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Generation and reactions of thiirenium ions by the Cation Pool method

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Dedicated to Professor Kenneth Laali on the occasion of his 65th anniversary

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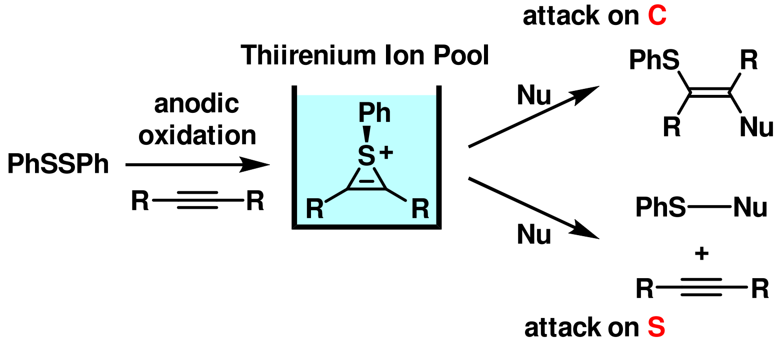
Abstract

Thiirenium ions generated and accumulated by low-temperature electrochemical oxidation of disulfides in the presence of alkynes were successfully observed by low-temperature NMR, Raman, and mass spectroscopies and were found to be stable at temperatures below −40 °C. The thiirenium ions showed ambident reactivity toward subsequently added nucleophiles to give either disubstituted alkenes or alkynes depending on the nature of the nucleophiles.



Keywords: Electrosynthesis, cations, thiirenium ions, reactive intermediates, ambident reactivity

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Introduction

Thiirenium ions[1] are important reactive intermediates in difunctionalization of alkynes. Because of their instability, thiirenium ions are conventionally generated by the reaction of alkynes with RS^+ equivalents in special solvents such as liquid SO_2.[2-5] Some thiirenium ions having bulky substituent groups can be isolated and characterized by X-ray crystal structural analysis.[6] Recently, Poleschner *et al*. reported the synthesis of thiirenium ions in CH_2Cl_2 by the reaction of disulfides with alkynes having bulky substituent groups using XeF_2 as an one-electron oxidant and silylcarborate salt Me_3Si^+ $CHB_{11}Cl_{11}^-$ as a F^- acceptor.[7] However, generation and accumulation of the thiirenium ions which do not have bulky substituent groups in normal organic solvents are still challenging[8] because nucleophiles derived from the RS^+ equivalents such as Cl^- and MeSSMe reacts with thiirenium ions even at low temperatures and even in highly acidic media.[2-5] Also, their generation in the presence of strong nucleophiles prevents studies on their reactivity towards various nucleophiles. Therefore, there is still room for a method for generating and accumulating thiirenium ions in normal organic solvents in the absence of strong nucleophiles.

Electrochemical oxidation[9-15] serves as a powerful method for generating and accumulating highly reactive cationic species. (For recent papers on organic electrosynthesis, see for example, refs 16-18) Electrochemical oxidation in solvents normally used in organic syntheses can be carried out by the cation pool method.[19-21] We have reported that the electrochemical oxidation of diaryl disulfides (ArSSAr) leads to the formation of $ArS(ArSSAr)^+$, which can be accumulated in solution at low temperatures (Figure 1).[22-26] This reaction presumably proceeds by generation of "ArS^+" followed by its reaction with ArSSAr. Therefore, we envisaged that the anodic oxidation of ArSSAr in the presence of alkynes leads to the formation of thiirenium ions (Figure 1). The method would enable not only characterization of thiirenium ions but also a study of their reactivity towards various nucleophiles which can be added after their generation. Herein, we report the generation of thiirenium ions having no bulky substituent groups by the "cation pool" method, their spectroscopic characterization, and their reactions with subsequently added nucleophiles.

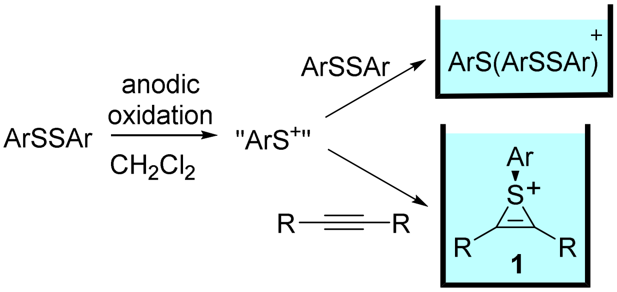


Figure 1. Generation and accumulation of $ArS(ArSSAr)^+$ and thiirenium ions.

Results and Discussion

To generate and accumulate thionium ion **1a** (Ar = Ph, R = Pr), electrochemical oxidation of PhSSPh (**2**) in the presence of 4-octyne was carried out under constant current conditions at −78 °C in an H-type divided cell equipped with an anode consisting of fine carbon fibers and a platinum plate cathode in 0.3 M Bu_4PBF_4/CD_2Cl_2 (Figure S1).[27] After 2.1 *F* of electricity was applied, the resulting anodic solution was analyzed by ^1H and ^{13}C NMR spectroscopies at −78 °C (Figure 2). In the ^1H and ^{13}C NMR spectra no signal of the disulfide **2** was observed. Only signals which can be attributed to **1a** were observed. All signals were assigned as shown in

Figure 2 by using HMQC and HMBC measurements (Figures S2 and S3). Correlation between $H_{a,a'}$ and $H_{o,m}$ in NOE spectrum (Figure S4) indicates the generation and accumulation of thiirenium ion **1a** in the solution. The chemical shift of the alkenyl carbons (106.8 ppm) is consistent with those of a thiirenium ion having *tert*-butyl groups reported in the literature (114.52[6] and 113.17[7]). Notably, two signals assigned to H_a and $H_{a'}$ and two signals assigned to H_b and $H_{b'}$ were observed at around 3.0 and 1.7 ppm, respectively (Figure 2a, inset), indicating that **1a** has a pyramidal sulfur atom whose inversion is prohibited or slow compared to the NMR time scale. The pyramidal structure of **1a** is consistent with the reported X-ray structure of the thiirenium ions bearing bulky *tert*-butyl groups.[6,7]

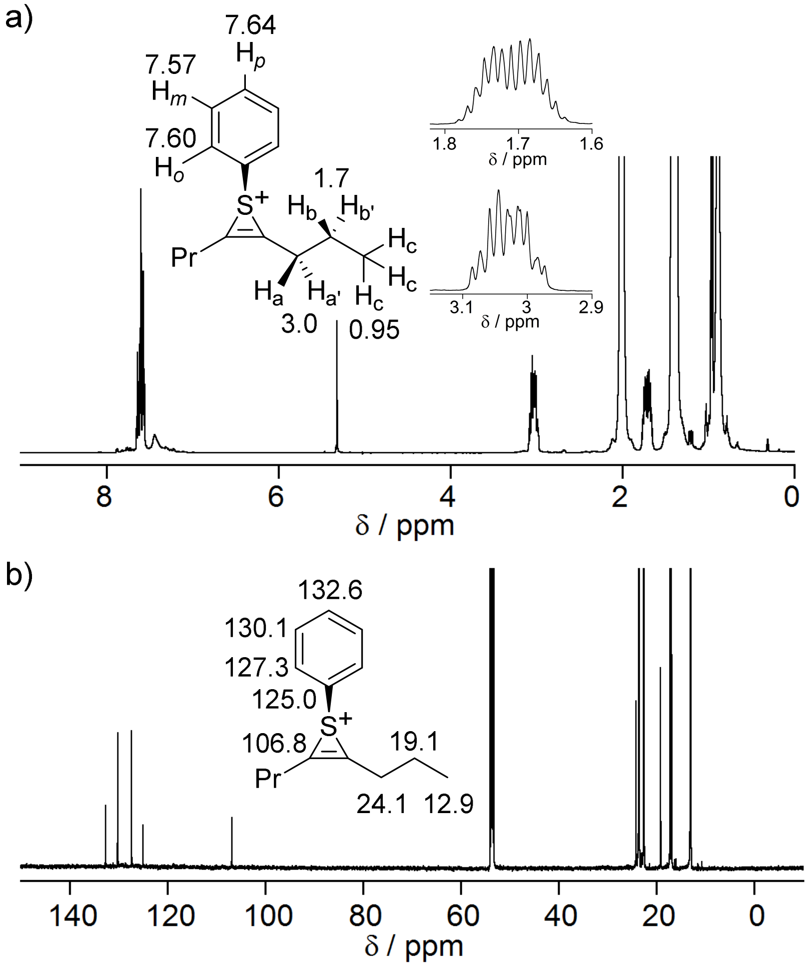


Figure 2. a) ^{1}H NMR and b) ^{13}C NMR spectra of **1a** at −78 °C in Bu_4PBF_4/CD_2Cl_2.

Thiirenium ion **1a** generated in $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ instead of Bu_4PBF_4/CD_2Cl_2 was analyzed by cold-spray-ionization mass spectroscopy (CSI-MS)[28] at 0 °C.[29] The signal assigned to **1a** was successfully observed (Figure S5).

Raman spectra were measured during the electrochemical oxidation at −78 °C (Figure 3a).[30,31] The solution of ArSSAr (Ar = 4-FC_6H_4) and 4-octyne in Bu_4NBF_4/CH_2Cl_2 was electrochemically oxidized to give **1b** (Ar = 4-FC_6H_4, R = Pr).[32] Increase of the electricity applied strengthened the signal at 1874 cm^{-1}, which is assigned to the stretching of the C−C double bond of **1b** by DFT calculations (1862 cm^{-1}, scaling factor: 0.9614[33]). The vibration frequencies of the C−C triple bond of 4-octyne, the C-C double bond of **1b,** and the C-C double bond of *cis*-4-octene show linear correlation with the C−C bond lengths obtained by DFT calculations (Figure 3b), which is similar to the tendency of seleniranium ions reported in the literature.[34] The higher frequency and the shorter bond length of **1b** than those of *cis*-4-octene is not because of the bond order of the C–C double bond of **1b** (1.91) and *cis*-4-octene (1.93) but because of the higher s-character of the carbon atoms of **1b** (41.1%, $sp^{1.43}$) than that of *cis*-4-octene (39.5%, $sp^{1.53}$).

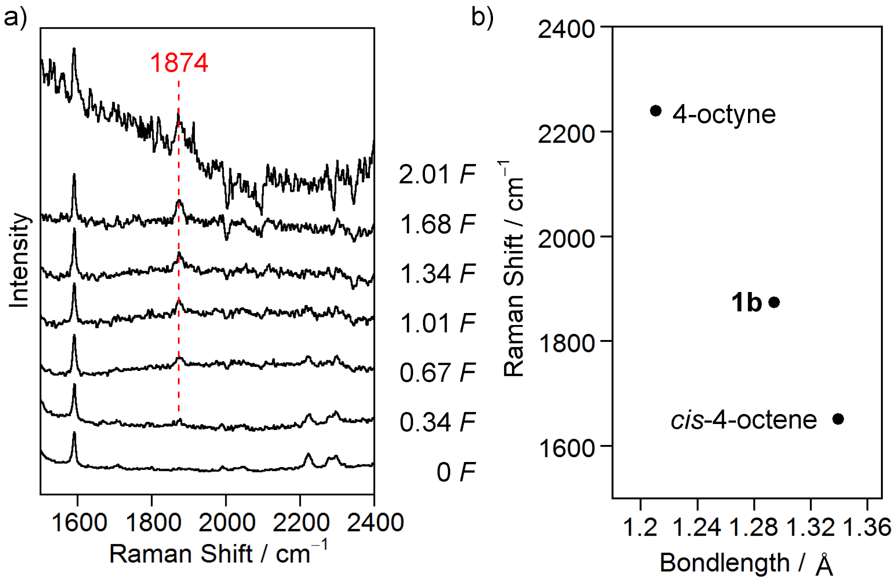


Figure 3. (a) Raman spectra of the reaction mixture during anodic oxidation at −78 °C in Bu_4NBF_4/CH_2Cl_2. (b) Relation between the observed C–C vibrations and C–C bond lengths obtained by DFT calculations of 4-octyne, **1b**, and *cis*-4-octene.

The thermal stability of thiirenium ion **1a** was investigated.[35] After a solution of **1a** was kept at the second temperature for 30 min, the resulting solution was recooled to −78 °C. Then, Bu_4NCl (10 equiv) was added and the mixture was stirred at −78 °C for 30 min. After work-up the yields of products, chloro-substituted alkene **2a** and fluoro-substituted alkene **2b** were determined by gas chromatography. Plots of the yield of **2a** against the temperature (Figure 4) indicates that **1a** is stable at temperatures lower than −40 °C. At the temperatures higher than –20 °C, the yield of **2a** decreased and the yield of **2b** increased with an increase in the temperature. Presumably, alkene **2b** was produced by the reaction of **1a** with the supporting electrolyte BF_4^- (*vide infra*).

Reactions of thiirenium ion **1a** with various nucleophiles were investigated (Table 1). After electrochemical generation and accumulation of the thiirenium ion, a nucleophile was added to the solution. The resulting solution was stirred at –78 °C for 30 min and then at 20 °C for 30 min. Cl^- reacted with **1a** to give **2a** in a good yield. When a nucleophile was not added intentionally, **2b** was obtained in a good yield (entry 2). Presumably F^- derived BF_4^- reacted with **1a**. Br^-, I^-, ArO^- (Ar = $4\text{-}O_2N\text{-}C_6H_4$), AcO^-, TfO^-, and SCN^-, reacted with **1a** to give the corresponding substituted alkenes **2c**-**2h** (entries 3-8). Stereochemistry of the alkenes was determined to be *E* by the NOE measurements. MeOH reacted with **1a** to give ketone **4**, which was probably formed via methoxy alkene (entry 9). Lithium acetylide gave a mixture of **2i** and **3a** (entry 10). Enyne **2i** was formed by the nucleophilic attack of the acetylide on C, whereas phenylthio-substituted alkyne **3a** was formed by the attack of the acetylide on S. Dimethylketene methyl trimethylsilyl acetal and Et_2NH attacked the sulfur atom of **1a** to give compounds **3b** and **3c**, respectively (entries 11 and 12). Recovery of the alkyne was confirmed by the reaction using 8-hexadecyne and Et_2NH (entry 13). These results indicate that **1a** acts as an ambident electrophile.[36]

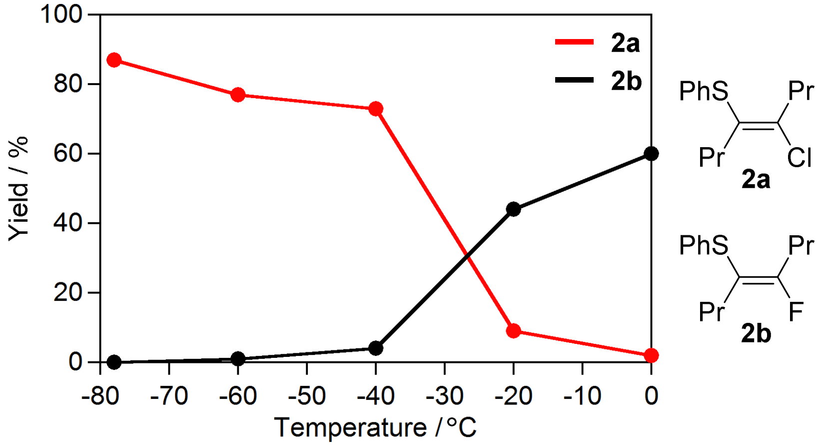
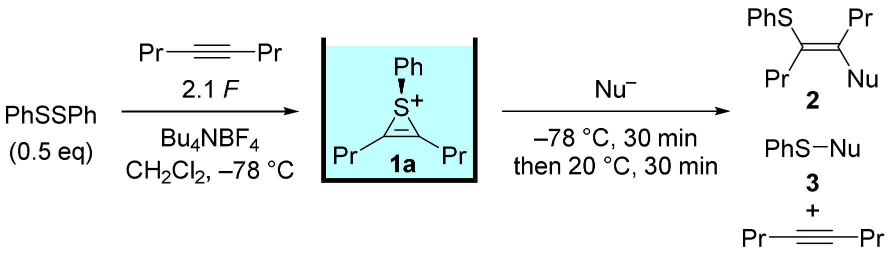


Figure 4. Thermal stability of the thiirenium ion **1a** in Bu_4NBF_4/CH_2Cl_2. Yields of **2a** (red line) and **2b** (black line).

Table 1. Reactions of thiirenium ion **1a** with nucleophiles[a]



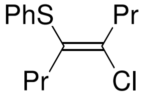
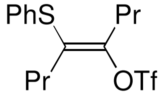
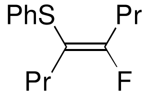
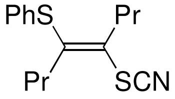
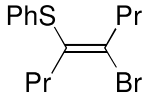
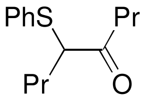
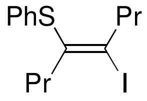
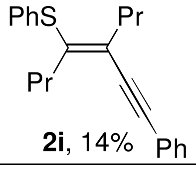
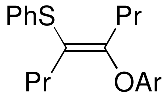
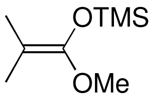
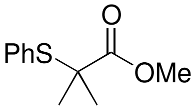
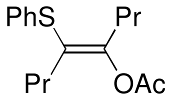
Entry	Nu^-	product **2**	Entry	Nu^-	product **2**	product **3**
1	Bu_4NCl	 **2a**, 87%[b]	7	Bu_4NOTf	 **2g**, 45%	
2	Bu_4NBF_4	 **2b**, 92%	8	Bu_4NSCN	 **2h**, 67%	
3	Bu_4NBr	 **2c**, 82%	9	MeOH	 **4**, 66%	
4	Bu_4NI	 **2d**, 69%	10	Li—≡—Ph	 **2i**, 14%	PhS—≡—Ph **3a**, 60%

Table 1. Continue

Entry	Nu⁻	product 2	Entry	Nu⁻	product **2**	product **3**
5	Bu_4NOAr^c Ar = $C_6H_4NO_2$-4	 **2e**, 40%	11			 **3b**, 50%
6	Bu_4NOAc	 **2f**, 61%	12	Et_2NH		PhS−NEt_2 **3c**, 58%
			13[d]	Et_2NH		PhS−NEt_2 **3c**, 82%

[a] PhSSPh (0.125 mmol) was electrochemically oxidized (2.1 *F*) in the presence of 4-octyne (0.25 mmol) in a 0.3 M solution of Bu_4NBF_4 in CH_2Cl_2 at –78 °C. 10 equiv of nucleophile was added. Isolated yields are shown unless otherwise stated. [b] The yields were determined by GC using an internal standard. [c] 7.1 eq of Bu_4NOAr was added. [d] 8-Hexadecyne was used instead of 4-octyne. 94% of 8-hexadecyne was recovered.

To obtain a deeper insight into the reactivity of the thiirenium ion we carried out DFT calculations. These calculations show that the LUMO of **1a** has large coefficients on the sulfur and the two carbon atoms of the three-membered ring (Figure 5a), indicating that nucleophiles can attack both sulfur and carbon atoms. The DFT calculation also shows that the carbon atom has higher positive potential than the sulfur atom although the thiirenium ion formally has a positive charge on the sulfur atom (Figure 5b).

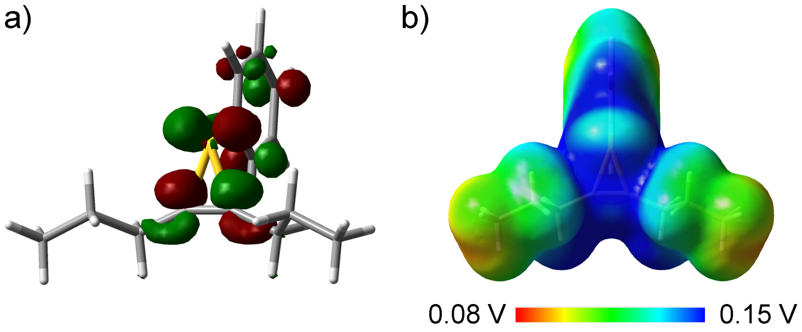


Figure 5. a) LUMO and b) electrostatic potential of **1a**.

The following mechanistic arguments may be reasonable (Figure 6). The ketene silyl acetal and Et_2NH attack the sulfur atom, which has a formal positive charge, to give **3** and the acetylene (*path a*), whereas halide, acetate, triflate, and SCN anions and methanol attack the carbon atom to give **2** (*path b*). The lithium acetylide attacks both the carbon and sulfur atoms of **1**. In the case of halide, acetate, and triflate ions as nucleophiles the reverse reaction of *path a* might be possible, because such nucleophiles are also good leaving groups. If such an equilibrium exists, **2** can be produced even if *path a* is preferable. To examine such a possibility, the experiments using an externally added acetylene having different R groups were carried out. The equilibrium would lead to the exchange of acetylenes and the formation of thiirenium ion **1** with different R groups, which eventually gives **2** with different R groups.

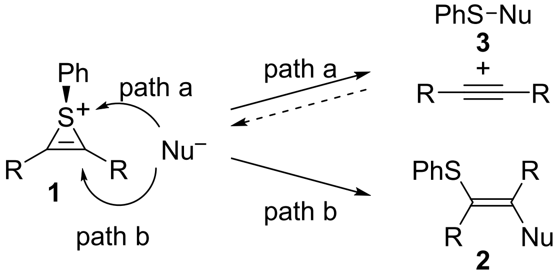


Figure 6. Plausible explanation for the product selectivity.

5-Decyne (1 equiv) was added to a solution of **1a** and the mixture was reacted with Bu_4NCl. **2a** was obtained as the major product (68%) in addition to **2j** (14%) (Figure 7). The reaction via *path a* gives **3** and 4-octyne, which might go out of the solvent cage. The reverse reaction of **3** with 5-decyne in the bulk solution gives **1c**, which react with Cl$^-$ via *path b* to give **2j**. This means the equilibrium discussed above does exist, although it does not play a major role. Another possibility to be considered is that an acetylene exchange reaction took place between **1a** and 5-decyne to give **1c** prior to the reaction with Cl$^-$.

In a second experiment, 4-octyne (1 equiv) was added to a solution of **1c** which was electrochemically generated from 5-decene and PhSSPh, and the mixture was reacted with Bu_4NCl. **2j** was obtained as the major product (94%) in addition to a small amount of **2a** (2%).

These experiments revealed that in the reaction of **1** with Cl$^-$ *path b* is faster than *path a*, although a small amount of **2** might be produced via **3** through *path a* and its reverse reaction.

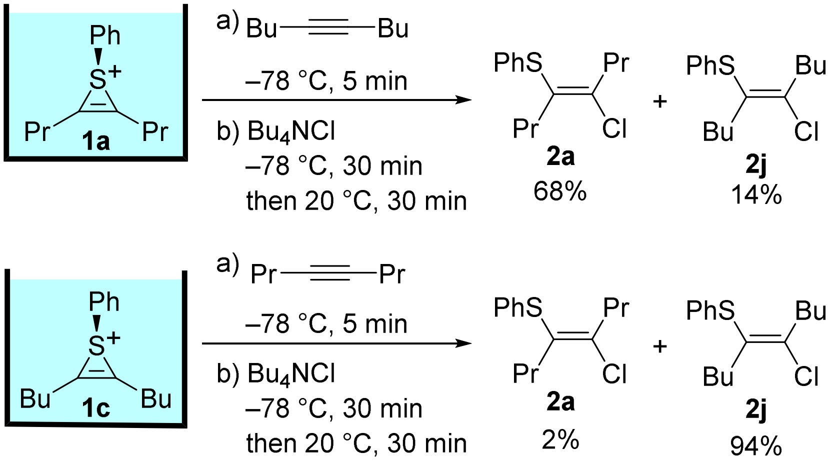


Figure 7. Reactions of **1** with Cl$^-$ in the presence of alkynes.

Conclusions

In conclusion, we show that thiirenium ions having no bulky substituent groups can be generated and accumulated in CH_2Cl_2 by electrochemical oxidation of disulfide in the presence of alkynes at low temperatures such as –78 °C. The thiirenium ions were successfully characterized by NMR, MS, and Raman spectroscopic analyses and exhibited two types of reactivity depending on the nature of nucleophiles.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Varian Mercury plus-400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) spectrometer, or JEOL ECA-600P spectrometer (^{1}H: 600 MHz, ^{13}C: 150 MHz) with tetramethylsilane as an internal standard unless otherwise noted. Mass spectra were obtained on JEOL JMS-SX102A mass spectrometer (EI). GC analysis was performed on a Shimadzu GC-2014 gas chromatograph equipped with a flame ionization detector using a fused silica capillary column (column, CBP1; 0.22 mm × 25 m). Merck precoated silica gel F254 plates (thickness 0.25 mm) was used for thin-layer chromatography (TLC) analysis. Flash chromatography was carried out on silica gel (Kanto Chem. Co., Silica Gel N, spherical, neutral, 40−100 µm) unless otherwise noted. All reactions were carried out under argon atmosphere unless otherwise noted. The anodic oxidation was carried out using an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon GF-20-P21E, ca. 160 mg for 0.25 mmol scale, dried at 300 °C/1 mmHg for 3 h before use) and a platinum plate cathode (10 mm × 10 mm) (Figure S1). Although we used a cell of our original design, similar electrochemical cells are commercially available at Adams & Chittenden Scientific Glass (http://adamschittenden.com/gallery.html?category=4) and EC Frontier.,Inc. (http://www.ec-frontier.co.jp/VB-9.html). A Kikusui PMC350-0.2A was used as DC power supply for the electrolysis.

Bu_4NBF_4 was purchased from TCI and dried at 25 °C/1 mmHg for 12 h. 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 4Å molecular sieves. Dichloromethane-d_2 (CD_2Cl_2 D-99.80%) was purchased and stored over molecular sieves 4A. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Bis(4-fluorophenyl)disulfide was prepared according to a reported procedure.[37,38] Compounds **2a**,[39] **2b**,[40] **2c**,[39] **2d**,[39] **2f**,[41] **2h**,[39] and **3c**[42] were oil, and were characterized by comparison of their ^{1}H NMR spectra with those reported in the literature.

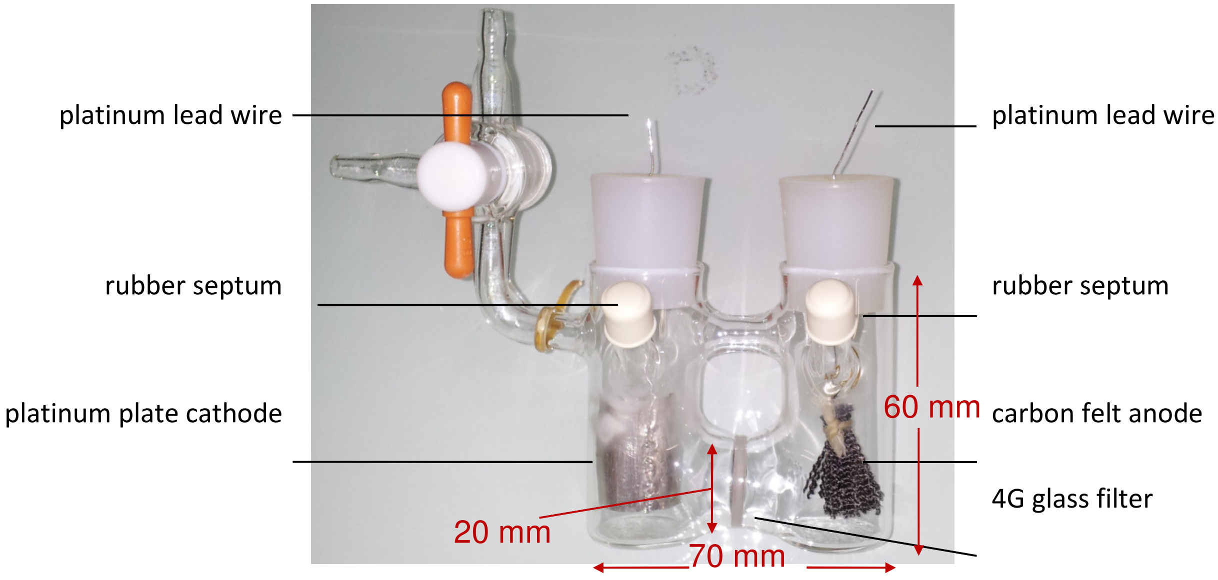
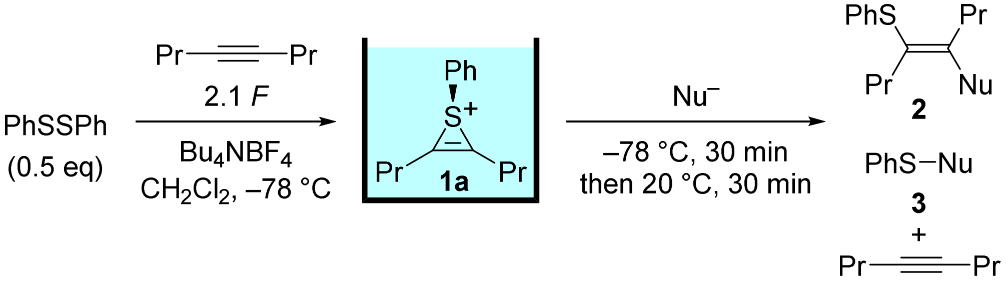


Figure 8. An H-type divided cell for electrolysis.

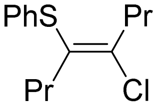
Generation and accumulation of thiirenium ion. The anodic oxidation was carried out in an H-type divided cell equipped with a carbon felt anode and a platinum plate cathode. In the anodic chamber was placed a solution of PhSSPh (0.5 equiv) and 4-octyne (1 equiv) in 0.3 M Bu_4PBF_4, $Bu_4NB(C_6F_5)_4$, or Bu_4NBF_4 in CH_2Cl_2 (10 mL). In the cathodic chamber were placed 0.3 M Bu_4PBF_4, $Bu_4NB(C_6F_5)_4$, or Bu_4NBF_4 in CH_2Cl_2 (10 mL) and trifluoromethanesulfonic acid (60 µl). The constant current electrolysis (8.0 mA) was carried out at −78 °C with magnetic stirring until 2.1 *F* of electricity was applied.

Reactions of thiirenium ion with nucleophiles. The electrolysis of PhSSPh (27.3 mg, 0.125 mmol) in the presence of 4-octyne (28.6 mg, 0.250 mmol) was carried out as described above. To a solution of the thiirenium ion thus generated in the anodic chamber was added a solution of nucleophile (2.50 mmol) in CH_2Cl_2 at −78 °C and the reaction mixture was stirred at −78 °C for 30 min, and then at 20 °C for 30 min. The solution in the anodic chamber was collected and the solvent was removed under reduced pressure and the residue was quickly filtered through a short column (2 x 3 cm) of silica gel to remove Bu_4NBF_4. After removal of the solvent under reduced pressure, the crude product was purified by flash chromatography and GPC to obtain the products.

Reactions of thiirenium ion with nucleophiles



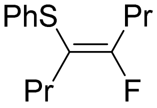
(*E*)-4-Chloro-5-phenylthio-4-octene (2a)



2a

The electrolysis (2.1 *F*) of PhSSPh (27.6 mg, 0.126 mmol) in the presence of 4-octyne (27.7 mg, 0.251 mmol), and subsequent treatment with 2.5 M Bu_4NCl/CH_2Cl_2 (1 mL) gave the title compound (87% yield). The yield was determined by GC analysis using hexadecane as internal standard.

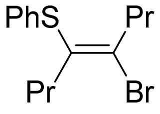
(*E*)-4-Fluoro-5-phenylthio-4-octene (**2b**)



2b

The electrolysis (2.1 *F*) of PhSSPh (76.0 mg, 0.348 mmol) in the presence of 4-octyne (74.5 mg, 0.676 mmol) followed by flash chromatography (hexane/EtOAc 100:0, then 10:3) gave the title compound (148.3 mg, 92% yield).

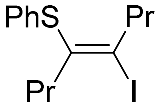
(*E*)-4-Bromo-5-phenylthio-4-octene (2c)



2c

The electrolysis (2.1 *F*) of PhSSPh (31.6 mg, 0.145 mmol) in the presence of 4-octyne (31.2 mg, 0.283 mmol), and the subsequent treatment with 2.5 M Bu_4NBr/CH_2Cl_2 (1 mL) followed by a short column of silica gel (hexane/EtOAc 1:1) and GPC gave the title compound (61.5 mg, 82%).

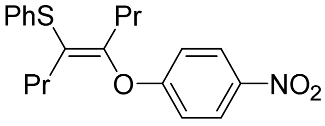
(*E*)-4-Iodo-5-phenylthio-4-octene (2d)



2d

The electrolysis (2.1 *F*) of PhSSPh (31.5 mg, 0.144 mmol) in the presence of 4-octyne (31.7 mg, 0.288 mmol), and the subsequent treatment with a solution of Bu_4NI (923 mg, 2.50 mmol) in CH_2Cl_2 (1.0 mL) followed by a short column of silica gel (hexane/EtOAc 1:1) and GPC gave the title compound (55.7 mg, 69%).

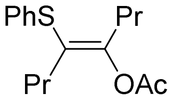
(*E*)-4-(4-Nitrophenoxy)-5-phenylthio-4-octene (2e)



2e

The electrolysis (2.1 *F*) of PhSSPh (27.8 mg, 0.127 mmol) in the presence of 4-octyne (26.9 mg, 0.244 mmol), and the subsequent treatment with a solution of $Bu_4NO(C_6H_4\text{-}p\text{-}NO_2)$ (660 mg, 1.74 mmol) in CH_2Cl_2 (4.0 mL) followed by a short column of silica gel (hexane/EtOAc 1:1) and GPC gave the title compound (34.7 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* 9.3 Hz, 2H), 7.35−7.20 (m, 4H), 7.02 (d, *J* 9.3 Hz, 2H), 2.63 (t, J 7.8 Hz, 2H), 2.13 (t, *J* 7.7 Hz, 2H), 1.58−1.42 (m, 4H), 0.92 (t, *J* 7.4 Hz, 3H), 0.78 (t, *J* 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 154.7, 142.4, 135.0, 129.08, 129.07, 126.4, 126.1, 124.5, 116.0, 32.0, 31.8, 21.3, 20.9, 13.67, 13.63; LRMS (EI) *m/z* 357 (M^+); HRMS (EI) calcd for $C_{20}H_{23}NO_3S$ (M^+): 357.1399, found: 357.1391.

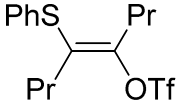
(*E*)-4-Acetoxy-5-phenylthio-4-octene (2f)



2f

The electrolysis (2.1 *F*) of PhSSPh (27.2 mg, 0.125 mmol) in the presence of 4-octyne (25.6 mg, 0.232 mmol), and the subsequent treatment with a solution of Bu_4NOAc (754 mg, 2.50 mmol) in CH_2Cl_2 (1.0 mL) followed by a short column of silica gel (hexane/EtOAc 1:1) and GPC gave the title compound (39.2 mg, 61%).

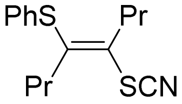
(*E*)-4-Trifluoromethanesulfonyloxy-5-phenylthio-4-octene (**2g**)



2g

The electrolysis (2.1 *F*) of PhSSPh (27.4 mg, 0.126 mmol) in the presence of 4-octyne (27.6 mg, 0.250 mmol), and the subsequent treatment with a solution of Bu_4NOTf (979 mg, 2.50 mmol) in CH_2Cl_2 (1.0 mL) followed by a short column of silica gel (hexane/EtOAc 1:1) and GPC gave the title compound (41.5 mg, 45%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33−7.21 (m, 5H), 2.78 (t, *J* 7.5 Hz, 2H), 2.27 (t, *J* 7.5 Hz, 2H), 1.67−1.49 (m, 4H), 0.96 (t, *J* 7.5 Hz, 3H), 0.84 (t, *J* 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 133.4, 129.9, 129.5, 129.2, 126.9, 118.4 (q, J_{C-F} = 36.1 Hz), 33.6, 32.5, 21.1, 20.3, 13.4, 13.2; LRMS (EI) *m/z* 368 (M^+); HRMS (EI) calcd for $C_{15}H_{19}F_3O_3S_2$ (M^+): 368.0728, found: 368.0730.

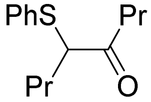
(*E*)-4-Thiocyanato-5-phenylthio-4-octene (**2h**)



2h

The electrolysis (2.1 *F*) of PhSSPh (27.4 mg, 0.126 mmol) in the presence of 4-octyne (27.6 mg, 0.250 mmol), and the subsequent treatment with the solution of Bu_4NSCN (752 mg, 2.50 mmol) in CH_2Cl_2 (1.0 mL) followed by a short column of silica gel (hexane/EtOAc 1:1) and GPC gave the title compound (46.3 mg, 67%).

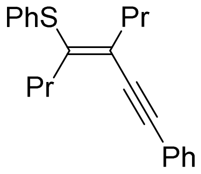
5-(Phenylthio)octan-4-one (**4**)



4

The electrolysis (2.1 *F*) of PhSSPh (24.3 mg, 0.111 mmol) in the presence of 4-octyne (23.2 mg, 0.27 mmol), and the subsequent treatment with CH_3OH (81.2 mg, 2.53 mmol) followed by flash chromatography (hexane/EtOAc 100:0, then 5:1) to the title compound (32.7 mg, 66 %). ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.33 (m, 2H), 7.31−7.22 (m, 3H), 3.64 (t, *J* 7.5 Hz, 1H), 2.55 (t, *J* 7.7 Hz, 2H), 1.85−1.75 (m, 1H), 1.72−1.62 (m, 1H), 1.60−1.53 (m, 2H), 1.51−1.44 (m, 1H), 1.42−1.31 (m, 1H), 0.92 (t, *J* 7.5 Hz, 3H), 0.88 (t, *J* 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.5, 133.3, 132.3, 129.0, 127.7, 56.7, 41.2, 32.5, 20.6, 17.3, 13.77, 13.72; LRMS (EI) m/z 236 (M^+); HRMS (EI) calcd for $C_{14}H_{20}OS$ (M^+): 236.1235, found: 236.1231.

(*E*)-4-Phenylthio-5-phenylethynyl-4-octene (2i)



2i

The electrolysis (2.1 *F*) of PhSSPh (27.5 mg, 0.126 mmol) in the presence of 4-octyne (27.6 mg, 0.25 mmol), and the subsequent treatment with the solution of 1.0 M lithium phenylacetylide/THF (2.5 mL) followed by a short column of silica gel (hexane/EtOAc 1:1) and GPC gave **2i** (10.8 mg, 14 %) and **3a** (31.8 mg, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.42 (m, 2H), 7.35−7.26 (m, 7H), 7.24−7.19 (m, 1H), 2.58 (t, *J* 7.5 Hz, 2H), 2.52 (t, *J* 7.5 Hz, 2H), 1.71−1.62 (m, 2H), 1.61−1.52 (m, 2H), 0.98 (t, *J* 7.5 Hz, 3H), 0.88 (t, *J* 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 134.9, 131.3, 130.6, 128.9, 128.3, 128.0, 126.9, 126.6, 123.7, 94.4, 89.3, 37.0, 36.2, 22.1, 22.0, 13.69, 13.62; LRMS (EI) *m/z* 320 (M^+); HRMS (EI) calcd for $C_{22}H_{24}S$ (M^+): 320.1599, found: 320.1598.

We could not determine the stereochemistry of **2i** by NOE measurement because the chemical shift of the protons of two methylene groups next to the alkene moiety are very close (2.52 and 2.58 ppm).

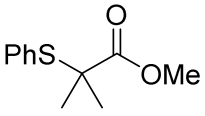
Phenyl(phenylethynyl)sulfane (3a)

PhS—≡—Ph

3a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.47 (m, 4H), 7.37−7.33 (m, 5H), 7.25−7.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.9, 131.7, 129.2, 128.6, 128.4, 126.5, 126.2, 122.9, 97.9, 75.4; LRMS (EI) m/z 210 (M^+); HRMS (EI) calcd for $C_{14}H_{10}S$ (M^+):210.0503, found: 210.0494.

Methyl 2-methyl-2-(phenylthio)propionate (3b)



3b

The electrolysis (2.1 *F*) of PhSSPh (27.5 mg, 0.126 mmol) in the presence of 4-octyne (27.6 mg, 0.250 mmol), and subsequent treatment with dimethylketene methyl trimethylsilyl acetal (436 mg, 2.50 mmol) followed by a short column of silica gel (hexane/EtOAc 1:1) and GPC gave the title compound (26.6 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.44 (m, 2H), 7.40−7.30 (m, 3H), 3.66 (s, 3H), 1.49 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 136.7, 131.4, 129.4, 128.6, 52.2, 51.0, 25.8; LRMS (EI) *m/z* 210 (M^+); HRMS (EI) calcd for $C_{11}H_{14}O_2S$ (M^+):210.0715, found: 210.0714.

Diethyl(phenylthio)amine (3c)

$PhS{-}NEt_2$

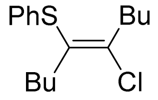
3c

The electrolysis (2.1 *F*) of PhSSPh (27.6 mg, 0.126 mmol) in the presence of 8-hexadecyne (56.1 mg, 0.252 mmol), and subsequent treatment with diethylamine (185 mg, 2.53 mmol) followed by a short column of silica gel (hexane/EtOAc 1:1) and GPC gave the title compound (37.3 mg, 82%) and 8-hexadecyne (52.9 mg, 94%).

Thermal stability. After generating thionium ion from PhSSPh (27.3 mg, 0.125 mmol) and 4-octyne (28.6 mg, 0.25 mmol) at −78 °C as described above, the solution was stirred at *T* °C (*T* = −78, −60, −40, −20, and 0) for 30 min. The solution was recooled to −78 °C, added Bu_4NCl (2.5 mmol) in CH_2Cl_2 and stirred at −78 °C for 30 min and then at 20 °C for 30 min. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (2 x 3 cm) of silica gel to remove Bu_4NBF_4. The silica gel was washed with hexane/EtOAc 1:1. After removal of the solvent under reduced pressure, the crude product was analyzed by gas chromatography.

Reference reaction. In the anodic chamber were placed 4-octyne or 5-decyne (0.25 mmol), and PhSSPh (0.125 mmol), Bu_4NBF_4 (3.0 mmol), and CH_2Cl_2 (10 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (60 µL), Bu_4NBF_4 (3.0 mmol) and CH_2Cl_2 (10 mL). The constant current electrolysis (8.0 mA) was carried out at −78 °C with magnetic stirring until 2.1 *F* of electricity was passed. To the anodic chamber was added another alkyne (0.25 mmol). The solution was stirred for 10 min at −78 °C. To the anodic chamber was added 2.5 M Bu_4NCl/CH_2Cl_2 (1 mL), and to the cathodic chamber CH_2Cl_2 (1 mL) was added at −78 °C. The solution was stirred for 30 min at −78 °C, and then 30 min at 20 °C. The solution in the anodic chambers was collected and the solvent was removed under reduced pressure. The residue was filtered through a short column (2 x 4 cm) of silica gel to remove Bu_4NBF_4 by using hexane/EtOAc (1:1 v/v) as an eluent. After removal of the solvent under reduced pressure the crude product was analyzed by GC using tetradecane as an internal standard.

(E)-5-Chloro-6-phenylthio-5-hexene (2j)



2j

In the anodic chamber were placed 5-decyne (34.6 mg, 0.25 mmol) and diphenyl disulfide (27.5 mg, 0.126 mmol). Electrochemical oxidation (2.1 *F*) and subsequent addition of the solution of 2.5 M Bu_4NCl/CH_2Cl_2 (1 mL) followed by a short column of silica gel (hexane/EtOAc 1:1) gave the crude of the title compound. After removal of the solvent under reduced pressure the crude product was analyzed by GC using tetradecane as an internal standard (99% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.27−7.19 (m, 4H), 7.17−7.12 (m, 1H), 2.80 (t, *J* 7.5 Hz, 2H), 2.37 (t, *J* 7.9 Hz, 2H), 1.62−1.54 (m, 4H), 1.53−1.45 (m, 4H), 0.91 (t, *J* 7.2 Hz, 3H), 0.84 (t, *J* 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 135.5, 129.5, 128.9, 128.8, 126.1, 37.0, 33.8, 30.1, 29.9, 22.2, 21.8, 13.90, 13.89; LRMS (EI) *m/z* 282 (M^+); HRMS (EI) calcd for $C_{16}H_{27}ClS$ (M^+): 282.1209, found: 282.1208.

NMR analyses. A solution of thiirenium ion 1a generated and accumulated from PhSSPh (49.4 mg, 0.226 mmol) and 4-octyne (48.5 mg, 0.440 mmol) in 0.3 M Bu_4PBF_4 in CD_2Cl_2 (6.0 mL) was transferred to Ar-flushed NMR tubes at −78 °C by Ar-flushed 1 mL syringe cooled with dry ice. NMR measurements were carried out using JEOL ECA-600P spectrometer (^{1}H: 600 MHz, ^{13}C: 150 MHz). Spectra so obtained are presented in the Supplementary File.

MS analyses; typical procedure. In the anodic chamber were placed 4-octyne (118.6 mg, 1.08 mmol), PhSSPh (114.6 mg, 0.525 mmol), $Bu_4NB(C_6F_5)_4$ (923.9 mg, 1.0 mmol), and CH_2Cl_2 (10 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (120 µL, 1.37 mmol), Bu_4NBF_4 (926 mg, 1.0 mmol), and CH_2Cl_2 (10 mL). The constant current electrolysis (15.0 mA) was carried out at −78 °C with magnetic stirring until 2.1 *F* of electricity was passed. The reaction mixture of the anodic chamber was analyzed by CSI-MS (spray temperature; 0 °C): HRMS (CSI) *m/z* calcd for $C_{14}H_{19}S^+$ (M^+): 219.1202, found: 219.1209.

Raman analyses. A laser beam from a fiber-coupled output of cw laser, Toptica XTRA, 250 mW at 785 nm, was conducted through the solution in the anodic chamber of the electrochemical cell. Scattered light was collected in the direction perpendicular to the axis of the laser beam by using a combination of quartz lenses focusing the light on the surface of the entrance cross section of the bundle of forty optical fibers with a 100 µm diameter for each. The optical components were contained in a vacuum-tight glass tube sealed with rubber *o*-rings and partly dipped into the reactant solution. The electrochemical cell was independently purged with N_2 gas to avoid humidity in air. For the measurement, the vacuum seal of the optical component was crucial in avoiding frost, which scatters both the excitation and signal beams.

The collected light was conducted through the optical fibers to a spectrometer for dispersion, Acton 320 PI (1200 G/mm blazed at 500 nm or 600 G/mm blazed at 1000 nm), and detected by using a liquid-nitrogen cooled CCD array detector, PyLoN:256-OE 1024 x 256 pixels of 26 x 26 µm^2. To minimize stray light, a sharp-edge long-pass filter, Semrock RazorEdge 785R (o.d. <10^{-6} at 785 nm), was placed in front of the entrance slit of the spectrometer, where the image of the exit cross section of the fiber bundle with vertically aligned forty optical fibers was focused. Spectra were accumulated for 6 min 40 sec (a 4-sec exposure time by 100 times accumulation) for each and redundantly stored one by one for 4 hours (400 sec by 60 spectra) during the electrolysis. Spectral resolution was ~0.2 nm, which corresponds to ~3 cm^{-1} at 815 nm where a Raman band of 470 cm^{-1} was observed.

DFT calculations. DFT calculations were conducted with the Gaussian 09 program.[43] All geometry optimizations were carried out at the B3LYP level of density functional theory with the 6-31G(d) basis set. The bond order and s-character were obtained by the natural bond orbital (NBO) analysis. See Supplementary file.

Acknowledgements

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Supplementary Material

Experimental procedures and spectroscopic data for new compounds.

References and Notes

1. Capozzi, G.; Lucchini, V.; Modena, G. *Res. Chem. Intermed.* **1979**, *2*, 347.
https://doi.org/10.1007/BF03156004

2. Capozzi, G.; De Lucchi, O.; Lucchini, V.; Modena, G. *J. Chem. Soc., Chem. Commun.* **1975**, 248.
https://doi.org/10.1039/c39750000248
3. Capozzi, G.; Lucchini, V.; Modena, G.; Scrimin, P. *Tetrahedron Lett.* **1977**, *18*, 911.
https://doi.org/10.1016/S0040-4039(01)92789-3
4. Capozzi, G.; Da Col. L.; Lucchini, V.; Modena, G.; Valle, G. *J. Chem. Soc., Perkin Trans. 2* **1980**, 68.
https://doi.org/10.1039/p29800000068
5. Lucchini, V.; Modena, G. Valle, G.; Capozzi, G. *J. Org. Chem.* **1981**, *46*, 4720.
https://doi.org/10.1021/jo00336a019
6. Destro, R.; Lucchini, V.; Modena, G.; Pasquato, L. *J. Org. Chem.* **2000**, *65*, 3367.
https://doi.org/10.1021/jo991731o
7. Poleschner, H.; Seppelt, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 12838.
https://doi.org/10.1002/anie.201307161
8. In ref 3, dimethylacetylene was reacted with methanesulfenyl chloride and antimony pentachloride in dichloromethane frozen at −120 °C followed by slow warming to −80 °C to give precipitation of trimethylthiirenium hexachloroantimonate. However, we cannot evaluate the stability of the thiirenium ion because the yield of the thiirenium ion was not reported.
9. Moeller, K. D. *Tetrahedron* **2000**, *56*, 9527.
https://doi.org/10.1016/S0040-4020(00)00840-1
10. Sperry, J. B.; Wright, D. L. *Chem. Soc. Rev.* **2006**, *35*, 605.
https://doi.org/10.1039/b512308a
11. Yoshida, J.; Kataoka, K.; Horcajada, R.; Nagaki, A. *Chem. Rev.* **2008**, *108*, 2265.
https://doi.org/10.1021/cr0680843
12. Frontana-Uribe, B. A.; Little, R. D.; Ibanez, J. G.; Palma, A.; Vasquez-Medrano, R. *Green Chem.* **2010**, *12*, 2099.
https://doi.org/10.1039/c0gc00382d
13. Ogawa, K. A.; Boydston, A. J. *Chem. Lett.* **2015**, *44*, 10.
https://doi.org/10.1246/cl.140915
14. Horn, E. J.; Rosen, B. R.; Baran, P. S. *ACS Cent. Sci.* **2016**, *2*, 302.
https://doi.org/10.1021/acscentsci.6b00091
15. Chiba, K.; Okada, Y. *Curr. Opin. Electrochem.* **2017**, *2*, 53.
https://doi.org/10.1016/j.coelec.2017.03.014
16. Horn, E. J.; Rosen, B. R.; Chen, Y.; Tang, J.; Chen, K.; Eastgate, M. D.; Baran, P. S. *Nature*, **2016**, *533*, 77.
https://doi.org/10.1038/nature17431
17. Hayashi, R.; Shimizu, A.; Yoshida, J. *J. Am. Chem. Soc.* **2016**, *138*, 8400.
https://doi.org/10.1021/jacs.6b05273
18. Llorente, M. J.; Nguyen, B. H.; Kubiak, C. P.; Moeller, K. D. *J. Am. Chem. Soc.* **2016**, *138*, 15110.
https://doi.org/10.1021/jacs.6b08667
19. Yoshida, J.; Suga, S.; Suzuki, S.; Kinomura, N.; Yamamoto, A.; Fujiwara, K. *J. Am. Chem. Soc.* **1999**, *121*, 9546.
https://doi.org/10.1021/ja9920112
20. Yoshida, J.; Suga, S. *Chem. Eur. J.* **2002**, *8*, 2651.
https://doi.org/10.1002/1521-3765(20020617)8:12<2650::AID-CHEM2650>3.0.CO;2-S
21. Yoshida, J.; Ashikari, Y.; Matsumoto, K.; Nokami, T. *J. Synth. Org. Chem., Jpn*. **2013**, *71*, 1136.
https://doi.org/10.5059/yukigoseikyokaishi.71.1136

22. Suga, S.; Matsumoto, K.; Ueoka, K.; Yoshida, J. *J. Am. Chem. Soc.* **2006**, *128*, 7710. https://doi.org/10.1021/ja0625778
23. Fujie, S.; Matsumoto, K.; Suga, S.; Nokami, T.; Yoshida, J. *Tetrahedron* **2010**, *66*, 2823. https://doi.org/10.1016/j.tet.2010.02.049
24. Matsumoto, K.; Suga, S.; Yoshida, J. *Org. Biomol. Chem.* **2011**, *9*, 2586. https://doi.org/10.1039/c0ob01070g
25. Matsumoto, K.; Kozuki, Y.; Ashikari, Y.; Suga, S.; Kashimura, S.; Yoshida, J. *Tetrahedron Lett*. **2012**, *53*, 1916. https://doi.org/10.1016/j.tetlet.2012.01.131
26. Matsumoto, K.; Sanada, T.; Shimazaki, H.; Shimada, K.; Hagiwara, S.; Fujie, S.; Ashikari, Y.; Suga, S.; Kashimura, S.; Yoshida, J. *Asian J. Org. Chem.* **2013**, *2*, 325. https://doi.org/10.1002/ajoc.201300017
27. Although Bu_4N^+ is generally used as a supporting electrolyte, protons of Bu_4N^+ were overlapped with the protons of **1a** at 2.95-3.10 ppm. Therefore, Bu_4PBF_4 was used as the supporting electrolyte.
28. Yamaguchi, K. *J. Mass Spectrom.* **2003**, *38*, 473. https://doi.org/10.1002/jms.488
29. Compound **1a** generated in Bu_4NBF_4/CH_2Cl_2 was not observed by MS measurement probably because of the presence of BF_4^-, which reacts with **1a** to give **2b**.
30. Matsumoto, K.; Miyamoto, Y.; Shimada, K.; Morisawa, Y.; Zipse, H.; Suga, S.; Yoshida, J.; Kashimura, S.; Wakabayashi, T. *Chem. Commun.* **2015**, *51*, 13106. https://doi.org/10.1039/C5CC03585F
31. Marui, T.; Kajita, S.; Katayama, Y.; Chiba, K. *Electrochem. Commun.* **2007**, *9*, 1331. https://doi.org/10.1016/j.elecom.2007.01.040
32. The use of PhSSPh caused precipitation during the electrochemical oxidation, which disturbed the Raman analysis.
33. Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502. https://doi.org/10.1021/jp960976r
34. Poleschner, H. Seppelt, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 6461 https://doi.org/10.1002/anie.200801691
35. Suga, S.; Suzuki, S.; Yamamoto, A.; Yoshida, J. *J. Am. Chem. Soc.* **2000**, *122,* 10244. https://doi.org/10.1021/ja002123p
36. Mayr, H.; Breugst, M.; Ofial, A. R. *Angew. Chem., Int. Ed.* **2011**, *50*, 6470. https://doi.org/10.1002/anie.201007100
37. Hirano, M.; Yakabe, S.; Monobe, H.; Morimoto, T. *J. Chem. Res. (S)* **1998**, 472.
38. Becker, D. P.; Villamil, C. I.; Barta, T. E.; Bedell, L. J.; Boehm, T. L.; DeCrescenzo, G. A.; Freskos, J. N.; Getman, D. P.; Hockerman, S.; Heintz, R.; Howard, S. C.; Li, M. H.; McDonald, J. J.; Carron, C. P.; Funckes-Shippy, C. L.; Mehta, P. P.; Munie, G. E.; Swearingen, C. A. *J. Med. Chem.*, **2005**, *48*, 6713. https://doi.org/10.1021/jm0500875
39. Taniguchi, N. *Tetrahedron* **2009**, *65*, 2782 https://doi.org/10.1016/j.tet.2009.01.094
40. Benati, L.; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc. Perkin Trans. 1* **1990**, 1691. https://doi.org/10.1039/P19900001691
41. Benati, L.; Casarini, D.; Montevecchi, P. C. Spagnolo, P. *J. Chem. Soc. Perkin Trans. 1* **1989**, 1113. https://doi.org/10.1039/P19890001113

42. Shiro, D.; Fujiwara, S.; Tsuda, S.; Iwasaki, T.; Kuniyasu, H.; Kambe, N. *Tetrahedron Lett.* **2015**, *56*, 1531. https://doi.org/10.1016/j.tetlet.2015.01.096
43. Gaussian 09, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.;Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2010.