction

Alkoxycarbenium ions, carbocations stabilized by a neighboring alkoxy group, are important intermediates in organic synthesis.[1] Usually alkoxycarbenium ions are generated from acetals using Lewis acids such as BF_3–OEt_2, $SnCl_4$, and $TiCl_4$ in the presence of a nucleophile (Scheme 1). Although benzylic alkoxycarbenium ions and di- and tri(alkoxy)carbenium ions are stable and are well characterized spectroscopically,[2] simple alkylalkoxycarbenium ions are unstable and are difficult to characterize spectroscopically. The generation processes for such unstable alkoxycarbenium ions are reversible, and their equilibrium concentrations are usually very low. In fact, extensive NMR studies on the reaction of acetals with Lewis acids revealed the presence of Lewis acid–acetal complexes, but alkoxycarbenium ions were not detected.[3]



Scheme 1.

The electrochemical method is also effective for generation of alkoxycarbenium ions.[4] Recently we have developed the 'cation pool' method, in which organic cations are generated and accumulated in the absence of nucleophiles by low-temperature electrolysis.[5] The cation pool method serves as a powerful tool not only for mechanistic studies on highly reactive organic cations but also for rapid parallel synthesis. The method has been successfully applied to alkoxycarbenium ions,[6] in addition to *N*-acyliminium ions,[7] diarylcarbenium ions,[8] organosilicon cations,[9] and iodine cations.[10] α-Silyl ethers serve as effective precursors of alkoxycarbenium ion pools (Scheme 2). Silyl groups serve as effective electroauxiliaries, which lower the oxidation potentials and control the regiochemistry by virtue of selective C–Si bond cleavage.[11] Alkylalkoxycarbenium ions thus generated are well characterized by NMR spectroscopy, which exhibits very similar spectra to those generated in super acid media.[12] In the next step, the cations react with carbon nucleophiles such as allylsilanes to give the corresponding carbon–carbon bond formation products.



Scheme 2.

We have been searching for alternative precursors of alkoxycarbenium ion pools and have been interested in thioacetals as precursors because of the following reasons: 1) An arylthio group is also an effective electroauxiliary for electrochemical oxidation.[13] 2) Thioacetals can be easily prepared. In preliminary communications,[14] we have reported generation of alkoxycarbenium ion pools from thioacetals by low-temperature electrolysis (direct cation pool method) and by the action of $ArS(ArSSAr)^+$, which is generated by low-temperature electrolysis of ArSSAr (indirect cation pool method) (Scheme 3). In this paper we report full details of these studies.

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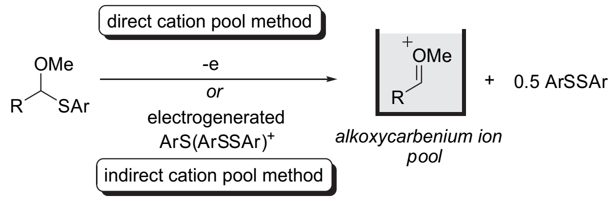
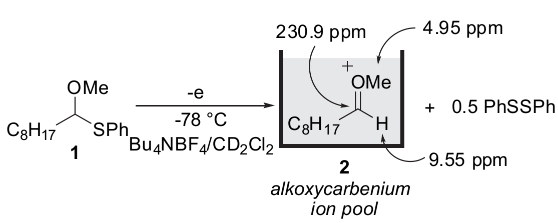


Scheme 3.

2. Result and discussion

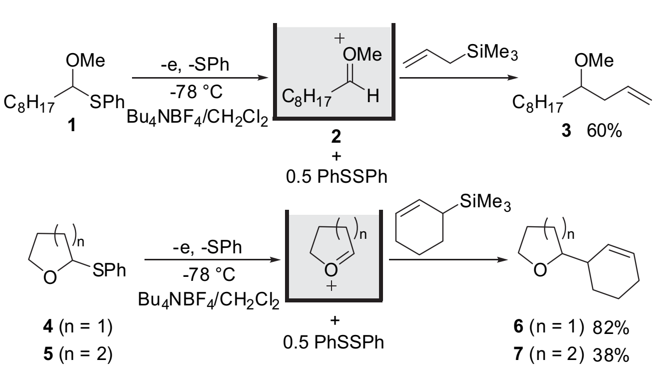
2.1. Direct cation pool method

At first, we examined the direct electrochemical method using thioacetal **1** as a precursor of an alkoxycarbenium ion. Thus, a solution of **1** was electrolyzed in Bu_4NBF_4/CD_2Cl_2 at −78 °C using an H-type divided cell (Scheme 4). After the electrolysis (1.4 F/mol), the resulting solution was analyzed by NMR spectroscopy at −80 °C. ^1H and ^{13}C NMR spectra (−80 °C) indicated the formation of alkoxycarbenium ion (**2**) by selective cleavage of the C–S bond. ^1H NMR exhibited a signal at δ 9.55 ppm due to the methine proton. ^{13}C NMR exhibited a signal at δ 230.9 ppm due to methine carbon. These chemical shifts are quite similar to those obtained by the direct electrochemical oxidation of $C_8H_{17}CH(OMe)SiMe_3$ (9.55 and 231.0 ppm),[6a] suggesting that the alkoxycarbenium ion is efficiently generated and accumulated as a single species in irreversible fashion. Though PhSSPh is generated by the oxidation of **1**, the oxidation potential of **1** (RDE decomposition potential: 1.30 V vs. SCE) is lower than that of PhSSPh (1.42 V), indicating that PhSSPh cannot be a mediator for the oxidation of **1**.



Scheme 4.

The reaction of **2** with allyltrimethylsilane gave the allylated product **3** in 60% (Scheme 5). The electrochemical method was found to be applicable to cyclic thioacetals (**4** and **5**), which were effectively oxidized under similar conditions. After the electrolysis, the resulting solutions were allowed to react with an allylsilane to give the corresponding C–C bond formation products **6** and **7** in 82% and 38% yields, respectively.



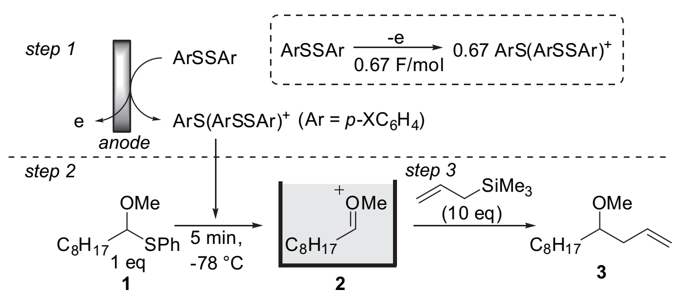
Scheme 5.

2.2. Indirect cation pool method

Because electrochemical reactions take place only on the surface of the electrode, alkoxycarbenium ions generated in an early stage of the electrolysis should stay in the solution until the electrolysis is completed. This means the application of direct cation pool method strongly depends on the stability of accumulated alkoxycarbenium ions.[15] During the accumulation, unstable alkoxycarbenium ions might decompose. To solve this problem, we examined indirect electrochemical method.[16] In the first step, an active chemical reagent is generated by the electrolysis, which is allowed to react with a precursor to generate an alkoxycarbenium ion pool in the second step. The second reaction can be faster than the electrolysis because it takes place in a homogeneous solution.

We envisaged that 'ArS^+'[17] generated by the electrochemical oxidation of ArSSAr might be suitable for the conversion of thioacetals to alkoxycarbenium ion pools. It is known in the literature that 'ArS^+'[18] or its equivalent $ArS(ArSSAr)^+$[19] serves as a powerful and highly thiophilic reagent, though the nature of the generated species has not yet been fully elucidated.[20]

Thus, the electrolysis of ArSSAr (Ar=*p*-XC_6H_4) (oxidation potential: X=F: 1.47 V, X=CH_3: 1.34 V, X=OMe: 1.47 V, X=Cl: 1.27 V, 2 equiv based on thioacetal **1**) was carried out in Bu_4NBF_4/CH_2Cl_2 at −78 °C using an H-type divided cell (Scheme 6, *step 1*). In the next step, the electrogenerated $ArS(ArSSAr)^+$ was reacted with thioacetal **1** to generate alkoxycarbenium ion **2** (*step 2*). This process requires only 5 min at −78 °C. In the third step, allyltrimethylsilane (10 equiv) was added to obtain the final product **3**.



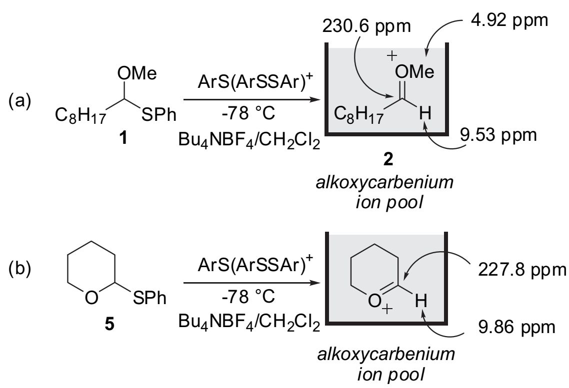
Scheme 6.

The results obtained under various conditions are summarized in Table 1. Electrolysis with 1.34 F/mol based on **1** (0.67 F/mol based on ArSSAr) gave the best yield of **3** (entry 2). 0.67 F/mol is the theoretical amount of electricity to convert ArSSAr to $ArS(ArSSAr)^+$. This means that 1.34 equiv of $ArS(ArSSAr)^+$ based on **1** was formed, because 2 equiv of ArSSAr based on **1** was used. Almost quantitative yield of **3** (98%) suggests that alkoxycarbenium ion **2** was generated almost quantitatively. High reactivity of $ArS(ArSSAr)^+$ and homogeneity of the reaction system seem to be responsible for fast and quantitative generation of **2**. Use of 1.5 equiv of ArSSAr led to a decrease in the yield of **3** (entry 5). Use of 3.0 equiv of ArSSAr also led to a decrease in the yield of **3** (entry 6). Other ArSSAr (Ar=C_6H_5, *p*-$CH_3C_6H_4$, *p*-$MeOC_6H_4$ and *p*-ClC_6H_4) were also effective, although the yield of **3** depends on the nature of the substituent on the aryl group (entries 7–10).

Table 1
Optimization of the indirect cation pool method

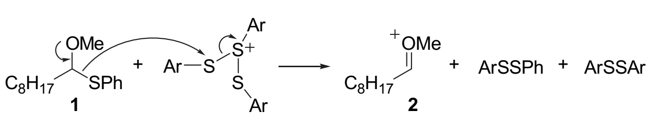
Entry	X	ArSSAr (equiv based on **1**)	Electricity (F/mol based on ArSSAr)	Yield (%) of **3**
1	F	2	0.50	69
2	F	2	0.67	98
3	F	2	0.75	91
4	F	2	1.0	87
5	F	1.5	0.67	73
6	F	3	0.67	86
7	H	2	0.67	79
8	CH_3	2	0.67	79
9	OMe	2	0.67	69
10	Cl	2	0.67	96

The formation of **2** was confirmed by NMR spectroscopy at −80 °C. A solution obtained by the reaction of **1** with the electrogenerated $ArS(ArSSAr)^+$ ($Ar{=}p\text{-}FC_6H_4$) exhibited signals at 9.53 and 4.92 ppm due to the methine proton and methyl protons, respectively (^1H NMR), and a signal at 230.6 ppm due to the methine carbon (^{13}C NMR) (Scheme 7a). These chemical shifts are quite similar to those obtained by the direct electrochemical oxidation of $C_8H_{17}CH(OMe)SiMe_3$ (9.55, 4.95, and 231.0 ppm).[6a] Such similarity in chemical shifts indicated that the sulfur-containing byproducts, such as PhSSAr and ArSSAr, which should be present in the solution, did not change the nature of alkoxycarbenium ion **2** appreciably.[21] We also generated and analyzed an alkoxycarbenium ion by the reaction of **5** with $ArS(ArSSAr)^+$ ($Ar{=}p\text{-}FC_6H_4$). The cation exhibited a signal at 9.86 ppm due to the methine proton (^1H NMR) and a signal at 227.8 ppm due to the methine carbon (^{13}C NMR) (Scheme 7b).



Scheme 7.

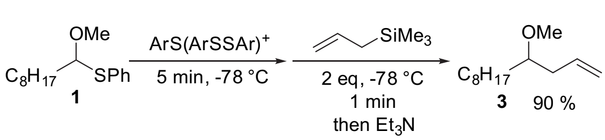
The detailed mechanism for the reaction of **1** with $ArS(ArSSAr)^+$ (*step 2*) has not been clarified as yet, but **2** seems to be generated according to Scheme 8. Though the possibility of a single electron-transfer mechanism cannot be ruled out, ionic mechanism seems to be more plausible. In the ionic mechanism $ArS(ArSSAr)^+$ acted as a thiophilic Lewis acid.



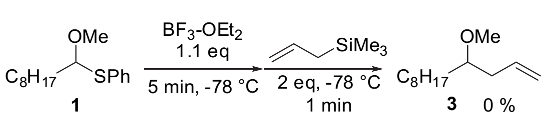
Scheme 8.

In order to get a deeper insight into the mechanism, reactions of **1** with other Lewis acids such as $BF_3\text{–}OEt_2$ and $SnCl_4$ were examined.[22] The resulting solution was analyzed by NMR spectroscopy at −80 °C, but alkoxycarbenium ion **2** was not detected at all.[3] Presumably these Lewis acids are not strong enough to generate **2** in a significant concentration. The equilibrium between **1** and **2** lies to **1**.

Much lower reactivity of $BF_3\text{–}OEt_2$ was confirmed by the following experiments. The reaction of thioacetal (**1**) with $ArS(ArSSAr)^+$ ($Ar{=}p\text{-}FC_6H_4$)in 5 min followed by treatment with allyltrimethylsilane in 1 min at −78 °C gave **3** in 90% yield Eq .(1). In contrast, the reaction using a $BF_3\text{–}OEt_2$ did not give **3** in an appreciable amount under similar conditions Eq. (2).



(1)



(2)

As described above, alkoxycarbenium ion **2** generated by the indirect method exhibited NMR spectra similar to that generated by the direct anodic oxidation of $C_8H_{17}CH(OMe)SiMe_3$.[6a] Thus, we next compared the thermal stability of **2** as follows: The cation pool generated at −78 °C was allowed to warm to a second temperature. After being kept there for 30 min, the pool was allowed to react with allyltrimethylsilane. The yield of **3** is plotted against the temperature in Figure 1. The cation pool of **2** generated by the indirect method exhibited thermal stability similar to that generated by the direct method of $C_8H_{17}CH(OMe)SiMe_3$.[6a]

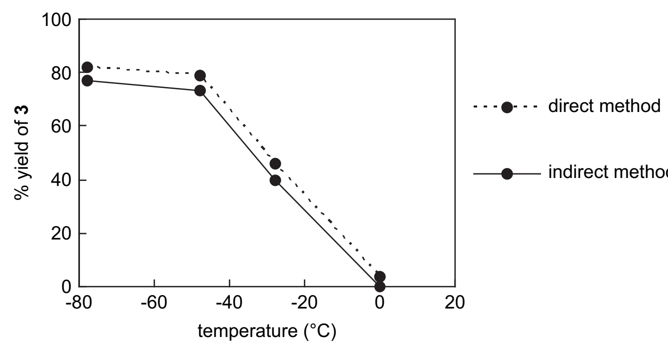
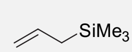
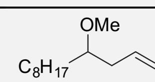
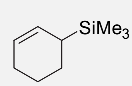
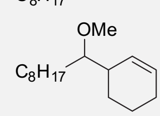
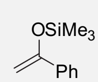
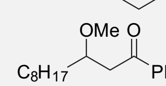
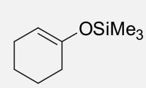
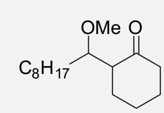
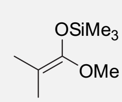
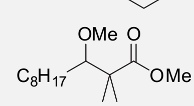
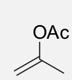
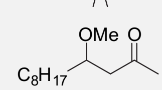
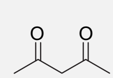
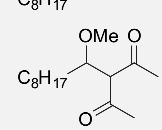


Figure 1. Thermal stability of alkoxycarbenium ion **2** generated by the direct method and the present indirect method.

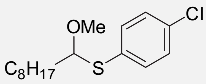
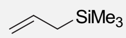
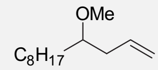
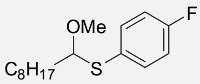
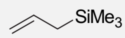
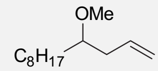
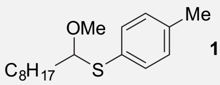
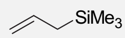
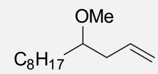
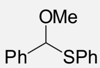
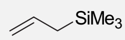
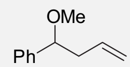
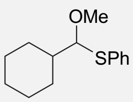
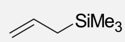
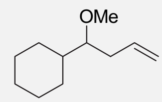
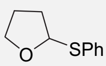
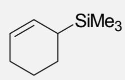
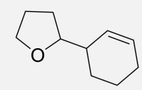
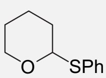
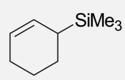
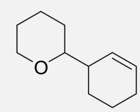
To test the applicability of the present indirect method, reactions with several carbon nucleophiles were examined (Table 2). Allylsilanes, enol silyl ethers, and ketene silyl acetals, and enol acetate were

Table 2
The reaction of alkoxycarbenium ion with various carbon nucleophiles[a]

Nu	Product		Yield (%)[b]
		**3**	89[c] (98)[c,d]
		**8**	91 (1.25:1)[e]
		**9**	79
		**10**	42 (2.45:1)[e]
		**11**	67
		**12**	63[f]
		**13**	43[d]

[a] ArSSAr ($Ar{=}p\text{-}FC_6H_4$, 0.40 mmol) was oxidized electrochemically in 0.3 M Bu_4NBF_4/CH_2Cl_2 at −78 °C using 0.67 F/mol of electricity. The solution thus obtained was allowed to react with 0.20 mmol of thioacetal at −78 °C for 5 min. Then a nucleophile (0.50 mmol, 2.5 equiv) was added, and the resulting solution was stirred at −78 °C for 15 min and the reaction was quenched with Et_3N (1 mL).
[b] Isolated yield.
[c] GC yield.
[d] 10 equiv of Nu was used.
[e] Diastereomer ratio.
[f] The reaction time with a nucleophile was 30 min.

Table 3
Indirect generation of various alkoxycarbenium ion pools followed by reactions with carbon nucleophiles

Substrate		Nu	Product		Yield[a] (%)
	**14**			**3**	82[b]
	**15**			**3**	83[b]
	**16**			**3**	72[b]
	**17**			**18**	91[c]
	**19**			**20**	68
	**4**			**6**	86 (ca. 9:1)[d]
	**5**			**7**	85 (ca. 7:1)[d]

[a] Isolated yield.
[b] GC yield.
[c] The acetal was reacted with ArS(ArSSAr)$^+$ for 10 min, and the resulting alkoxycarbenium ion was reacted with allyltrimethylsilane for 1 h.
[d] Diastereomer ratio.

effective as carbon nucleophiles, and the corresponding C–C bond formation products were obtained. 1,3-dicarbonyl compounds such as acetylacetone were also effective to form carbon–carbon bond.

Finally, we examined generation of alkoxycarbenium ion pools from several thioacetals. The p-ClC_6H_4S, p-FC_6H_4S, and p-MeC_6H_4S groups were also effective as electroauxiliaries. Aryl and alkyl substituted thioacetals, including cyclic substrates, were effective for generation of alkoxycarbenium ion pools. The resulting alkoxycarbenium ion pools reacted with carbon nucleophiles such as allylsilanes to give the corresponding C–C bond formation products in good yields as shown in Table 3.

3. Conclusions

In conclusion, we have developed a method for generation and accumulation of alkoxycarbenium ions from thioacetals by direct low-temperature electrolysis. We have also developed a sequential one-pot indirect method for generation and accumulation of alkoxycarbenium ions. In the first step, ArSSAr is oxidized by low-temperature electrolysis to generate and accumulate ArS(ArSSAr)$^+$, which is allowed to react with a thioacetal to generate and accumulate an alkoxycarbenium ion. The cation pool thus generated reacts with various carbon nucleophiles such as allylsilanes and silyl enol ethers. The direct and indirect methods for generation of alkoxycarbenium ion pools from thioacetals add a new dimension to organic cation chemistry and organic electrochemistry.

4. Experimental section

4.1. General remarks

GC analysis was performed on a gas chromatograph (SHIMADZU GC-14B) equipped with a flame ionization detector using a fused silica capillary. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Gemini 2000 (^{1}H 300 MHz, ^{13}C 75 MHz), Varian MERCURY plus-400 (^{1}H 400 MHz, ^{13}C 100 MHz), JEOL A-500 (^{1}H 500 MHz, ^{13}C 125 MHz), or JEOL ECA-600P (^{1}H 600 MHz, ^{13}C 150 MHz) spectrometer with Me_4Si as an internal standard unless otherwise noted. Mass spectra were obtained on JEOL JMS SX-102A mass spectrometer. IR spectra were measured with a SHIMADZU FTIR 1600 spectrometer. Thin layer chromatography (TLC) was carried out by using Merck precoated silica gel F254 plates (thickness 0.25 mm). Flash chromatography was carried out on a column of silica gel (Kanto Chem. Co., Silica Gel N, spherical, neutral, 40–100 mm). Gel permeation chromatography (GPC) was carried out on Japan Analytical Industry LC-908 equipped with JAIGEL-1H and 2H using $CHCl_3$ as eluent. All reactions were carried out under Ar atmosphere unless otherwise noted.

4.2. Materials

Dichloromethane was washed with water, distilled from P_2O_5, redistilled from dried K_2CO_3 to remove a trace amount of acid, and stored over molecular sieves 4A. Dry THF was used as obtained (Kanto Chemical Co., Inc.). ArSSAr (Ar=p-FC_6H_4) was prepared according to the procedures in the literatures,[23] and identified by the comparison of its spectral data with that of authentic sample.[24]

4.3. Thioacetals

1-Methoxy-1-phenylthiononane (**1**),[13c] 2-phenylthiotetrahydrofuran (**4**)[25] and 2-phenylthiotetrahydropyran (**5**)[25] were prepared according to the literature procedures.

*4.3.1. 1-Methoxy-1-(4-chlorophenylthio)nonane (**14**).* To a solution of 4-chlorobenzenethiol (5.19 g, 36.0 mmol) in tetrahydrofuran

(THF) (64 mL), was added triethylamine (7.2 mL, 52 mmol) and chloromethyl methyl ether (3.3 mL, 43 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 separated, washed with saturated aqueous $NaHCO_3$, and was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by distillation (130 °C, 14 mm Hg), to obtain (4-chlorophenylthio)methyl methyl ether (5.76 g, 30.5 mmol).

To a solution of (4-chlorophenylthio)methyl methyl ether (1.51 g, 8.0 mmol) in THF (20 mL), was added butyllithium (1.54 M in hexane, 6.4 mL, 10 mmol) at −78 °C. The mixture was stirred at −45 °C for 3 h and was cooled to −78 °C. 1-Iodooctane (2.62 g, 10.9 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 extracts were washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified by flash chromatography (hexane) to obtain the title compound (1.60 g, 5.3 mmol, 66%): TLC R_f 0.73 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J=6.8 Hz, 3H), 1.21–1.28 (m, 10H), 1.40–1.43 (m, 2H), 1.36–1.44 (m, 2H), 1.62–1.78 (m, 2H), 3.46 (s, 3H), 4.57 (t, J=6.8 Hz, 1H), 7.23–7.26 (m, 2H), 7.36–7.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 26.3, 29.2, 29.3, 29.5, 31.9, 35.6, 55.4, 90.9, 128.7, 131.6, 133.5, 134.6; IR (neat) 2953, 1476, 1130, 1092, 623 cm^{-1}; LRMS (EI) m/z 300 (M^+), 269 (M^+-OCH_3), 187 (M^+-C_8H_{17}), 157 (M^+-SC_6H_4 p-Cl); HRMS (EI) calcd for $C_{16}H_{25}OClS$: 300.1315, found: 300.1313.

*4.3.2. 1-Methoxy-1-(4-fluorophenylthio)nonane (**15**).* To a solution of pelargonaldehyde dimethyl acetal (4.03 g, 21.4 mmol) and p-fluorothiophenol (2.30 mL, 21.5 mmol) in toluene (180 mL), was added BF_3–OEt_2 (2.7 mL, 21.5 mmol) at −78 °C. The solution was stirred for 2 h. Saturated aqueous $NaHCO_3$ was added. The reaction mixture was partitioned between Et_2O and saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by flash chromatography (hexane/EtOAc 30:1) to give the title compound (**15**) (4.23 g, 14.9 mmol, 70%): TLC R_f 0.28 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J=6.8 Hz, 3H), 1.18–1.32 (m, 10H), 1.34–1.46 (m, 2H), 1.58–1.74 (m, 2H), 3.47 (s, 3H), 4.51 (t, J=6.4 Hz, 1H), 6.94–7.02 (m, 2H), 7.39–7.45 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.6, 26.2, 29.1, 29.2, 29.4, 31.8, 35.5, 55.5, 91.0, 115.8 (d, J=21.7 Hz), 127.9 (d, J=3.4 Hz), 136.1 (d, J=8.0 Hz), 162.7 (d, J=246.0 Hz); IR (neat) 2926, 1590, 1491, 830 cm^{-1}; LRMS (EI) m/z 284 (M^+), 157 (M^+-SC_6H_4p-F); HRMS (EI) calcd for $C_{16}H_{25}FOS$ (M^+) 284.1610, found 284.1605.

*4.3.3. 1-Methoxy-1-(4-methylphenylthio)nonane (**16**).* To a solution of 4-methylbenzenethiol (6.13 g, 49.4 mmol) in THF (100 mL), was added triethylamine (10 mL, 73 mmol) and chloromethyl methyl ether (4.69 g, 58.3 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 separated, washed with saturated aqueous $NaHCO_3$, and was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by distillation to obtain (4-methylphenylthio)-methyl methyl ether (6.71 g, 39.9 mmol).

To a solution of (4-methylphenylthio)methyl methyl ether (3.21 g, 19.1 mmol) in THF (45 mL), was added butyllithium (1.54 M in hexane, 15 mL, 23.1 mmol) at −78 °C. The mixture was stirred at −45 °C for 3 h and cooled to −78 °C. 1-Iodooctane (5.90 g, 24.6 mmol) was added, and the mixture was stirred at −78 °C for 30 min. Saturated aqueous NH_4Cl was added. The organic materials were extracted with ether, and the organic extracts were washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified by flash chromatography (hexane/EtOAc 50:1) to obtain the title compound (4.43 g, 15.8 mmol, 83%): TLC R_f 0.42 (hexane/EtOAc 20:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, J=6.6 Hz, 3H), 1.22–1.34 (m, 10H), 1.36–1.52 (m, 2H), 1.64–1.80 (m, 2H), 2.32 (s, 3H), 3.46 (s, 3H), 4.54 (t, J=6.6 Hz, 1H), 7.09 (m, 2H), 7.35 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 21.1, 22.6, 26.2, 29.1, 29.2, 29.4, 31.8, 35.6, 55.4, 91.1, 129.4, 129.4, 134.0, 137.5; IR (neat) 2924, 1466, 1088, 644 cm^{-1}; LRMS (EI) m/z 280 (M^+), 157 (M^+-SC_6H_4p-CH_3); HRMS (EI) calcd for $C_{17}H_{28}OS$: 280.1861, found: 280.1859.

*4.3.4. (Methoxy(phenylthio))methylbenzene (**17**).* To a toluene solution of benzaldehyde dimethyl acetal (786.8 mg, 5.17 mmol) and thiophenol (612.0 mg, 5.55 mmol), was added BF_3–OEt_2 (736.0 mg, 5.19 mmol) at −78 °C. The solution was stirred for 2 h. Dry pyridine (2.4 mL) was added. The mixture was diluted with ether and was washed with 1 M NaOH solution and water. After drying over Na_2SO_4 and removal of solvent, colorless oil thus obtained was purified by flash chromatography (hexane/EtOAc 50:1–10:1) to obtain the title compound (757.8 mg, 3.29 mmol, 64%).[26]

*4.3.5. (Methoxy(phenylthio)methyl)cyclohexane (**19**).* To a toluene solution of cyclohexanecarbaldehyde dimethyl acetal (774.0 mg, 4.89 mmol) and thiophenol (600 mg, 5.45 mmol) was added BF_3–OEt_2 (901.3 mg, 6.35 mmol) at −78 °C. The solution was stirred for 2 h, and dry pyridine (0.5 mL) was added. The mixture was diluted with ether and was washed with 1 M NaOH solution and water. After drying by Na_2SO_4 and removal of solvent, colorless oil thus obtained was purified by flash chromatography (hexane/EtOAc 50:1–10:1) and GPC to give the title compound (918.6 mg, 3.89 mmol, 79%).[26]

4.4. Generation of alkoxycarbenium ions (direct cation pool method)

4.4.1. Typical procedure. The anodic oxidation was carried out in an H-type divided cell (4 G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca. 320 mg, dried at 250 °C/1 mm Hg for 1 h before use) and a platinum plate cathode (40 mm×20 mm). In the anodic chamber was placed a solution of 1-methoxy-1-phenylthiononane (**1**) (94.9 mg, 0.356 mmol) in 0.3 M Bu_4NBF_4/CH_2Cl_2 (8.0 mL). In the cathodic chamber were placed 0.3 M Bu_4NBF_4/CH_2Cl_2 (8.0 mL) and trifluoromethanesulfonic acid (150.7 mg, 1.00 mmol). The constant current electrolysis (8 mA) was carried out at −78 °C with magnetic stirring until 2.5 F/mol of electricity was consumed.

4.5. NMR analysis of alkoxycarbenium ion (2) based on direct cation pool method

^{1}H and ^{13}C NMR spectra were recorded in CD_2Cl_2 on a JEOL A-500 spectrometer. Chemical shifts are reported using methylene signals of CH_2Cl_2 at δ 5.32 (^{1}H NMR) and δ 53.80 (^{13}C NMR) as standards. The anodic oxidation was carried out in a divided cell equipped with a carbon felt anode and a platinum plate cathode. In the anodic chamber were placed a solution of 1-methoxy-1-phenylthiononane (**1**) (49.9 mg, 0.187 mmol) in 3.7 mL of 0.3 M Bu_4NBF_4/CD_2Cl_2. In the cathodic chamber were placed trifluoromethanesulfonic acid (71.1 mg, 0.474 mmol) and 0.3 M Bu_4NBF_4/CD_2Cl_2 (3.7 mL). The constant current electrolysis (3.7 mA) was carried out at −78 °C with magnetic stirring. After 1.4 F/mol of electricity was consumed, the reaction mixture of the anodic chamber was transferred to a 5 mm φ NMR tube with a septum cap under Ar atmosphere at −78 °C. The NMR measurement was carried out at −80 °C: ^{1}H NMR (500 MHz, CD_2Cl_2, selected) δ 4.95 (s, 3H), 9.55 (s, 1H); ^{13}C NMR (125 MHz, CD_2Cl_2, selected) δ 40.7 ($CH_3OCH\underline{C}H_2$), 76.1 ($\underline{C}H_3OCH$), 230.9 ($CH_3O\underline{C}H$). In the NMR spectra the other signals could not be assigned because of overlap of the signals of Bu_4NBF_4 used as electrolyte. The signals due to the thiophenyl group leaving from **1** were also observed: ^{1}H NMR δ 7.2–8.0 (m); ^{13}C NMR δ 116.5, 119.0, 124.1, 130.3.

4.6. Reaction of alkoxycarbenium ion and carbon nucleophiles

*4.6.1. 4-Methoxy-dodec-1-ene (**3**) (a typical procedure of direct cation pool method).* The electrolysis of **1** (94.9 mg, 0.356 mmol) was carried out as described above. To the 'cation pool' thus generated in the anodic chamber, was added allyltrimethylsilane (99.7 mg, 0.873 mmol) at −78 °C and the reaction mixture was stirred for 15 min. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (2×3 cm) of silica gel to remove Bu_4NBF_4. The silica gel was washed with ether (150 mL). The GC analysis of the combined filtrate indicated that **3** was formed in 60% yield (GC ^tR 6.3 min, column, OV-1; 0.25 mm×25 m; initial oven temperature, 100 °C; rate of temperature increase, 10 °C/min). The isolated product was identified by the comparison of its spectral data with those of an authentic sample.[6a]

4.7. Generation of alkoxycarbenium ions (indirect cation pool method)

4.7.1. Typical procedure. The anodic oxidation was carried out in an H-type divided cell (4 G glass filter) equipped with a carbon felt anode and a platinum plate cathode (40 mm×20 mm). In the anodic chamber was placed a solution of ArSSAr (Ar=*p*-FC_6H_4) (101.9 mg, 0.401 mmol) in 0.3 M Bu_4NBF_4/CH_2Cl_2 (8.0 mL). In the cathodic chamber were placed 0.3 M Bu_4NBF_4/CH_2Cl_2 (8.0 mL) and trifluoromethanesulfonic acid (41.0 mg, 0.273 mmol). The constant current electrolysis (8 mA) was carried out at −78 °C with magnetic stirring until 0.67 F/mol of electricity was consumed. To the anodic chamber containing electrogenerated $ArS(ArSSAr)^+$, was added 1-methoxy-1-phenylthiononane (**1**) (53.3 mg, 0.200 mmol) and the mixture was stirred for 5 min at −78 °C. The solution thus obtained was used for the subsequent reaction.

4.8. NMR analysis of alkoxycarbenium ion based on indirect cation pool method

*4.8.1. Alkoxycarbenium ion (**2**) derived from **1**.* ^{1}H and ^{13}C NMR spectra were recorded in CH_2Cl_2/CD_2Cl_2 (10:1) on a JEOL ECA600P (^{1}H 600 MHz, ^{13}C 150 MHz) spectrometer. The anodic oxidation was carried out in a divided cell equipped with a carbon felt anode and a platinum plate cathode. In the anodic chamber were placed a solution of ArSSAr (Ar=*p*-FC_6H_4) (81.9 mg, 0.322 mmol) in 4.0 mL of 0.3 M $Bu_4NBF_4/CH_2Cl_2/CD_2Cl_2$ (10:1). In the cathodic chamber were placed trifluoromethanesulfonic acid (32.4 mg, 0.216 mmol) and 0.3 M $Bu_4NBF_4/CH_2Cl_2/CD_2Cl_2$ (10:1) (4.0 mL). The constant current electrolysis (4.0 mA) was carried out at −78 °C with magnetic stirring. After 0.67 F/mol of electricity was consumed, the reaction mixture of the anodic chamber (0.8 mL) was transferred to a 5 mm φ NMR tube with a septum cap under Ar atmosphere at −78 °C. 1-Methoxy-1-phenylthiononane (**1**) (10.2 mg, 0.0383 mmol) was added and the tube was shaken at the same temperature. The NMR measurement was carried out at −80 °C. Chemical shifts are reported using methylene signals of CH_2Cl_2 at δ 5.32 (^{1}H NMR) and δ 53.80 (^{13}C NMR) as standards. The huge signal coming from CH_2Cl_2 is reduced by usual pulse techniques[27]: ^{1}H NMR (600 MHz, CH_2Cl_2/CD_2Cl_2 (10:1), selected) δ 3.26 (t, *J*=6.3 Hz, 2H), 4.92 (s, 3H), 9.53 (s, 1H); ^{13}C NMR (150 MHz, CH_2Cl_2/CD_2Cl_2 (10:1), selected) δ 40.3 ($CH_3OCH\underline{C}H_2$), 75.6 ($\underline{C}H_3OCH$), 230.6 ($CH_3O\underline{C}H$). Other signals could not be assigned because of overlap with the signals of Bu_4NBF_4 used as the electrolyte.

*4.8.2. Alkoxycarbenium ion derived from **5**.* The anodic oxidation was carried out in a divided cell equipped with a carbon felt anode and a platinum plate cathode. In the anodic chamber was placed a solution of ArSSAr (Ar=*p*-FC_6H_4) (153.0 mg, 0.602 mmol) in 4.0 mL of 0.3 M $Bu_4NBF_4/CH_2Cl_2/CD_2Cl_2$ (10:1). In the cathodic chamber were placed trifluoromethanesulfonic acid (80.2 mg, 0.534 mmol) and 0.3 M $Bu_4NBF_4/CH_2Cl_2/CD_2Cl_2$ (10:1) (4.0 mL). The constant current electrolysis (4.0 mA) was carried out at −78 °C with magnetic stirring. After 0.67 F/mol of electricity was consumed, the reaction mixture of the anodic chamber (0.8 mL) was transferred to a 5 mm φ NMR tube equipped with a septum cap under Ar atmosphere at −78 °C. 2-(Phenylthio)tetrahydropyran (**5**) (16.4 mg, 0.084 mmol) was added and the tube was shaken at the same temperature. The NMR measurement was carried out at −80 °C. Chemical shifts are reported using methylene signals of CH_2Cl_2 at δ 5.32 (^{1}H NMR) and δ 53.80 (^{13}C NMR) as standards. The huge signal coming from CH_2Cl_2 is reduced by usual pulse techniques[27]: ^{1}H NMR (600 MHz, CH_2Cl_2/CD_2Cl_2 (10:1), selected) δ 1.88 (br t, *J*=5.8 Hz, 2H), 2.14 (br s, 2H), 3.49 (br t, *J*=5.2 Hz, 2H), 5.24 (br s, 2H), 9.86 (s, 1H); ^{13}C NMR (150 MHz, CH_2Cl_2/CD_2Cl_2 (10:1), selected) δ 12.1, 19.5, 35.4, 82.5, 227.8. Other signal could not be assigned because of overlap with the signals of Bu_4NBF_4 used as the electrolyte or CH_2Cl_2, which was used as the solvent.

4.9. Reaction of alkoxycarbenium ion and carbon nucleophiles

*4.9.1. 4-Methoxy-dodec-1-ene (**3**) (a typical procedure of indirect cation pool method).* The electrolysis of ArSSAr (Ar=*p*-FC_6H_4) (102 mg, 0.401 mmol) was carried out as described above. To the $ArS(ArSSAr)^+$ thus generated in the anodic chamber, was added 1-methoxy-1-phenylthiononane (**1**) (52.7 mg, 0.198 mmol) at −78 °C and the reaction mixture was stirred for 5 min. Then allyltrimethylsilane (56.6 mg, 0.495 mmol) was added and the resulting solution was stirred at −78 °C for 15 min. The reaction was quenched with Et_3N. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (2×3 cm) of silica gel to remove Bu_4NBF_4. The silica gel was washed with ether (150 mL). The GC analysis of the combined filtrate indicated that the title compound was formed in 89% yield (GC ^tR 7.1 min, column, CBP1; 0.22 mm φ×0.25 mm×25 m; initial oven temperature, 100 °C; rate of temperature increase, 10 °C/min). The isolated product was identified by the comparison of its spectral data with those of an authentic sample.[6a]

The other products, **6**,[6a] **7**,[6a] **8**,[6a] **9**,[6a] **10**,[6a] **11**,[6a] **12**,[6a] **13**,[6a] **18**[6c] and **20**[6a] were identified by the comparison of their spectral data with those of authentic samples.

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