## Oxidative Conversion of Tetraaryldihydrodibenzothiepins into Elemental Sulfur and Stable Cationic Dyes Accompanied by Dual UV-vis and CD Spectral Changes

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Upon oxidation of the title heterocycles with dimethylamino groups, elemental sulfur is extruded to form dicationic dyes, which regenerate the heterocycles by the reaction with  $Na_2S$ . The electrolysis of the heterocycles induces a drastic change in UV–vis spectrum exhibiting several isosbestic points. The bayregion substituents enhance configurational stability, so the optically pure heterocycle can be obtained in terms of helicity of one-handedness, and its chromism is accompanied by a large chiroptical response as detected by CD spectroscopy.

Organosulfur compounds exhibit unique reactivities that are absent in the oxygen congeners. For example, redox activation of sulfur enables various transformations that are useful in organic synthesis<sup>1</sup> and materials chemistry.<sup>2</sup> Oxidation of sulfides commonly induces oxygenation of sulfur to give the corresponding sulfoxides and sulfones (eq 1).<sup>3</sup> On the other hand, desulfurization accompanied by C–S bond fission is another reaction path that is often found in the strained thiiranes.<sup>4</sup> The C–S bond in an aryl benzyl sulfide is cleaved readily under electron-transfer conditions.<sup>5</sup> Based on the facile C–S bond mesolysis,<sup>6</sup> we envisaged that the novel reaction giving elemental sulfur and two cationic species would be realized (eq 2) upon oxidation of sulfides with cation-stabilizing substituents, such as bis(triarylmethyl) sulfides **1**.

$$R_2S \xrightarrow{\text{oxdn}} R_2S=0 \xrightarrow{\text{oxdn}} R_2SO_2$$
 (1)

$$R_2S \xrightarrow{\text{oxdn}} 2R^+ + 1/8S_2$$
 (2)

Although parent bis(triphenylmethyl) sulfide has been known for a century,7 its properties and reactivities were scarcely investigated,<sup>8</sup> and only few derivatives are known to date.9 During the course of our studies on novel redox-based response systems,<sup>10</sup> we found that, upon treatment with Na<sub>2</sub>S, biphenyl-2,2'-diylbis[bis(4-dimethylaminophenyl)carbenium]  $(3a^{2+})$  was converted to  $2a^{11}$  the first member of 5,5,7,7tetraaryl-5,7-dihydrodibenzo[*c*,*e*]thiepin, which is the "clamped" analogue of bis(triarylmethyl) sulfide 1a. Here, we found that 2a as well as newly prepared 2b undergo an oxidative desulfurization, giving rise to elemental sulfur and the corresponding dicationic dyes  $3a^{2+}$  and  $3b^{2+}$ , respectively (Scheme 1); this is the successful demonstration of the reaction illustrated in eq 2. "Unclamped" sulfide 1a was also prepared from bis(4-dimethylaminophenyl)phenylcarbenium (MG<sup>+</sup>), and its properties and reactivities are also examined in this study.

When  $MG^+BF_4^-$  was allowed to react with 5 equiv of  $Na_2S$  in  $CH_3CN/H_2O/CH_2Cl_2$  (5/1/1 v/v), characteristic deep blue color of the cationic dye gradually disappeared, affording **1a**<sup>12</sup> as



**Scheme 1.** Oxidative desulfurization of bis(triarylmethyl) sulfides.

a pale colored powder in 67% yield. Similarly, "clamped" analogue **2a** was obtained upon treatment of  $3a^{2+}(BF_4^{-})2^{13}$  with 5 equiv of Na<sub>2</sub>S in CH<sub>3</sub>CN/H<sub>2</sub>O (5/1 v/v) as a white powder. The quantitative yield of 2a was accomplished despite congestion around the suflur atom by the two triarylmethyl units.<sup>11,14</sup> To minimize steric hindrance, 2a adopts a skewed conformation with a twisted biphenyl skeleton as in  $3a^{2+}$ (Figure S1).<sup>15</sup> Thus, both 2a and  $3a^{2+}$  are endowed with a chiral element of helicity and axial chirality, respectively, although interconversion between enantiomers proceeds easily at room temperature<sup>11</sup> (Scheme 2). Thiepin derivative 2b with benzyloxy groups was then designed with anticipation that the bulky bay-region substituents would increase the racemization barrier to allow optical resolution. The M enantiomer of  $2b^{12}$ was obtained in 90% yield upon Na2S-treatment of the corresponding dicationic dye salt (R)-**3b**<sup>2+</sup>(BF<sub>4</sub><sup>-</sup>)<sub>2</sub>,<sup>12</sup> which was prepared from diol (R)-4b<sup>12</sup> derived from diester (R)-5b (Scheme 3). The optically pure diester  $5b^{16}$  was facilely synthesized in a stereoselective manner and was therefore chosen as a suitable starting material in this study. All these hexabenzyloxy derivatives are configurationally stable, and there were no signs of racemization upon transformation or standing.

According to the voltammetric analyses,<sup>17</sup> sulfide **1a** and thiepins **2a** and **2b** are strong electron donors. They undergo irreversible electrochemical oxidation at  $E_{1/2} = +0.71$ , +0.57, and +0.59 V vs. SCE, respectively (Figure S2).<sup>15</sup> Upon treatment of **1a** with 3 equiv of iodine in CH<sub>2</sub>Cl<sub>2</sub>, a deep green powder of MG<sup>+</sup>I<sub>3</sub><sup>-</sup> was obtained in 92% yield. Considering



Scheme 2. Configurational stability of biphenyl moiety.



Scheme 3. Preparation of optically pure (M)-2b.

steric congestion around the sulfur atom,<sup>14</sup> the S–I bond forming process may not be an essential initiation to cause desulfurization. In fact, treatment of **1a** with (4-BrC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>N<sup>++</sup>SbCl<sub>6</sub><sup>-</sup> (2 equiv) similarly induced effective formation of cationic salt, MG<sup>+</sup>SbCl<sub>6</sub><sup>-</sup> (y. 93%). Unimolecular cleavage<sup>5</sup> of C–S bond in **1a**<sup>++</sup> would be a plausible key step to furnish MG<sup>+</sup> (Scheme S1).<sup>15</sup> Thus, the conversion of **1a** was also induced electrochemically. When the electrolysis of **1a** was conducted in CH<sub>2</sub>Cl<sub>2</sub>, a continuous change exhibiting several isosbestic points was observed by UV–vis spectroscopy (Figure 1), demonstrating that the oxidation reaction of Scheme 1a is accompanied by a chromic response with a vivid change in color from colorless to deep blue.

When thiepin **2a** was allowed to react with 3 equiv of iodine in CH<sub>2</sub>Cl<sub>2</sub>, a dark purple powder of  $3a^{2+}(I_3^{-})_2^{12}$  was obtained in 88% yield. From the filtrate, elemental sulfur was also isolated.<sup>18</sup> When the electrolysis of **2a** was conducted in CH<sub>2</sub>Cl<sub>2</sub>, a characteristic deep blue color developed, and a continuous change exhibiting several isosbestic points was observed by UV–vis spectroscopy (Figure S3).<sup>15,19</sup> Considering that the twisted  $\pi$ -systems exhibit strong circular dichroism (CD) signals by exciton coupling mechanism,<sup>20</sup> it is expected that the electrochemical oxidation of (*M*)-**2b** [ $\lambda_{ext}$  306 nm ( $\Delta \varepsilon$  + 30.3), 265 (+54.8), 243 (-67.6)] would exhibit a large change in the CD spectrum. In fact, clean conversion exhibiting isosbestic points was observed not only in the UV–vis but also



**Figure 1.** A continuous change in UV–vis spectrum upon constant current electrochemical oxidation of **1a**  $(5.0 \times 10^{-6} \text{ M})$  in CH<sub>2</sub>Cl<sub>2</sub> containing 0.05 M Bu<sub>4</sub>NBF<sub>4</sub> (5  $\mu$ A, every 4 min). The newly appeared absorptions are identical to those of MG<sup>+</sup>.



**Figure 2.** Continuous changes in UV–vis (upper) and CD (lower) spectra upon constant current electrochemical oxidation of (M)-**2b**  $(9.1 \times 10^{-6} \text{ M})$  in CH<sub>2</sub>Cl<sub>2</sub> containing 0.05 M Bu<sub>4</sub>NBF<sub>4</sub> (5  $\mu$ A, every 8 min).

in the CD spectra (Figure 2).<sup>19</sup> Thus, oxidative desulfurization reaction of title heterocycles can be accompanied by electrochiroptical response when the biphenyl moiety in 2 and  $3^{2+}$  is attached with the proper substituents (e.g., OBn) to enhance configurational stability.

Further studies on the oxidative desulfurization of the sulfides and related compounds with cation-stabilizing substituents are now in progress.

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- 17 Cyclic voltammetry was conducted in MeCN containing 0.1 M Et<sub>4</sub>NClO<sub>4</sub> as a supporting electrolye (E/V vs. SCE, Pt electrode, scan rate 100 mV s<sup>-1</sup>). The oxidation wave is irreversible in all cases, and the oxidation potentials were estimated as  $E^{\text{peak}} 0.03$  V. Ferrocene undergoes one-electron oxidation at +0.38 V under the similar conditions.
- 18 To a solution of **2a** (905 mg, 1.31 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added iodine (1.04 g, 4.10 mmol). After stirring for 24 h at room temperature, the mixture was diluted with ether. The resulting suspension was filtered to give  $3a^{2+}(I_3^{-})_2$  (1.73 g, y. 88%) as a dark purple powder. The filtrate was treated with P(OMe)<sub>3</sub> to remove remaining iodine, and chromatographic separation (Al<sub>2</sub>O<sub>3</sub>, ether) gave elemental sulfur (12.9 mg), which corresponds to 31% of the calculated amount according to eq 2.
- 19 The newly appeared absorptions are not identical to those of dication 3<sup>2+</sup> (ref 15) since the C–S mesolysis of 2<sup>•+</sup> would afford a cationic intermediate that needs further oxidation to cleave another C–S bond before furnishing 3<sup>2+</sup> (Scheme S1) (ref 15).
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