

## Formation and Isolation of the Dithioether Dications of Cyclic Dithioethers in the Reactions of the Corresponding *S*-Oxides and *S*-Imine in Concentrated Sulfuric Acid

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The dithioether dication of 1,5-dithiacyclooctane (1,5-DTCO) is formed in the reaction of the corresponding *S*-oxide and *S*-imine with concentrated H<sub>2</sub>SO<sub>4</sub>; it can be isolated in crystalline form. In the cyclic six-, nine-, and ten-membered ring and acyclic dithioethers, the reaction of the corresponding *S*-oxides with concentrated H<sub>2</sub>SO<sub>4</sub> similarly affords the dithioether dications. All were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Furthermore, the cyclic dithioether dication bearing benzylic carbon (a dibenzodithiocin derivative) can be generated in the reaction of the corresponding *S*-oxide with concentrated H<sub>2</sub>SO<sub>4</sub>.

Electron transfer from sulfides to generate the corresponding cation radicals is an important phenomenon in chemical and biological redox reactions, and the intermediacy of cation radicals and dications of thioethers has been extensively studied.<sup>1-8</sup> We have previously reported the isolation of the crystalline dithioether dication of 1,5-dithiacyclooctane (1,5-DTCO) from the reaction of 1,5-DTCO 1-oxide or 1-imine with concentrated H<sub>2</sub>SO<sub>4</sub>.<sup>9</sup> We have also reported formation of the dication of the dibenzodithiocin by the same reaction.<sup>10</sup> We have also found that the Pummerer reaction of 1,5-DTCO 1-oxide with acetic anhydride takes place via the dithioether dication.<sup>11</sup> These results indicate that when a positive charge develops on one sulfur atom in appropriate cyclic dithioethers, transannular interaction occurs with the second sulfur atom.

This paper describes <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic evidence for formation of dications in the reaction of several cyclic and acyclic dithioether mono-*S*-oxides or *S*-imine and their deuteriated derivatives with concentrated H<sub>2</sub>SO<sub>4</sub>.

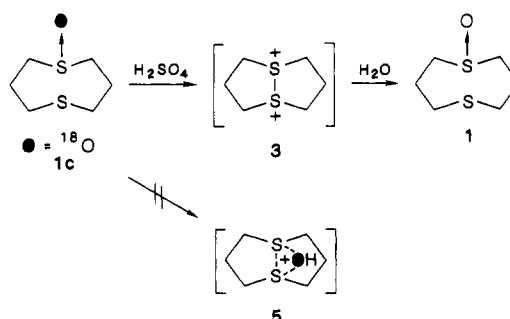
When 1,5-DTCO 1-oxide (1) was dissolved in 98% D<sub>2</sub>SO<sub>4</sub>, the solution became pale yellow, and <sup>1</sup>H and <sup>13</sup>C NMR spectra of the solution were recorded immediately. The signals of 1 previously observed in CDCl<sub>3</sub> disappeared, and two sets of new peaks appeared at δ 4.32-3.40 and 3.32-2.10 in a 2:1 ratio (Figure 1). Musker et al.<sup>1</sup> reported that the dication (BF<sub>4</sub>) salt has broad <sup>1</sup>H NMR signals at δ 4-2 in CD<sub>3</sub>CN, while his <sup>13</sup>C NMR spectra agreed roughly with ours. These spectra of 1,5-DTCO in D<sub>2</sub>SO<sub>4</sub> did not change after standing for 24 h at room temperature (Table I). Treatment of the D<sub>2</sub>SO<sub>4</sub> solution of 1 with water and workup led to the starting *S*-oxide 1 in 72% yield. Similar treatment of 2,2,8,8-tetradeuterio-1,5-dithiacyclooctane 1-oxide (1a) in D<sub>2</sub>SO<sub>4</sub> showed similar chemical shifts in the <sup>1</sup>H NMR spectra, but the peak ratio was 1:1 (Figure

**Table I. NMR Spectral Data for Compounds 1, 2, 3, 7, 8, 8c, 9, 10, 13, 14, 15, 16, and 17<sup>a</sup>**

1	<sup>1</sup> H: 3.23-3.04 [m, 4 H, S(O)CH <sub>2</sub> ], 2.76-2.54 (m, 4 H, SCH <sub>2</sub> ), 2.43-2.18 (m, 4 H, CH <sub>2</sub> ) <sup>13</sup> C: 56.6, 30.2, 23.7
2	<sup>1</sup> H: 7.81 (d, 2 H, <i>J</i> 6.6 Hz, ArH), 7.23 (d, 2 H, <i>J</i> = 6.6 Hz, ArH), 3.41-3.22 [m, 4 H, S(NTs)CH <sub>2</sub> ], 2.78-2.54 (m, 4 H, SCH <sub>2</sub> ), 2.39 (s, 3 H, Me), 2.39-2.17 (m, 4 H, CH <sub>2</sub> ) <sup>13</sup> C: 50.8, 30.4, 25.3 for ring carbon
3	<sup>1</sup> H: 4.32-3.40 (br m, 8 H, S <sup>+</sup> CH <sub>2</sub> ), 3.32-2.10 (br m, 4 H, CH <sub>2</sub> ) <sup>13</sup> C: 56.3, 38.6
7	<sup>1</sup> H: 3.53-2.86 [m, 4 H, S(O)CH <sub>2</sub> ], 2.86-2.51 (m, 4 H, SCH <sub>2</sub> ), 2.51-1.51 (m, 6 H, CH <sub>2</sub> ) <sup>13</sup> C: 47.5, 46.1, 31.9, 29.2, 26.2, 19.1, 17.4
8	<sup>1</sup> H: 3.72-2.90 [m, 4 H, S(O)CH <sub>2</sub> ], 2.90-2.62 (m, 4 H, SCH <sub>2</sub> ), 2.29-1.57 (m, 8 H, CH <sub>2</sub> ) <sup>13</sup> C: 49.9, 31.8, 25.7, 19.6
8c	<sup>1</sup> H: 4.14-3.29 (br m, 8 H, S <sup>+</sup> CH <sub>2</sub> ), 2.31-1.25 (br m, 8 H, CH <sub>2</sub> )
9	<sup>1</sup> H: 3.02-2.53 (m, 4 H, CH <sub>2</sub> ), 2.59 [s, 3 H, S(O)Me], 2.37-1.90 (m, 2 H, CH <sub>2</sub> ), 2.12 (s, 3 H, SMe)
10	<sup>1</sup> H: 3.77-3.43 (m, 2 H, SCH <sub>2</sub> -a), 3.22-2.91 [m, 4 H, S(O)CH <sub>2</sub> ], 2.70-2.40 (m, 2 H, SCH <sub>2</sub> -e) <sup>13</sup> C: 46.9, 18.8
13	<sup>1</sup> H: 7.64-6.77 (m, 8 H, Ph), 5.11, 4.08 [AB q, <i>J</i> = 14 Hz, S(O)CH <sub>2</sub> ], 4.15, 3.96 (AB q, <i>J</i> = 14 Hz, SCH <sub>2</sub> ) <sup>13</sup> C: 61.3, 35.6 for methylene carbon
14	<sup>1</sup> H: 7.82-6.96 (m, 8 H, Ph), 5.61, 5.17 (AB q, <i>J</i> = 15.6 Hz, S <sup>+</sup> CH <sub>2</sub> ) <sup>13</sup> C: 63.6 for methylene carbon
15	<sup>1</sup> H: 8.30-8.01 (m, 2 H, Ph), 7.69-7.01 (m, 6 H, Ph), 4.56, 3.87 (AB q, <i>J</i> = 15 Hz, SCH <sub>2</sub> )
16	<sup>1</sup> H: 7.92-6.98 (m, 8 H, Ph), 5.57, 5.20 (AB q, <i>J</i> = 15 Hz, S <sup>+</sup> CH <sub>2</sub> )
17	<sup>1</sup> H: 7.96-7.15 (m, 8 H, Ph), 5.64, 4.18 [AB q, <i>J</i> = 12 Hz, S(O)CH <sub>2</sub> ], 4.06, 3.82 [AB q, <i>J</i> = 13 Hz, S(O)CH <sub>2</sub> ]

<sup>a</sup> <sup>1</sup>H and <sup>13</sup>C data (δ) for the sulfoxides in CDCl<sub>3</sub>, relative to Me<sub>4</sub>Si; data for dications in D<sub>2</sub>SO<sub>4</sub> relative to sodium 4,4-dimethyl-4-silapentanesulfonate (DSS).

**Scheme I**



2). Treatment of the D<sub>2</sub>SO<sub>4</sub> solution of deuteriated sulfoxide 1a with water led to 76% recovery of the *S*-oxide. The <sup>1</sup>H NMR spectrum of the recovered sulfoxide indi-

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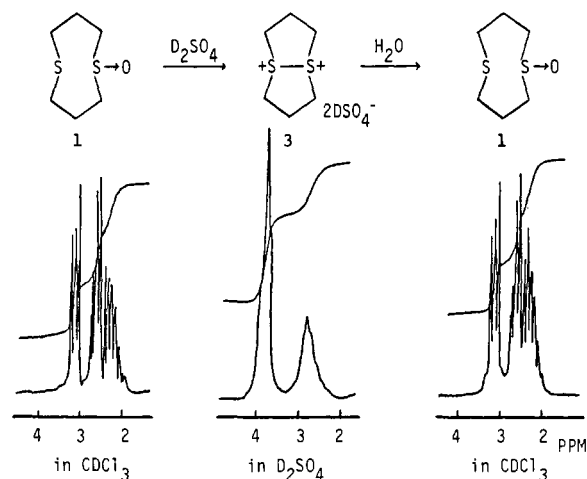
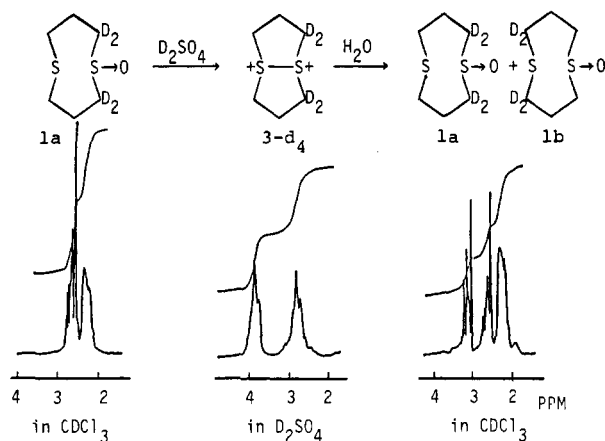
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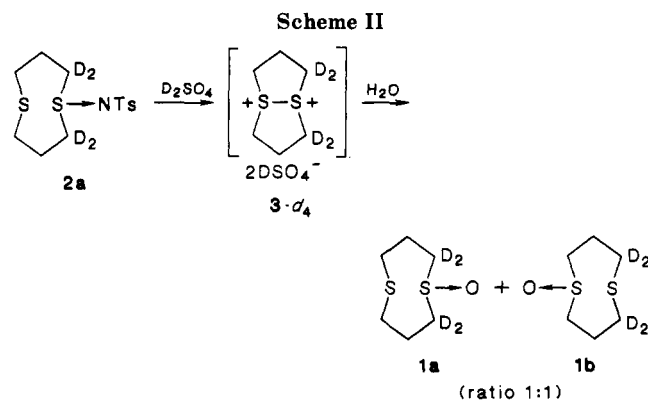
Figure 1.  $^1\text{H}$  NMR spectra.Figure 2.  $^1\text{H}$  NMR spectra.

cated that it was a 1:1 mixture of **1a** and the 4,4,6,6-tetradeuteriated sulfoxide (**1b**) and also that no H-D exchange with  $\text{H}_2\text{SO}_4$  took place during the reaction. These results indicate that sulfoxides **1** and **1a** are converted into the symmetrical intermediate dications **3** and **3-d<sub>4</sub>**. Hydrolysis of dication **3** should give a 1:1 mixture of **1a** and **1b** if water attacks equally the two sulfur atoms of the dication **3-d<sub>4</sub>**.

Although the results seem to indicate the formation of the dithioether dication from **1** in  $\text{H}_2\text{SO}_4$ , they could also be explained by formation of the symmetrical oxydisulfonium salt **5** (Scheme I). To explore this alternative,  $^{18}\text{O}$ -labeled dithioether 1-oxide (**1c**,  $^{18}\text{O}$  content 42.1 excess atom %) was synthesized and dissolved in concentrated  $\text{H}_2\text{SO}_4$ . If the oxydisulfonium salt **5** was formed as an intermediate, the  $^{18}\text{O}$  label should remain more or less on the recovered sulfoxide after treatment of the  $\text{H}_2\text{SO}_4$  solution with water. However, upon treatment of the  $\text{H}_2\text{SO}_4$  solution of **1c** with cold anhydrous diethyl ether and subsequently with ice-water, no  $^{18}\text{O}$  was incorporated into the recovered sulfoxide as shown by mass spectrometry. This result seems to rule out the formation of **5** and is consistent with conversion of **1c** into the dication **3**.

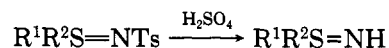
The dithioether dication **3** of 1,5-DTCO was isolated by pouring its  $\text{H}_2\text{SO}_4$  solution into ice-cooled anhydrous diethyl ether, whereupon colorless crystals of **3** precipitated. The crystalline salt was very hygroscopic, becoming liquid on exposure to air; it was identified as the bis(hydrogen sulfate) salt **4** of the dication of 1,5-DTCO. Hydrolysis of salt **4** gave the starting *S*-oxide **1**.

The ESR spectrum of the  $\text{H}_2\text{SO}_4$  solution of **1** showed signals due to the cation radical **6** of 1,5-DTCO and was



consistent with that reported by Musker.<sup>12</sup> On the other hand, the UV spectra of  $\text{H}_2\text{SO}_4$  solutions of **1** showed absorption maxima of the dication at 230 nm (lit.<sup>1</sup> 233 and 212 nm) but no absorption due to a radical cation at 420 nm. We assume that the intermediate in this reaction is mainly the dithioether dication **3** in equilibrium with a low concentration of the cation radical **6**. Glass and Wilson<sup>13</sup> suggested from electrochemical studies that it is easier to remove an electron from 1,5-DTCO cation radical than from 1,5-DTCO itself, hence the cation radical **6** should be oxidized easily to the dication **3**.

Similarly, 1,5-DTCO *N*-tosylimine (**2**) was dissolved in 98%  $\text{D}_2\text{SO}_4$  and the  $^1\text{H}$  NMR spectrum of this solution was taken immediately. The chemical shifts observed agreed well with those expected for a 1:1 mixture of dication **3** and *p*-toluenesulfonamide (Table I), although in general *N*-tosylimines undergo cleavage of the N-S bond to afford the corresponding *S*-imines on treatment with concentrated  $\text{H}_2\text{SO}_4$ .<sup>14</sup> Hydrolysis of the  $\text{D}_2\text{SO}_4$  solution of *S*-



imine **2** gave the *S*-oxide **1** in 81% yield. These results suggest that *S*-imine **2** is converted directly into the dithioether dication **3** by transannular S-S interaction instead of by cleavage of the N-S bond, since **2** has a conformationally feasible structure for this interaction. X-ray crystallographic analysis of **2** indicates that the ring has a boat-chair conformation with a short transannular S...S contact of 3.143 Å, which is considerably shorter than the sum of the S...S van der Waals radii (3.70 Å).<sup>15</sup> Other relatively strong transannular S...S interactions in 1,5-DTCO derivatives have been reported.<sup>22,23</sup>

2,2,8,8-Tetradeuterio-1,5-dithiacyclooctane *N*-tosylimine (**2a**) was dissolved in 98%  $\text{D}_2\text{SO}_4$ , and treatment of the solution with water and workup led to quantitative recovery of a 1:1 mixture of **1a** and **1b** (Scheme II).

The cyclic dithioether *S*-oxides 1,5-dithiacyclononane 1-oxide (**7**) and 1,6-dithiacyclodecane 1-oxide (**8**) and their tetradeuterio derivatives **7a** and **8a** were treated with 98%  $\text{H}_2\text{SO}_4$  and  $\text{D}_2\text{SO}_4$  in the same manner as **1**. The  $^1\text{H}$  NMR spectra of the  $\text{H}_2\text{SO}_4$  solution of **8** and **8a** could be explained by the formation of dication **8c** of 1,6-dithiacyclodecane, but the  $^1\text{H}$  NMR spectra of  $\text{H}_2\text{SO}_4$  solutions of **7** and **7a** were complex (Table I). Hydrolysis of the  $\text{D}_2\text{SO}_4$  solutions of **7a** and **8a** gave 1:1 mixtures of deuteriated *S*-oxides analogous to **1a** and **1b**. These results indicate

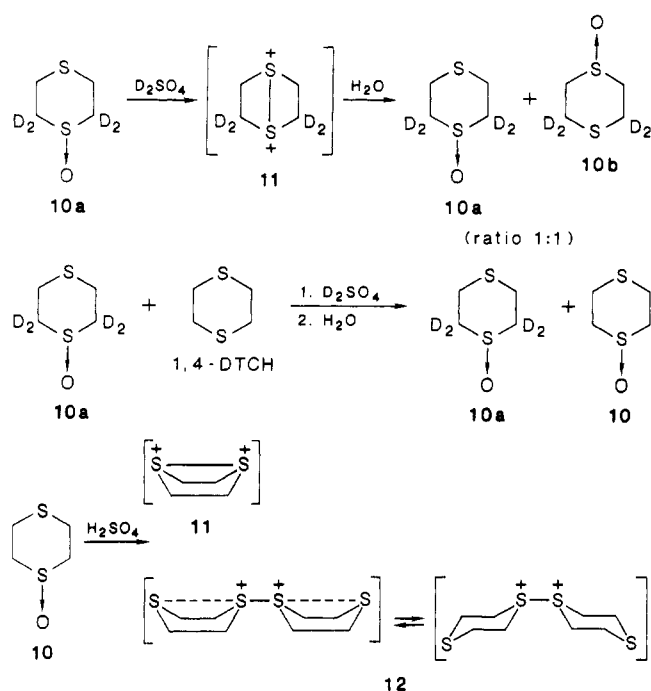
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Scheme III

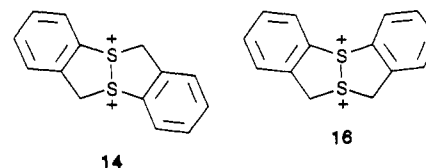


that dications can be formed in nine- and ten-membered ring dithioethers.

Similar results were obtained when the acyclic compound 1,1,1,3,3-pentadeuterio-2,6-dithiaheptane 2-oxide (**9a**) was dissolved in  $D_2SO_4$ ; sulfoxides analogous to **1a** and **1b** were obtained on hydrolysis of the  $D_2SO_4$  solution.

In 1,4-dithiacyclohexane 1-oxide (**10**), transannular interaction of the two sulfur atoms at 1,4 positions should be minimal. Compound **10** was dissolved in 98%  $D_2SO_4$ , and the  $^1H$  and  $^{13}C$  NMR spectra were taken immediately. These spectra showed complex multiplets, and their signals could not be assigned. Nevertheless, when the  $D_2SO_4$  solution was treated with water, only the starting sulfoxide **10** was obtained. 2,2,6,6-Tetradeuterio-1,4-dithiacyclohexane 1-oxide (**10a**) was synthesized and dissolved in concentrated  $D_2SO_4$ . The  $^1H$  NMR spectrum similarly showed unassignable multiplets. However, surprisingly a 1:1 mixture of sulfoxides **10a** and 3,3,5,5-tetradeuterio-1,4-dithiacyclohexane 1-oxide (**10b**) was obtained by hydrolysis of the  $D_2SO_4$  solution (Scheme III). The  $^1H$  NMR spectrum of the mixture of **10a** and **10b** is consistent with that of the mixture of sulfoxides obtained by oxidation of 2,2,6,6-tetradeuterio-1,4-dithiacyclohexane. Furthermore, **10a** was treated with  $D_2SO_4$  in the presence of an equimolar amount of 1,4-dithiacyclohexane (1,4-DTCH). The  $^1H$  NMR spectrum was so complex that it could not be analyzed. When this  $D_2SO_4$  solution was treated with water, a 1:1 mixture of **10a** and undeuterated 1,4-dithiacyclohexane *S*-oxide was obtained. The ratio was determined by mass spectrometry. However, no sulfoxide **10** was obtained by hydrolysis of a solution of 1,4-DTCH in concentrated  $H_2SO_4$ ; 1,4-DTCH was recovered quantitatively. These results suggest that the reaction of **10** in  $H_2SO_4$  leads to both intramolecular (**11**) and intermolecular (**12**) S-S bonded intermediates (Scheme III). Asmus et al.<sup>16</sup> reported the formation of 1,4-DTCH cation radical with an intramolecular S-S bond when 1,4-DTCH was oxidized with hydroxyl radical generated by pulse radiolysis at low concentration of sulfide.

When 6*H*,12*H*-dibenzo[*b,f*]-1,5-dithiocin *S*-oxide (**13**) was dissolved in 98%  $D_2SO_4$  the solution became yellow, and the reaction was followed immediately by  $^1H$  and  $^{13}C$  NMR spectroscopy. In the  $^1H$  NMR spectrum, two methylene signals adjacent to the sulfenyl and sulfinyl groups for **13** in  $CDCl_3$  disappeared and new AB quartets appeared which must be the benzylic methylene of **14**. In



the  $^{13}C$  NMR spectrum, two signals due to the corresponding methylene carbon atoms in **13** in  $CDCl_3$  coalesced into one singlet in  $D_2SO_4$  (Table I). Treatment of the  $D_2SO_4$  solution of **13** with ice-water and workup afforded only the original mono-*S*-oxide **13** in 82% isolated yield. Similar treatment of the deuterated *S*-oxide **13a** in  $D_2SO_4$  led to similar changes in the  $^1H$  NMR spectrum, and hydrolysis led to 80% recovery of the *S*-oxide. The  $^1H$  NMR spectrum indicated a 1:1 mixture of the 6,6- and 12,12-dideuterated *S*-oxides analogous to **1a** and **1b**. No H-D exchange of **13a** with  $H_2SO_4$  was observed. These results demonstrate clearly that **13** and **13a** are converted into symmetrical intermediate dications.

In a similar way, the reaction of 5*H*,7*H*-dibenzo[*b,g*]-1,5-dithiocin 12-oxide (**15**) with concentrated  $D_2SO_4$  was followed by  $^1H$  NMR spectroscopy, and the spectra suggest the formation of a symmetrical dication **16** analogous to **3**. Treatment of this solution with water afforded the oxygen-migrated *S*-oxide 5*H*,7*H*-dibenzo[*b,g*]-1,5-dithiocin 6-oxide (**17**) in good yield, and no **15** could be detected.

## Experimental Section

**Physical Measurements.** Electronic absorption spectra were recorded on a Hitachi Model 200-20 spectrophotometer.  $^1H$  NMR spectra were measured on a Hitachi R-600 FT NMR spectrometer.  $^{13}C$  NMR spectra were recorded on JEOL-FX100 spectrometer. The IR spectra were obtained on a JASCO A-3 spectrometer. ESR spectra were determined on a JEOL-ME spectrometer. Mass spectra were taken with a Hitachi RMU-6MG mass spectrometer. Elemental analyses were carried out by the Chemical Analysis Center at this University.

**Materials.** All reagents were obtained from Wako Pure Chemical Industries, Ltd., Tokyo Kasei Co. Ltd., or Aldrich Chemical Co. The reagents used as reaction solvents were further purified by general methods.

**Preparation of Mesocyclic or Acyclic Dithioethers.** 1,5-Dithiacyclooctane was synthesized by a modification of the method of Meadow and Reid;<sup>17</sup> yield 29%; bp 97–100 °C/3 mmHg [lit.<sup>17</sup> bp 245–246 °C].

1,5-Dithiacyclononane was synthesized by a modification of the method of Musker et al.;<sup>1</sup> yield 6%; mp 58.5–60.0 °C (lit.<sup>1</sup> mp 58.5–60.0 °C).

1,6-Dithiacyclodecane was synthesized by a modification of the procedure of Ochrymowycz et al.;<sup>18</sup> yield 3%; mp 92.0–93.5 °C.

2,6-Dithiaheptane was synthesized by a modification of the procedure of Protina et al.;<sup>19</sup> yield 45%; bp 64.0 °C/5 mmHg [lit.<sup>19</sup>

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bp 92 °C/15 mmHg].

**6*H*,12*H*-Dibenzo[*b,f*][1,5]dithiocin** was synthesized by a modification of the method of Ollis et al.<sup>20</sup> yield 31%; mp 174–175 °C [lit.<sup>20</sup> mp 170–173 °C].

**5*H*,7*H*-Dibenzo[*b,g*][1,5]dithiocin** was prepared by a modification of the method of Ollis et al.<sup>21</sup> yield 55%; mp 129–130 °C [lit.<sup>21</sup> mp 128–130 °C].

**Dithioether mono-*S*-oxides** were obtained by oxidation using NaIO<sub>4</sub> or *m*-chloroperbenzoic acid (*m*-CPBA). The <sup>1</sup>H and <sup>13</sup>C NMR data are described in Table I. The melting points and spectroscopic data for the sulfoxides are listed below:

**1,5-Dithiacyclooctane 1-oxide (1):** yield 96%; mp 27–29 °C; IR (neat) 1010 cm<sup>-1</sup> (S=O).

**1,5-Dithiacyclononane 1-oxide (7):** yield 71%; mp 75.0–76.5 °C; IR (KBr) 1010 cm<sup>-1</sup> (S=O).

**1,6-Dithiacyclodecane 1-oxide (8):** yield 57%; mp 68.5–70.0 °C; IR (KBr) 1030 cm<sup>-1</sup> (S=O).

**2,6-Dithiaheptane 2-oxide (9):** yield 65%; IR (KBr) 1040 cm<sup>-1</sup> (S=O).

**1,4-Dithiacyclohexane 1-oxide (10):** yield 36%; mp 125.5–127.0 °C; IR (KBr) 1020 cm<sup>-1</sup> (S=O).

**6*H*,12*H*-Dibenzo[*b,f*][1,5]dithiocin 1-oxide (13):** yield 72%; mp 119 °C; IR (KBr) 1038 cm<sup>-1</sup> (S=O). Anal. calcd for C<sub>14</sub>H<sub>12</sub>OS<sub>2</sub>: C, 64.58; H, 4.64. Found C, 64.44; H, 4.62.

**5*H*,7*H*-Dibenzo[*b,g*][1,5]dithiocin 6-oxide (17):** yield 83%; mp 178–180 °C; IR (KBr) 1075, 1040 cm<sup>-1</sup>. Anal. Calcd for C<sub>14</sub>H<sub>12</sub>OS<sub>2</sub>: C, 64.58; H, 4.64. Found: C, 64.51; H, 4.65.

**5*H*,7*H*-Dibenzo[*b,g*][1,5]dithiocin 12-oxide (15)** was prepared by cyclization of the corresponding bis(*o*-(bromomethyl)phenyl) sulfoxide with sodium sulfide hydrate in ethanol: yield 78%; mp 195–196 °C; IR (KBr) 1078, 1040 cm<sup>-1</sup> (S=O). Anal. Calcd for C<sub>14</sub>H<sub>12</sub>OS<sub>2</sub>: C, 64.58; H, 4.64. Found: C, 64.50; H, 4.61.

**Preparation of 1,5-Dithiacyclooctane *N*-Tosylimine (2).** To a stirred solution of 1,5-dithiacyclooctane (0.74 g, 5 mmol) in 10 mL of ethanol was added dropwise a solution of *N*-chloro-4-methylbenzenesulfonamide sodium salt (Chloramine-T) (1.55 g, 5.5 mmol) in 10 mL of ethanol. The mixture was stirred at room temperature for 5 h. After the mixture was filtered and concentrated, the residue was recrystallized from ethanol to give 1.30 g of compound 2: yield 82%; mp 175–178 °C; IR (KBr) 1270, 1140 (S=O), 1000 cm<sup>-1</sup> (S=N). Anal. Calcd for C<sub>13</sub>H<sub>19</sub>O<sub>2</sub>NS<sub>2</sub>: C, 49.18; H, 6.01; N, 4.41. Found: C, 49.11; H, 6.02; N, 4.38. The <sup>1</sup>H and <sup>13</sup>C NMR spectra are described in Table I.

#### Preparation of Deuteriated Dithioether Mono-*S*-oxide.

A typical procedure is as follows: To a ca. 40% solution of sodium deuterium oxide in 3 mL of deuterium oxide (D content 99.8%) was added a solution of 1 (199 mg, 1.21 mmol) in 1 mL of deuterium oxide. After the mixture was stirred under a N<sub>2</sub> atmo-

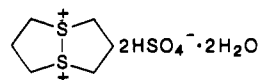
sphere at 100 °C for 24 h, the solvent was concentrated under reduced pressure. The mixture was extracted with chloroform. The combined organic phase was dried over anhydrous MgSO<sub>4</sub>. After removing the solvent, the residue was separated with alumina column chromatography using chloroform affording 200 mg of 2,2,8,8-tetradeuterio-1,5-dithiacyclooctane 1-oxide (1a). The content of deuterium was >95% as determined by <sup>1</sup>H NMR spectroscopy.

**Preparation of Deuteriated Compounds 2a and 13a.** The deuteration was accomplished by heating 13 with NaOD–D<sub>2</sub>O–tetrahydrofuran in a sealed tube at 85 °C for 7 h; deuterium content of 13a was >95 atom %. The compound 2a was prepared in a similar way: deuterium content 81 atom %.

**Preparation of <sup>18</sup>O-Labeled 1,5-Dithiacyclooctane 1-Oxide (1c).** To a solution of 1,5-dithiacyclooctane (32.8 mg, 0.22 mmol) in 0.1 mL of acetic acid were added 0.1 mL of H<sub>2</sub><sup>18</sup>O (<sup>18</sup>O content = 98 atom %) and the bromine complex of 1,4-diazabicyclo[2.2.2]octane (48.0 mg, 0.11 mmol). The heterogeneous mixture was stirred under a N<sub>2</sub> atmosphere at room temperature for 0.5 h. After removing the solvent, the residue was separated with alumina column chromatography using chloroform as eluent affording the crude product. The crude product was further purified with preparative liquid chromatography to give 21.8 mg of <sup>18</sup>O-labeled 1,5-dithiacyclooctane 1-oxide (1c). <sup>18</sup>O content was 42.1 excess atom % by mass spectroscopy.

**Oxidation of 2,2,6,6-Tetradeuterio-1,4-dithiacyclohexane (18).** The oxidation of compound 18 was carried out with NaIO<sub>4</sub> in MeOH–H<sub>2</sub>O. The *S*-oxides 10a and 10b were obtained in a 1:1 ratio by <sup>1</sup>H NMR spectroscopy. The sulfide 18 was prepared by the reduction of 10a using lithium aluminum deuteride in tetrahydrofuran: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.01–2.82 (br s, 4 H, SCH<sub>2</sub>).

**Isolation of Dithioether Dication 4 of 1,5-DTCO.** Compound 1 was dissolved in concentrated H<sub>2</sub>SO<sub>4</sub>; then the solution was poured into ice-cooled anhydrous diethyl ether and colorless crystals formed. The crystals were collected, washed with anhydrous diethyl ether, and dried under reduced pressure. The colorless crystals were very hygroscopic and were identified as the salt of dithioether dication 4 of 1,5-DTCO. 4: mp 66–69 °C. Anal. Calcd for C<sub>8</sub>H<sub>18</sub>O<sub>10</sub>S<sub>4</sub>: C, 19.04; H, 4.26. Found: C, 18.93; H, 4.22.



**Observation of Cation Radical of 1,5-DTCO.** In a degassed and sealed ESR tube, compound 1 was dissolved in concentrated H<sub>2</sub>SO<sub>4</sub>. The ESR spectrum was obtained by using a JEOL-ME spectrometer. Temperature, room temperature; field; 3268 + 50 G; gain, 5 × 100; response, 1 s; mod. width, 2.0 × 1 G; power, 1.4 mW; sweep time, 10 min.

(23) Musker, W. K.; Olmstead, M. M.; Goodrow, M. H. *Acta Crystallogr., Sect. C* 1983, C39, 887.