Electrochemical Synthesis of Thienoacene Derivatives: Transition Metal-Free Dehydrogenative C–S Coupling Promoted by a Halogen Mediator

Koichi Mitsudo,*[a] Ren Matsuo,[a] Toki Yonezawa,[a] Haruka Inoue,[a] Hiroki Mandai,[b] and Seiji Suga*[a]

Abstract: The first electrochemical dehydrogenative C–S bond formation leading to thienoacene derivatives is described. Several thienoacene derivatives were synthesized via dehydrogenative C–H/S–H coupling. The addition of $^{n}Bu_4NBr$, which catalytically promoted the reaction as a halogen mediator, was essential.

The formation of a carbon–sulfur bond is one of the most fundamental and significant transformations in organic synthesis because C–S bonds are an abundant and significant skeleton in the field of pharmaceuticals[1] and material science[2] (Figure 1). Example compounds include the antidepressant vortioxetine,[3] and an antifungal medication sertaconazole[4]. π-Expanded benzo[*b*]thiophene derivatives, such as [1]benzothieno[3,2-*b*][1]benzothiophene (BTBT)[5] and dinaphtho[2,3-*b*:2',3'-*d*]thiophene (DNT),[6] have received considerable attention as key building blocks for use in organic field effect transistors.

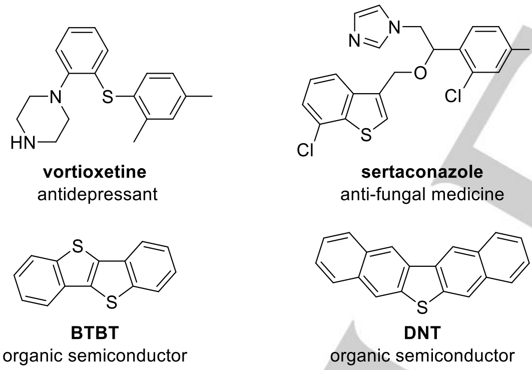

Figure 1. Representative medicines and semiconductors having C–S bonds.

One of the most conventional methods for the construction of C–S bonds is transition metal-catalyzed cross-coupling between aryl halides and thiols.[7] Recently, transition metal-catalyzed dehydrogenative C–S coupling reactions have attracted attention as an improved method for the formation of C–S bonds with high atom-economy.[8]

Meanwhile, electrochemical carbon–heteroatom bond formation is known to be as an environmentally benign strategy that proceeds under mild conditions.[9] Recently, several novel electrochemical carbon–heteroatom coupling reactions, such as those for C–N[10] and C–O,[11] have been reported. For instance, Lin and co-workers reported the 1,2-diazidation of alkenes,[10a] and Baran reported electrochemical allylic oxidation.[11a,b] Electrochemical approaches are also effective for C–S bond formation.[12] Lei reported electro-oxidative intermolecular C–S bond formation via C–H/S–H bond cleavage (Scheme 1 (i)).[12a] Intramolecular dehydrogenative coupling between an arene and a thiocarbonyl group was also effective for constructing C–S bonds (Scheme 1 (ii)).[12d,g] While electrochemical transformations have been studied intensively, to the best of our knowledge, there has been no report on electrochemical carbon–heteroatom bond formation for the construction of π-expanded heteroacene derivatives, which are candidates for useful organic materials.

We are interested in the development of new methods for the synthesis of thienoacenes,[13] acene derivatives that contain a thiophene skeleton. We were inspired to investigate electrochemical approaches[14] for the synthesis of thienoacenes. We first assumed that intramolecular dehydrogenative C–H/S–H coupling of 2-arylbenzene-1-thiol would form π-expanded thiophenes, but the desired product was not obtained (Scheme 1 (iii)). During the course of further study, we eventually found that the desired dehydrogenative C–S bond formation proceeded smoothly in the presence of electrogenerated [Br^+] as a powerful promoter (Scheme 1 (iv)). This strategy was effective for the synthesis of π-expanded thienoacenes such as [1]benzothieno[3,2-*b*]benzo[2,3-*d*]furan (BTBF) and BTBT. We report here the first electro-oxidative dehydrogenative C–S bond formation promoted by electrogenerated [Br^+] for the synthesis of BTBFs and BTBTs.

As a model compound, 2-(benzo[*b*]furan-2-yl)benzenethiol (**1a**) was chosen and electro-oxidation was performed in 0.1 M $LiClO_4$ solution in CH_3CN (Table 1). When simple electrolysis without an additive was carried out at 25 °C, the desired cyclized product **2a** was not obtained and disulfide **3a** was obtained in 42% yield (entry 1). We next included some additives. With 1.0 equiv of $^{n}Bu_4NBr$ at 25 °C, disulfide **3a** was obtained in 73% yield as a major compound along with the desired product **2a** in 11% yield (entry 2). With an increase in the reaction temperature, the yield of **2a** increased: 90% yield at 60 °C (entry 4). At 70 °C, the yield of **2a** decreased to 62%, but then increased to 91% with the use of 2.0 equiv of $^{n}Bu_4NBr$ (entry 5). The use of

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[a] Dr. K. Mitsudo, R. Matsuo, T. Yonezawa, Prof. Dr. S. Suga
Division of Applied Chemistry, Graduate School of Natural Science and Technology, Okayama University
3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530 (Japan)
E-mail: mitsudo@okayama-u.ac.jp; suga@cc.okayama-u.ac.jp
[b] Dr. H. Mandai
Department of Medical Technology, Gifu University of Medical Science
4-3-3 Nijigaoka, Kani, Gifu 509-0293 (Japan)

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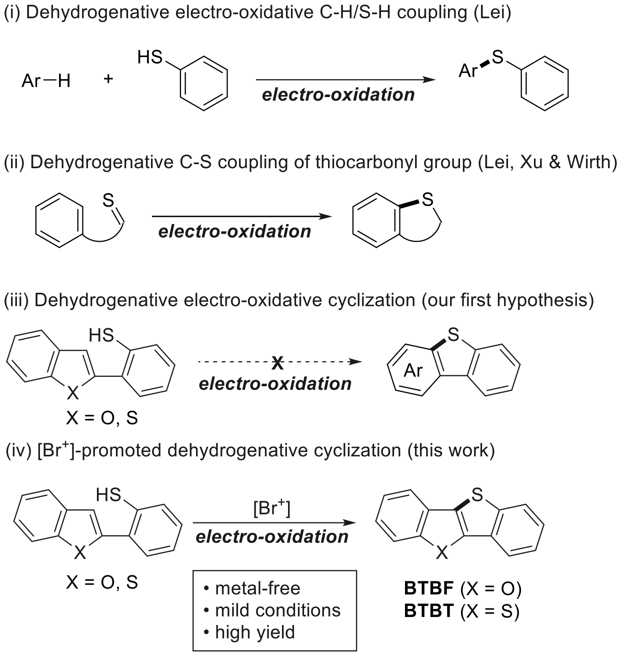
$^{n}\mathrm{Bu_4NCl}$ and $^{n}\mathrm{Bu_4NI}$ predominantly gave disulfide **3a** (entries 6 and 7).

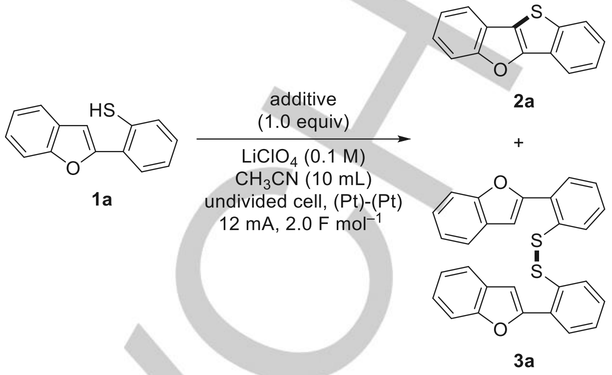


Scheme 1. Representative electrochemical dehydrogenative C–S bond formation and this work

The product distribution strongly depends on the amount of charge (Table 2). With 1.0 F mol^{-1} of charge (the theoretical amount for one-electron oxidation of the substrate), while only a trace amount of **2a** was obtained, **3a** was obtained in 96% yield (entry 1). With an increase in the amount of charge, the yield of **3a** decreased and that of **2a** drastically increased. The yield of **2a** reached 94% with 2.4 F mol^{-1} of charge (entry 4). During further optimization, we found that the amount of charge could be reduced by further stirring of the reaction mixture after electrolysis. With 15 min of additional stirring after electrolysis at 2.0 F mol^{-1}, **2a** was obtained in an excellent yield (94% NMR yield; 97% isolated yield). These results indicate that the electro-oxidation of **1a** initially gave **3a** selectively, and **3a** was then converted to the desired product **2a**. The latter transformation should be slower than the first step, and required several minutes to be finished. Since the conversion of **1a** to **2a** is a two-electron oxidation, the electron efficiency of the reaction is quite high.

We next reduced the amount of $^{n}\mathrm{Bu_4NBr}$ for the electro-oxidation (Table 3). With 0.5 equiv of $^{n}\mathrm{Bu_4NBr}$, the yield of **2a** decreased to 90% (entry 1). With a further decrease in the amount of $^{n}\mathrm{Bu_4NBr}$ (0.1–0.2 equiv), the yield of **2a** drastically decreased (entries 2 and 3). The low yield of **2a** would be due to the over-oxidation of **1a** and **2a**. To suppress this over-oxidation, electro-oxidation was carried out with 2 mA of current. As expected, the yield of **2a** drastically improved to 93% (entry 4). The amount of electrolyte could be reduced to 0.05 M (95% yield).

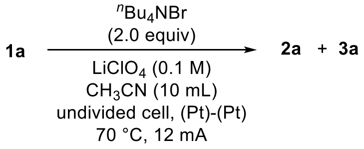
Table 1: Optimization of the additive for the electro-oxidation of **1a**



Entry	Additive	Temp [°C]	**2a** [%][a]	**3a** [%][a]
1	none	25	0	42
2	$^{n}\mathrm{Bu_4NBr}$	25	11	73
3	$^{n}\mathrm{Bu_4NBr}$	50	71	11
4	$^{n}\mathrm{Bu_4NBr}$	60	90 (89)[b]	4 (9)[b]
5	$^{n}\mathrm{Bu_4NBr}$	70	62 (91)[b]	28 (trace)[b]
6	$^{n}\mathrm{Bu_4NCl}$	60	trace	40
7	$^{n}\mathrm{Bu_4NI}$	60	0	77

[a] NMR yield. [b] Performed with 2.0 equiv of $^{n}\mathrm{Bu_4NBr}$.

Table 2: Effect of charge in the electro-oxidation of **1a**



Entry	Charge [F mol^{-1}]	**2a** [%][a]	**3a** [%][a]
1	1.0	trace	96
2	1.5	17 (54)c	76 (38)[b]
3	2.0	91 (94)[b] (97)[b,c]	trace (0)[b]
4	2.4	94	N.D.

[a] NMR yield. [b] After electrolysis, the mixture was stirred for an additional 15 min. [c] Isolated yield.

Under the optimized conditions, we examined the scope of the reaction (Table 4). Precursors with an electron-donating group such as a methyl group gave the cyclization products in high yields (**2b**, 93%; **2c**, 98%, **2d**, 93%). When a precursor with an electron-withdrawing group such as a fluoro group was used in the reaction, the desired compound **2e** was obtained in 94% yield. More π-expanded compound was obtained by a similar method. With a precursor bearing a naphthyl group, a five-ring fused thienofuran **2f** was obtained in 95% yield with 0.3 equiv of ^{n}Bu$_4$NBr. With 0.1 equiv of ^{n}Bu$_4$NBr, decomposition of **2f** took place probably due to the low oxidation potential of **2f**, but this decomposition was suppressed by the use of 0.3 equiv of ^{n}Bu$_4$NBr. A precursor bearing benzo[*b*]thiophene gave BTBT (**2g**) in 98% yield. Several BTBT derivatives bearing electron-donating or -withdrawing groups could be obtained in high yield (**2h–k**). Benzo[*b*]thieno[2,3-*d*]thiophene derivatives **2l–n** were also obtained in excellent yield. A more π-expanded thienothiophene such as **2o** was readily obtained from a corresponding precursor which has two thiols.

Table 3: Electro-oxidation of **1a** with catalytic amount of ^{n}Bu$_4$NBr

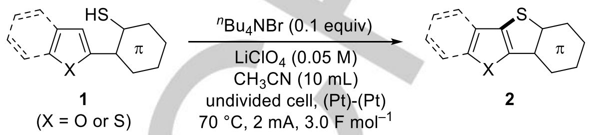
$$\mathbf{1a} \xrightarrow[\substack{\text{LiClO}_4\ (0.1\ \text{M}) \\ \text{CH}_3\text{CN}\ (10\ \text{mL}) \\ \text{undivided cell, (Pt)-(Pt)} \\ 70\ °\text{C},\ 2.0\ \text{F mol}^{-1}}]{^{n}\text{Bu}_4\text{NBr}} \mathbf{2a} + \mathbf{3a}$$

Entry	^{n}Bu$_4$NBr [equiv]	Current [mA]	**2a** [%][a]
1	0.5	12	90
2	0.2	12	37
3	0.1	12	11
4	0.1	2	93 (95)[b]

[a] NMR yield. [b] With 0.05 M of LiClO$_4$.

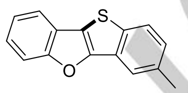
To gain further insight into the reaction mechanism, we performed some control experiments (Scheme 2). Without electrolysis, **1a** was not converted to **2a**, and mostly **1a** was recovered, (Scheme 2 (i)). We also attempted a reaction of **1a** with NBS without electrolysis. Under the conditions, **2a** was obtained in only 20% yield and dibrominated by-product **4a** was obtained in 20% yield (Scheme 2 (ii)). The reaction with 1.0 equiv of Br$_2$ instead of NBS gave disulfide **3a** quantitatively. Further addition of Br$_2$ (2.0 equiv) gave **2a** in 87% yield.[15] We also tried to use ^{n}Bu$_4$NBr$_3$, and found that **2a** was obtained quantitatively, while a stoichiometric amount of ^{n}Bu$_4$NBr$_3$ was required. While the exact structure of [Br$^+$] generated in situ is not yet clear, the behavior of [Br$^+$] should be similar to that of Br$_3^-$. This result was consistent with that of Nonaka's work on [Br$^+$].[16] While similar C–S bond formations proceed with Br$_2$ and ^{n}Bu$_4$NBr$_3$ instead of electrolysis, stoichiometric amounts of these reagents are required to accomplish the chemical transformations. In contrast, an advantage of Br$^-$-promoted electrochemical reactions is that only a catalytic amount of ^{n}Bu$_4$NBr, which is a low-toxic and stable compound, was required for this reaction.

Table 4: Electro-oxidative dehydrogenative cyclization of several precursors for the synthesis of **2** under the optimized conditions[a]

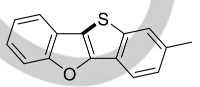


1
(X = O or S)

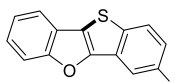
2



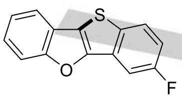
2b, 93%



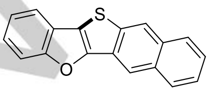
2c, 98%



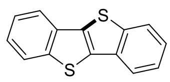
2d, 93%



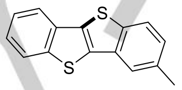
2e, 94%



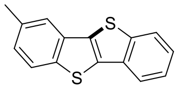
2f, 95%[b]



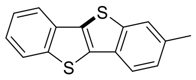
2g, 98%



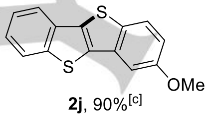
2h, 98%



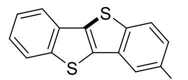
2h, 92%



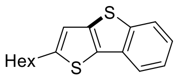
2i, 98%



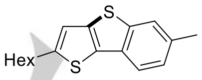
2j, 90%[c]



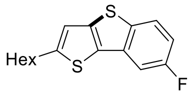
2k, 84%[c]



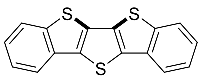
2l, 97%



2m, 93%



2n, 91%

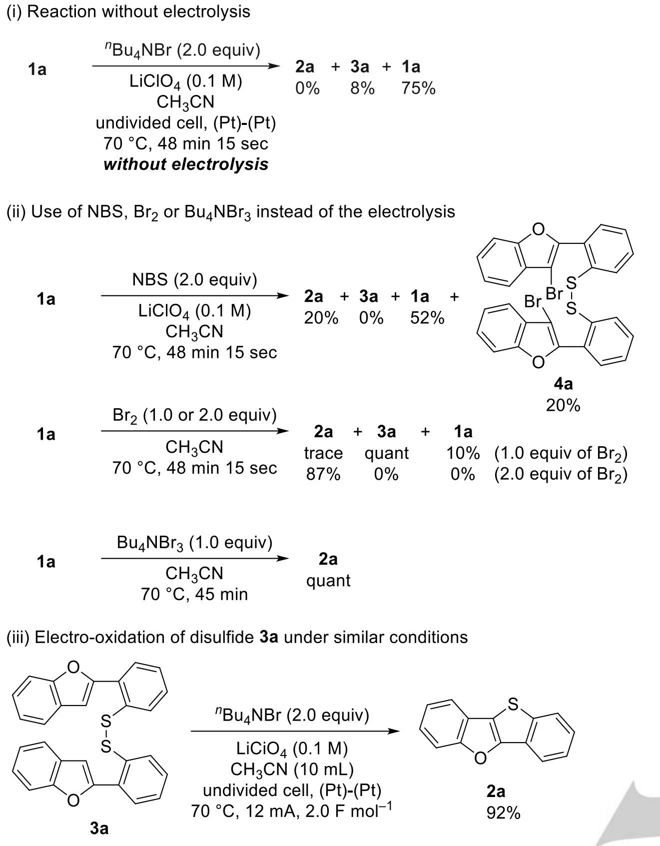


2o, 53%[d]

[a] Isolated yield. [b] With 0.3 equiv of ^{n}Bu$_4$NBr. [c] With ^{n}Bu$_4$NBr (2.0 equiv) and LiClO$_4$ (0.1 M). 12 mA, 2.0 F mol^{-1}. [d] With ^{n}Bu$_4$NBr (4.0 equiv) and LiClO$_4$ (0.1 M). 12 mA, 8.0 F mol^{-1}

According to the results shown in Table 2, **3a** should be the intermediate for the synthesis of **2a** from **1a**. Electro-oxidation of **3a** was carried out under similar conditions. When 2.0 F mol^{-1} of charge was passed, **3a** was completely consumed and **2a** was obtained in 92% yield (Scheme 2 (iii)). These results clearly indicate that **1a** was converted to **2a** through **3a**.

To clarify the role of ^{n}Bu$_4$NBr as a promoter of the transformation, the electrochemical properties of **1a**, **2a**, **3a**, and ^{n}Bu$_4$NBr were studied using cyclic voltammetry (Figure S2). The oxidation potential of ^{n}Bu$_4$NBr was the most negative (E_{onset} = 0.25 V), and E_{onset} of **1a** (0.83 V) was more negative than those of **2a** (0.96 V) and **3a** (0.99 V). These results suggest that the oxidation of ^{n}Bu$_4$NBr should occur first, and the oxidation of **1a** would be preferred compared to those of **2a** and **3a**. In the cyclic voltammograms of the mixture of **1a** and ^{n}Bu$_4$NBr, a catalytic current was observed.[17] This result suggests that a cationic species generated from Br$^-$ would oxidize **1a**.



Scheme 2. Control experiments

Based on these experiments, a plausible mechanism for the electro-oxidative dehydrogenative cyclization of **1** is illustrated in Figure 3. First, Br$^-$ of ^{n}Bu$_4$NBr would be oxidized to afford [Br$^+$].[16,18] **1** would be oxidized by [Br$^+$] to give disulfide **3** and Br$^-$, which would be oxidized to [Br$^+$] again on the anode. Next, disulfide **3** would react with [Br$^+$] to give cationic species **A**. Subsequent intramolecular cyclization would give cyclized product **B** and arylthiobromide **C**. Subsequent deprotonation of the intermediate **B** would give the desired product **2**. Intermediate **C** would be oxidized by anodic oxidation or [Br$^+$] to give disulfide **3**, which would react with [Br$^+$] to give **A**. The cathodic reaction would be the generation of hydrogen from H$^+$.

In conclusion, we have developed the first method for the construction of BTBFs and BTBTs by electro-oxidative dehydrogenative cyclization promoted by [Br$^+$]. This method realizes the construction of π-expanded thienoacenes under transition metal-free and mild conditions with a catalytic amount of halogen mediator. The scope of this methodology is under investigation in our laboratory.

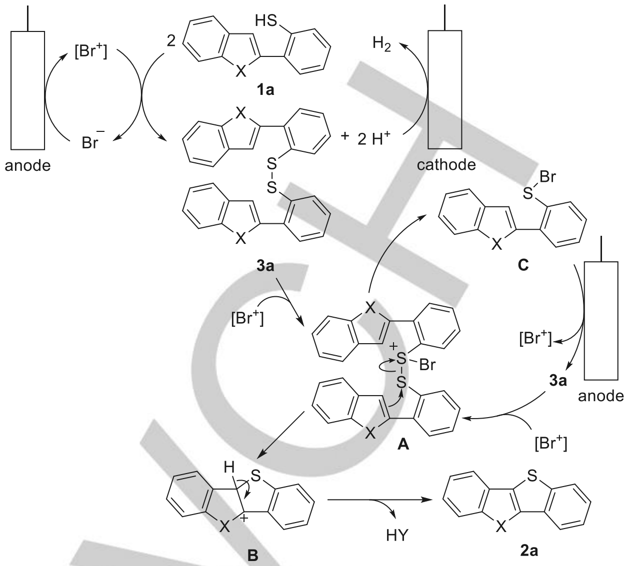


Figure 3. A plausible mechanism for the dehydrogenative cyclization of **1a**.

Acknowledgements

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Keywords: Electrochemistry • Sulfur heterocycles • C–S bond formation • Cross-coupling • Cyclization

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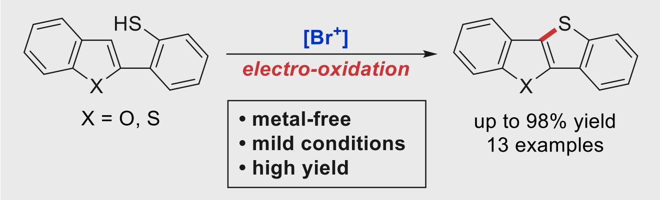

Electrochemical intramolecular C–S bond formation leading to derivatives is achieved. Bromide catalytically promoted the reaction as a halogen mediator.

Koichi Mitsudo, Ren Matsuo, Toki Yonezawa, Haruka Inoue, Hiroki Mandai, and Seiji Suga**

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Electrochemical Synthesis of Thienoacene Derivatives: Transition Metal-Free Dehydrogenative C–S Coupling Promoted by a Halogen Mediator