Anomalous Ring Cleavage of 1,3-Dithiole- and 1,3-Diselenole-2-thiones under the Cross-Coupling Conditions Using Triethyl Phosphite

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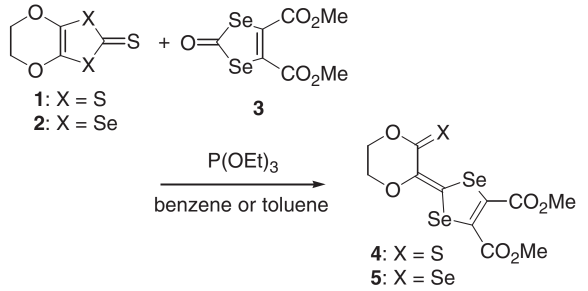
(Received February 23, 2004; CL-040200)

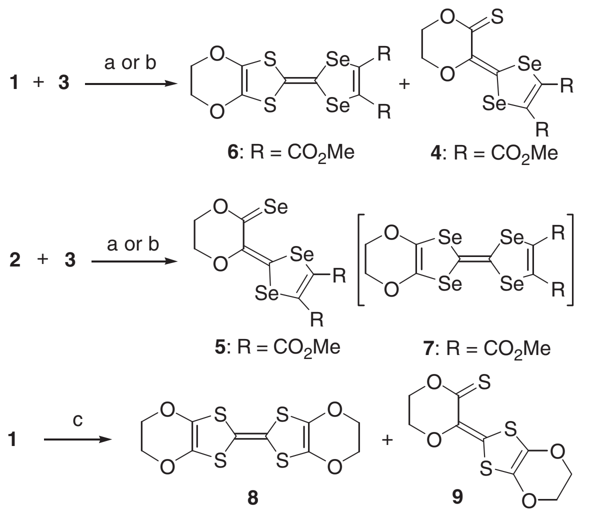
The ring cleavage of 4,5-ethylenedioxy-1,3-dithiole- and -1,3-diselenole-2-thiones, followed by the reaction with 4,5-bis(methoxycarbonyl)-1,3-diselenole-2-one took place under the phosphite-mediated cross-coupling conditions to afford 2-thioxo- and 2-(selenoxomethylidene)-1,3-diselenoles. The structure of 4,5-bis(methoxycarbonyl)-2-(thioxoalkylidene)-1,3-diselenole was confirmed by X-ray analysis.

There has been considerable interest in 1,3-dithioles and 1,3-diselenoles as synthetic blocks for constructing organic metals, organic ferromagnets, and other functional organic systems.[1] Thus, 2-methylidene-1,3-dithioles and dihydro-TTF derivatives have been employed as the donor units for highly conductive organic metals,[2] and a number of tetrathiafulvalene (TTF) and tetraselenafulvalene (TSF) derivatives containing alkylidene-1,3-dithiole and -1,3-diselenole units have been prepared to improve donor properties of TTF and TSF.[1] We recently found that the cross-coupling of 4,5-ethylenedioxy-1,3-dithiole or -1,3-diselenole-2-thiones (**1** or **2**) with 4,5- bis(methoxycarbonyl)-1,3-diselenol-2-one (**3**) using triethyl phosphite produces 2-(thioxomethylidene)- and 2-(selenoxomethylidene)-1,3-diselenoles (**4** or **5**) (Scheme 1). We report here the anomalous ring cleavage and coupling pathway, together with related reactions.



Scheme 1. Cross-coupling of the thione (**1** or **2**) with **3** using P(OEt)$_3$.

The cycloaddition of 3-thioxo-1,2-dithioles to acetylenedicarboxylate was reported to produce 2-(thioxoalkylidene)-1,3-dithioles.[3] Since this cycloaddition can be applied for the synthesis of both TTF vinylogues and useful sulfur-rich molecules, many related reactions have been reported until now.[4,5] In addition, tetrathiafulvaleno-quinone and -thioquinonemethides have been synthesized by Sugimoto et al. and the conducting and magnetic properties of their radical salts have been recently reported.[6] Taking into account the utility of 2-(thioxoalkylidene)-1,3-dithioles, 2-(selenoxomethylidene)-1,3-diselenoles can be expected to have potential multi-functionality. However, the cycloaddition methodology is unable to apply for the synthesis of the corresponding 1,3-diselenole derivatives, because of the difficulty in preparing 3-selenoxo-1,2-diselenoles.



Scheme 2. The reaction of the thione (**1** or **2**) with **3** in the presence of P(OEt)$_3$. Reagents and conditions: a) P(OEt)$_3$, toluene, reflux; b) P(OEt)$_3$, benzene, reflux; c) P(OEt)$_3$, 65 °C.

The phosphite-mediated cross-coupling of a 1,3-dithiole-2-thione containing an electron-donating substituent with a 1,3-dithiol-2-one containing an electron-withdrawing substituent results in the formation of the corresponding TTF derivative in a good yield as compared with a similar reaction of a 1,3-dithiol-2-one containing an electron-donating substituent with a 1,3-dithiole-2-thione containing an electron-withdrawing substituent.[7] By considering this selectivity in the phosphite-mediated cross-coupling, together with the reported procedure,[8] we carried out the synthesis of ethylenedioxy-1,3-diselena-1′,3′-dithiafulvalene diester (**6**). The reaction of **1** (1 equiv.) with **3**[9] (1.5 equiv.) in the presence of P(OEt)$_3$ (10 equiv.) in refluxing toluene for 2 h afforded **6** in 37% yield, together with an unexpected product **4** in 30% yield (Scheme 2).[10] In a similar manner, the P(OEt)$_3$-mediated reaction of **1** with **3** in refluxing benzene for 8 h gave **4** and **6** in 30 and 29% yields, respectively. In the P(OEt)$_3$-mediated coupling of **3** with **2**, which was prepared from 3,4-dibromodioxene in moderate yields,[11] the reaction in refluxing toluene or benzene led to **5** in 19 or 52% yield without the formation of the TSF derivative **7**. It was reported that the phosphite-mediated coupling of **1** produced BEDO-TTF (**8**) in low yields,[12] although the corresponding selone afforded **8** in moderate yields.[13] Under our reaction conditions, a solution of **1** in P(OEt)$_3$ (4 equiv.) was heated at 65 °C for 8 h to yield **8** (37%), together with **9** (15%). Thus, the formation of **9** suppressed the yield of **8**. The products **4**, **5**, and **9** are stable crystalline compounds, and can be stored at room temperature without decomposition.

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2-(Thioxomethylidene)-1,3-diselenole derivative **4** was recrystallized from CCl_4-methanol to afford orange single crystals. To determine the structure of **4**, the X-ray analysis was carried out.[14] As shown in Figure 1, the crystal lattice includes four crystallographically independent molecules, i.e., two pairs of the dimerized molecules (**A**···**B** and **C**···**D**), which form a column structure along the *c*-axis. The 2-thioxomethylidene units of these four molecules are almost planar, and the face-to-face distances **A**···**B**, **B**···**A′**, **C**···**D**, and **D**···**C′** are 3.84, 3.90, 3.68, and 4.07 Å, respectively. The four molecules show intramolecular Se···S contacts [Se(1)···S(1) 2.950(6), Se(3)···S(2) 2.936(6), Se(5)···S(3) 2.946(6), and Se(7)···S(4) 2.941(6) Å], which are much shorter than the Se···S van der Waals distance (3.85 Å). In addition, there are intermolecular Se···Se contacts [Se(2)···Se(3) 3.979(3) and Se(5)···Se(8) 3.977(3) Å], which may contribute to form the column structure.

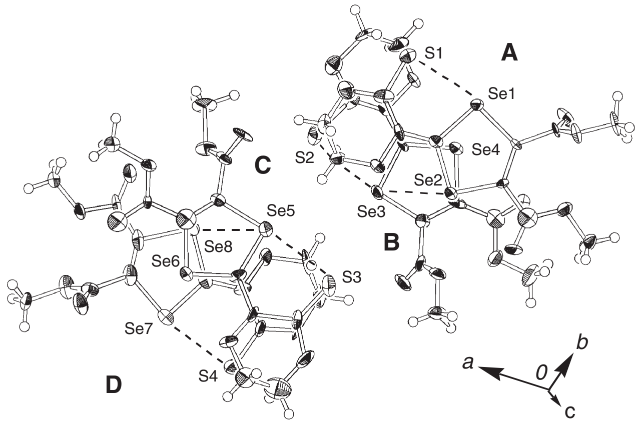

Figure 1. Crystal structure of **4**. Dotted lines indicate the Se···Se and Se···S short contacts.

Interestingly, **4**, **5**, and **9** produce the corresponding cation radicals. Thus, these molecules show an irreversible redox wave in the cyclic voltammetric analysis [**4**: $E_{\mathrm{p,ox}} = 0.77$ V, **5**: $E_{\mathrm{p,ox}} = 0.72$ V, and **9**: $E_{\mathrm{p,ox}} = 0.36$ V vs Fc/Fc^+].[15] The cation radicals derived from **4**, **5** and **9** may be stabilized by both the 1,3-diselenole or 1,3-dithiole ring and the vinylic oxygen.

Although the reaction mechanism for the formation of **4**, **5**, and **9** is not yet clear, the initial attack of $P(OEt)_3$ may take place on the thiocarbonyl group in **1** or **2** to cleave the adjacent C–S or C–Se bond. The phosphite mediated cross-coupling of the ring-cleaved intermediates with **1** or **3** results in the formation of **4**, **5**, or **9**.

The authors are grateful to Dr. Masashi Hasegawa for the X-ray analysis of **4** and to Dr. Yoshiyuki Kuwatani for helpful discussions. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas of Exploitation of Multi-Element Cyclic Molecules (No. 14044086) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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10 Physical and spectroscopic data. **4**: orange prisms, mp 144–145 °C, MALDI–TOF MS m/z 430 (M^+); ^1H NMR ($CDCl_3$) δ 4.58–4.56 (m, 2H), 4.38–4.36 (m, 2H), 3.90 (s, 3H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 186.47, 163.16, 162.00, 143.33, 142.96, 138.95, 137.10, 69.35, 64.02, 53.52, 53.38; UV–vis/CH_2Cl_2 $\lambda_{\max}$ ($\log \varepsilon$) 254 (4.30), 303 (3.85), 445 (4.25) nm. **5**: orange cryst., mp 160–162 °C, MALDI–TOF MS m/z 478 (M^+); ^1H NMR ($CDCl_3$) δ 4.52–4.51 (m, 2H), 4.43–4.41 (m, 2H), 3.90 (s, 3H), 3.89 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 189.11, 163.31, 161.94, 146.54, 143.68, 141.13, 138.02, 69.80, 64.09, 53.54, 53.38; UV–vis/CH_2Cl_2 $\lambda_{\max}$($\log \varepsilon$) 278 (4.31), 340 (3.95), 476 (4.22) nm. **9**: orange cryst., mp 201–203 °C; EI–MS m/z 276 (M^+); ^1H NMR ($CDCl_3$) δ 4.50–4.49 (m, 2H), 4.33 (s, 4H), 4.32–4.30 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 182.0, 139.3, 134.3, 129.3, 128.7, 68.2, 66.2, 66.0, 65.8.

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14 X-ray crystallographic data for **4**: $C_{11}H_{10}O_6SSe_2$, $M_r = 428.18$, triclinic, $P1$ (No. 1), $Z = 4$, $a = 12.504(2)$ Å, $b = 14.840(2)$ Å, $c = 7.733(1)$ Å, $\alpha = 95.09(1)^\circ$, $\beta = 94.07(1)^\circ$, $\gamma = 88.57(1)^\circ$, $V = 1425.4(3)$ Å^3, $D_{\mathrm{calcd}} = 1.995$ g cm^{-3}, $T = 298$ K, μ(Mo Kα) $= 53.55$ cm^{-1}, Rigaku AFC7R, Mo Kα ($\lambda = 0.71069$ Å), 7988 reflections were collected, 7984 unique ($R_{\mathrm{int}} = 0.020$), 7984 observed ($I > 2\sigma(I)$), 722 parameters, $R_1 = 0.051$, $wR_2 = 0.136$, GOF $= 1.73$.

15 The oxidation potentials of **4**, **5**, and **9** were determined by cyclic voltammetry [0.1 M Bu_4NClO_4, 1.4–1.5 mM in CH_2Cl_2, glassy carbon working and Pt counter electrodes, Ag/Ag^+ reference electrode, 100 mV s^{-1}, rt].

Published on the web (Advance View) April 12, 2004; DOI 10.1246/cl.2004.570