CHEMISTRY LETTERS, pp. 675-678, 1992.

Preparation of Sterically Congested 1,9-Disubstituted Dibenzoselenophenes by Ligand Coupling Reactions and Formation of New Dithia and Diselena Dications on Chemical and Electrochemical Oxidations

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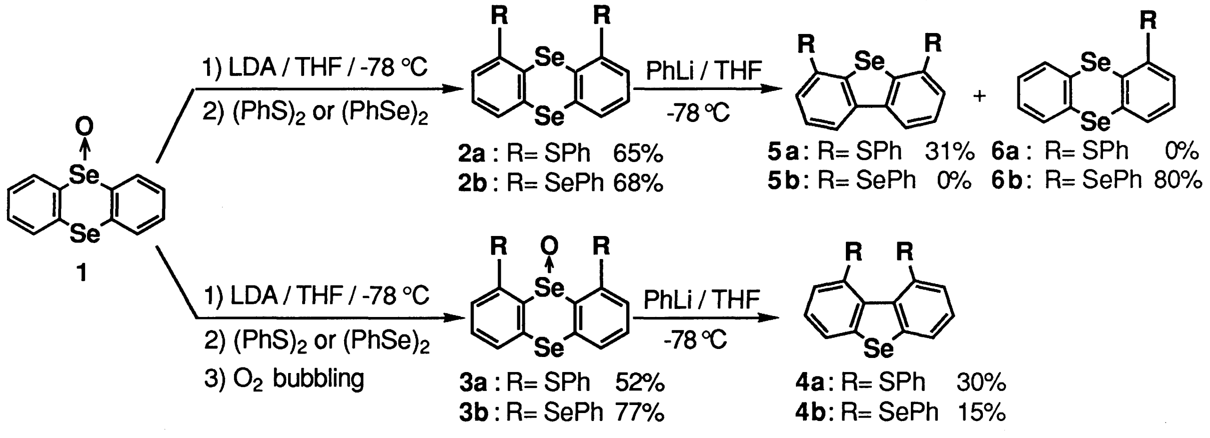
Sterically congested 1,9-bis(phenylthio)dibenzoselenophene (**4a**) and 1,9-bis(phenylseleno)dibenzoselenophene (**4b**) were prepared. New dithia dication and diselena dication were generated from **4a** and **4b**, respectively, in concd sulfuric acid.

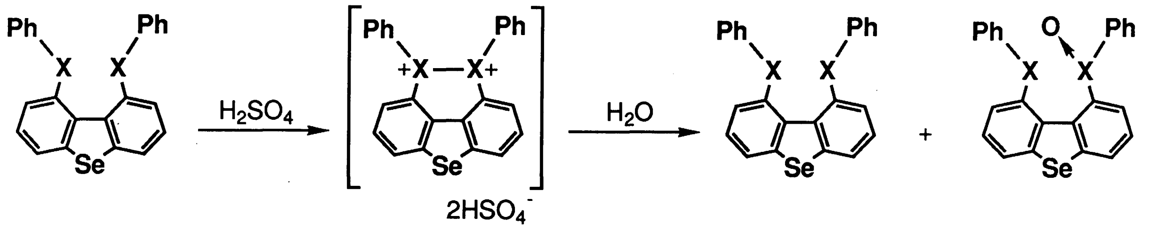
Recently, it has been reported that 4,6-disubstituted thianthrene-5-oxides undergo ring contraction by treatment with butyllithium to afford sterically hindered 1,9-disubstituted dibenzothiophenes in moderate yields.1) Similarly, sterically congested 1,9-bis(phenylthio)dibenzoselenophene (**4a**) and 1,9-bis(phenylseleno)dibenzoselenophene (**4b**) were prepared on treatment of 4,6-disubstituted selenanthrene-5-oxides with phenyllithium. This paper reports the convenient preparation of **4a,b** and the formation of new types of dithia and diselena dications by chemical and electrochemical oxidations.

Selenanthrene-5-oxide (**1**)2,3) was treated with three equivalents of lithium diisopropylamide (LDA) in THF at -78 °C and then with diphenyl disulfide or diphenyl diselenide resulting in the formation of 1,9-disubstituted selenanthrenes (**2a** and **2b**) in 65 and 68% yields respectively, but 4,6-disubstituted selenanthrene-5-oxides were not obtained at all demonstrating that the reduction of selenoxides took place probably by the thiophenolate anion or selenophenolate anion formed in the reactions.4) Therefore, after addition of electrophiles the reaction mixture was treated with oxygen gas which oxidized thiophenolate or selenophenolate anion. Thus, this procedure provided the desired 1,9-disubstituted selenanthrene-5-oxides (**3a**) and (**3b**) in 52 and 77% yields,



Scheme 1.

respectively. Since selenanthrene-5-oxide (**1**) was found to be converted to dibenzoselenophene in 35% yield by treating with phenyllithium in THF, the ring contraction was applied to 4,6-disubstituted selenanthrene-5-oxides (**3a** and **3b**) using phenyllithium in THF at -78 °C. The compound **3a** afforded 1,9-bis(phenylthio)-dibenzoselenophene (**4a**) in 30% yield together with the reduction product **2a** and 4,6-bis(phenylthio)dibenzoselenophene (**5a**) which was produced by the reaction of **2a** with phenyllithium in 25% and 3% yields, respectively.5,6) The facile Se-O bond cleavage have been observed in the ligand exchange and coupling reactions of diaryl selenoxides with phenyllithium.7) The structures of regio-isomers **4a** and **5a** were determined by the chemical shifts of the ^{1}H-NMR. Similarly **3b** gave 1,9-bis(phenylseleno)dibenzoselenophene (**4b**) in 15% yield (Scheme 1).8) These results indicate that the divalent selenium atom of the compounds **3a** and **3b** is also attacked by phenyllithium. However, the present procedure for ring contraction may proceed mainly via an initial attack by phenyllithium on the selenium atom of selenoxide to give the corresponding σ-selenurane which affords the sterically congested 1,9-disubstituted dibenzoselenophene by coupling of the two phenyl rings. On the other hand, we found that the X-ray crystallographic analysis of the dibenzothiophene analog of **4a** revealed the unusually short distance between the two outer sulfur atoms (3.012 Å) and hence a dithia dication was readily formed.9) Since the compounds **4a** and **4b** should have a short S-S or Se-Se distance, they may give rise to the dithia or diselena dication on oxidation. Initially, the compounds **4a** and **4b** were dissolved in concd sulfuric acid-d$_2$ (D_2SO_4) and their ^{1}H and ^{77}Se-NMR spectra were measured. The ^{77}Se-NMR chemical shifts of **4b** in concd D_2SO_4 were observed at 699.1 and 534.8 ppm, whereas **4b** has the ^{77}Se-NMR chemical shifts in $CDCl_3$ at 468.7 and 427.0 ppm (Fig. 1). The larger downfield shift of the two outer selenium atoms than that of the selenium atom in the selenophene ring demonstrates clearly that the dication **7b** is formed and the cations are localized preferentially on the outer selenium atoms by the formation of Se-Se σ-bond. In the ^{1}H-NMR spectra of **4b** the phenyl protons show the absorption at 7.10-7.04 (meta, para) and 6.99-6.94 (ortho) in $CDCl_3$. As shown in Fig. 2 when **4b** was dissolved in concd D_2SO_4, the phenylseleno protons shifted to the upfield at 6.38 ppm (4H, ortho) and 6.89 ppm (4H, meta) and to the downfield at 7.33 ppm (2H, para). These characteristic shifts in concd D_2SO_4 were also observed in the case of the dibenzothiophene derivatives as previously reported.9) Hydrolysis of **7a** and **7b** gave the corresponding sulfoxide **8a** in 81% yield and the selenoxide **8b** in 75% yield, respectively, demonstrating that the dications **7a** and **7b** should be formed in concd sulfuric acid (Scheme 2).10) Similarly, the sulfoxide **8a** and selenoxide **8b** were treated with concd D_2SO_4 to give the same NMR spectra of **7a** and **7b**, respectively.



4a : X=S
4b : X=Se

7a : X=S
7b : X=Se

4a : X=S 0%
4b : X=Se 15%

8a : X=S 81%
8b : X=Se 75%

Scheme 2.

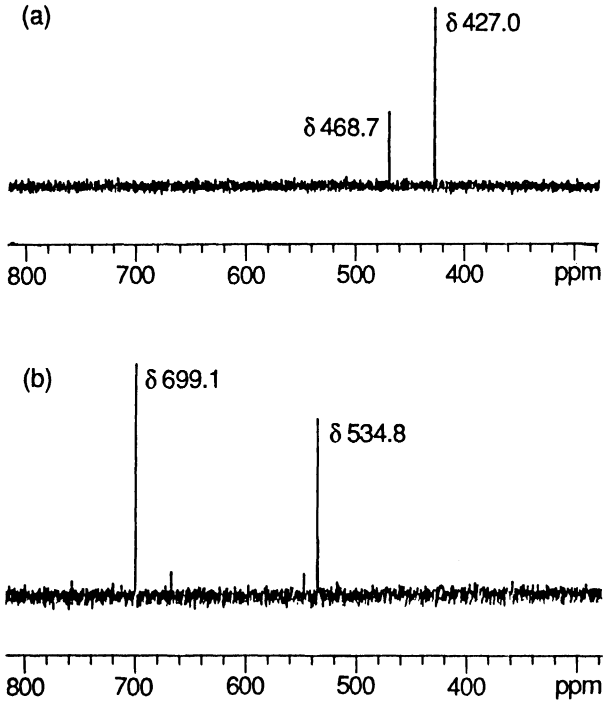


Fig. 1. 51 MHz ^{77}Se-NMR spectra of **4b** in $CDCl_3$ (a) and dication **7b** in D_2SO_4 (b).

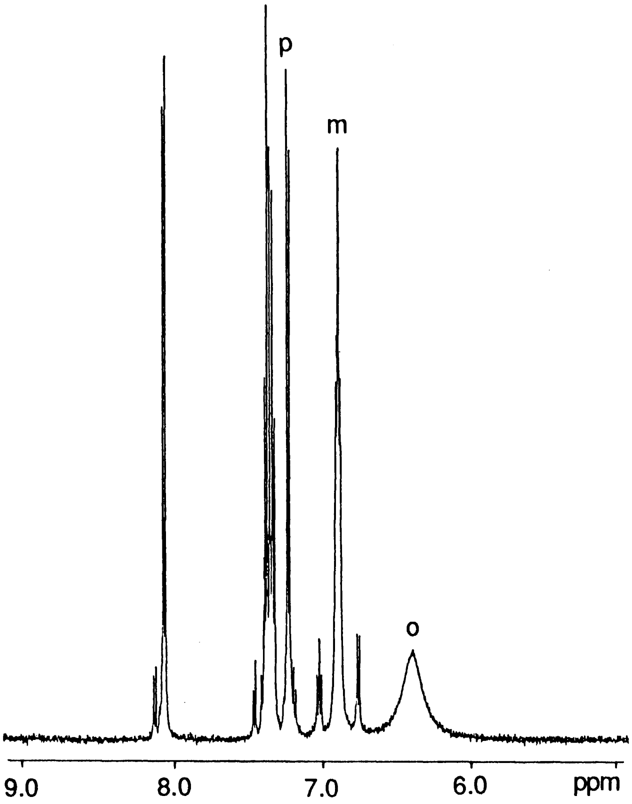


Fig. 2. 500 MHz ^{1}H-NMR spectrum of dication **7b** in D_2SO_4.

Furthermore, in order to confirm the formation of dications **7a** and **7b** in concd sulfuric acid, the fast atom bombardment (FAB) mass spectra of their dications were measured in the concd sulfuric acid matrix. These spectra reveal the first evidence for the formation of the dication salts in which HSO_4^- exists as a counter anion as follows: **7a**: m/z 643 ($[M+H]^+$), 545 ($[M-HSO_4]^+$); **7b**: m/z 737 ($[M+H]^+$), 639 ($[M-HSO_4]^+$). Electrochemical oxidations may also provide a strong evidence for formation of **7a** and **7b**. The oxidation potentials of **4a** and **4b** were measured with cyclic voltammetry, and the peak potentials measured are 0.85 V (**7a**) and 0.67 V (**7b**), respectively. These values are relatively low compared with those of **2a** (0.97 V), **2b** (0.98 V), **5a** (1.21 V), and dibenzoselenophene (1.02 V), supporting the strong evidence for the interaction between the two outer sulfur or the two outer selenium atoms on electrochemical oxidation.[11] Further studies on these new heterocycles are in progress.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency No. 03233101 from the Ministry of Education, Science and Culture, Japan. This work was also supported by a Special Grant from University of Tsukuba.

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3) Selenanthrene was oxidized with an equimolar amount of *m*-chloroperbenzoic acid (mCPBA) to give the monoxide (**1**) quantitatively. mp 203-204 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.99 (d, J=7.6 Hz, 2H, 4,6-ArH), 7.80 (d, J=7.6 Hz, 2H, 1,9-ArH), 7.58 (t, J=7.6 Hz, 2H, 3,7-ArH), 7.42 (t, J=7.6 Hz, 2H, 2,8-ArH); ^{77}Se-NMR (51 MHz, $CDCl_3$) δ 850.6, 390.4; IR (KBr) 822 cm^{-1} (SeO); MS m/z 312 (M^+-16); Anal. Found: C, 44.11; H, 2.46%. Calcd for $C_{12}H_8OSe_2$: C, 44.20; H, 2.47%.

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5) **4a**: Mp 176-177 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.83 (dd, J_1=7.8 Hz, J_2=1.1 Hz, 2H, 4,6-ArH), 7.58 (dd, J_1=7.8 Hz, J_2=1.1 Hz, 2H, 2,8-ArH), 7.33 (t, J=7.8 Hz, 2H, 3,7-ArH), 7.15-7.04 (m, 6H, *m,p*-PhH), 6.93-6.87 (m, 4H, *o*-PhH); ^{77}Se-NMR (51 MHz, $CDCl_3$) δ 470.6; MS m/z 448 (M^+); Anal. Found: C, 64.23; H, 3.43%. Calcd for $C_{24}H_{16}S_2Se$: C, 64.42; H, 3.60%.

6) **5a**: Mp 128-129 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, J_1=7.4 Hz, J_2=1.1 Hz, 2H, 1,9-ArH), 7.50 (dd, J_1=7.4 Hz, J_2=1.1 Hz, 2H, 3,7-ArH), 7.47 (t, J=7.4 Hz, 2H, 2,8-ArH), 7.30-7.21 (m, 8H, *o,m*-H) 7.19 (t, J=7.1 Hz, 2H, *p*-H); MS (m/z) 448 (M^+); Anal. Found: C, 64.33; H, 3.49%. Calcd for $C_{24}H_{16}S_2Se$: C, 64.42; H, 3.60%.

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8) **4b**: Mp 190 °C (decomp); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, J_1=7.8 Hz, J_2=1.0 Hz, 2H, 2,8-ArH), 7.75 (dd, J_1=7.8 Hz, J_2=1.0 Hz, 2H, 4,6-ArH), 7.27 (t, J=7.8 Hz, 2H, 3,7-ArH), 7.10-7.04 (m, 6H, *m,p*-PhH), 6.99-6.94 (m, 4H, *o*-PhH); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 141.1, 140.0, 137.1, 134.8, 131.0, 129.5, 128.9, 127.7, 126.6, 125.3; ^{77}Se-NMR (51 MHz, $CDCl_3$) δ 468.7, 427.0; MS m/z 542 (M^+); Anal. Found: C, 53.39; H, 2.87%. Calcd for $C_{24}H_{16}Se_3$: C, 53.27; H, 2.98%.

9) T. Kimura, Y. Horie, S. Ogawa, H. Fujihara, F. Iwasaki, and N. Furukawa, *Heterocycles*, **33**, 101 (1992); N. Furukawa, T. Kimura, Y. Horie, S. Ogawa, and H. Fujihara, *Tetrahedron Lett.*, in press.

10) **8a**: Mp 238 °C (decomp); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.96 (dd, J_1=7.8 Hz, J_2=1.1 Hz, 1H, 2-ArH), 7.93 (dd, J_1=7.8 Hz, J_2=1.1 Hz, 1H, 8-ArH), 7.77 (dd, J_1=7.8 Hz, J_2=1.1 Hz, 1H, 4-ArH), 7.68 (dd, J_1=7.8 Hz, J_2=1.1 Hz, 1H, 6-ArH), 7.68-7.63 (m, 2H, *o*-S(O)PhH), 7.51 (t, J=7.8 Hz, 1H, 3-ArH), 7.42 (t, J=7.8 Hz, 1H, 7-ArH), 7.14-7.04 (m, 3H, *m,p*-SPhH), 6.75-6.69 (m, 2H, *o*-SPhH); ^{77}Se-NMR (51 MHz, $CDCl_3$) δ 482.5; IR (KBr) 1027 cm^{-1} (SO); MS m/z 464 (M^+); **8b**: mp 184 °C (decomp); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.96 (dd, J_1=7.8 Hz, J_2=1.1 Hz, 1H, 2-ArH), 7.95 (dd, J_1=7.8 Hz, J_2=1.1 Hz, 1H, 8-ArH), 7.88-7.82 (m, 2H, *o*-Se(O)PhH), 7.81 (dd, J_1=7.8 Hz, J_2=1.1 Hz, 1H, 4-ArH), 7.78 (dd, J_1=7.8 Hz, J_2=1.1 Hz, 1H, 6-ArH), 7.50 (t, J=7.8 Hz, 1H, 3-ArH), 7.46-7.39 (m, 3H, *m,p*-Se(O)PhH), 7.38 (t, J=7.8 Hz, 1H, 7-ArH), 7.15-7.08 (m, 3H, *m,p*-SePhH), 6.91-6.85 (m, 2H, *o*-SePhH); ^{77}Se-NMR (51 MHz, $CDCl_3$) δ 894.1, 482.4, 420.7; IR (KBr) 812 cm^{-1} (SeO); MS m/z 542 (M^+-16).

11) Cyclic voltammetry was measured using Ag/0.01 M $AgNO_3$ as a reference electrode; scan rate: 200 mV/s at 25 °C in acetonitrile.

(Received January 29, 1992)