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First Systematic Synthesis and Electrochemical Oxidation of 4,7-Diisopropyl-1,2,3-benzotrichalcogenoles Containing Both Sulfur and Selenium Atoms

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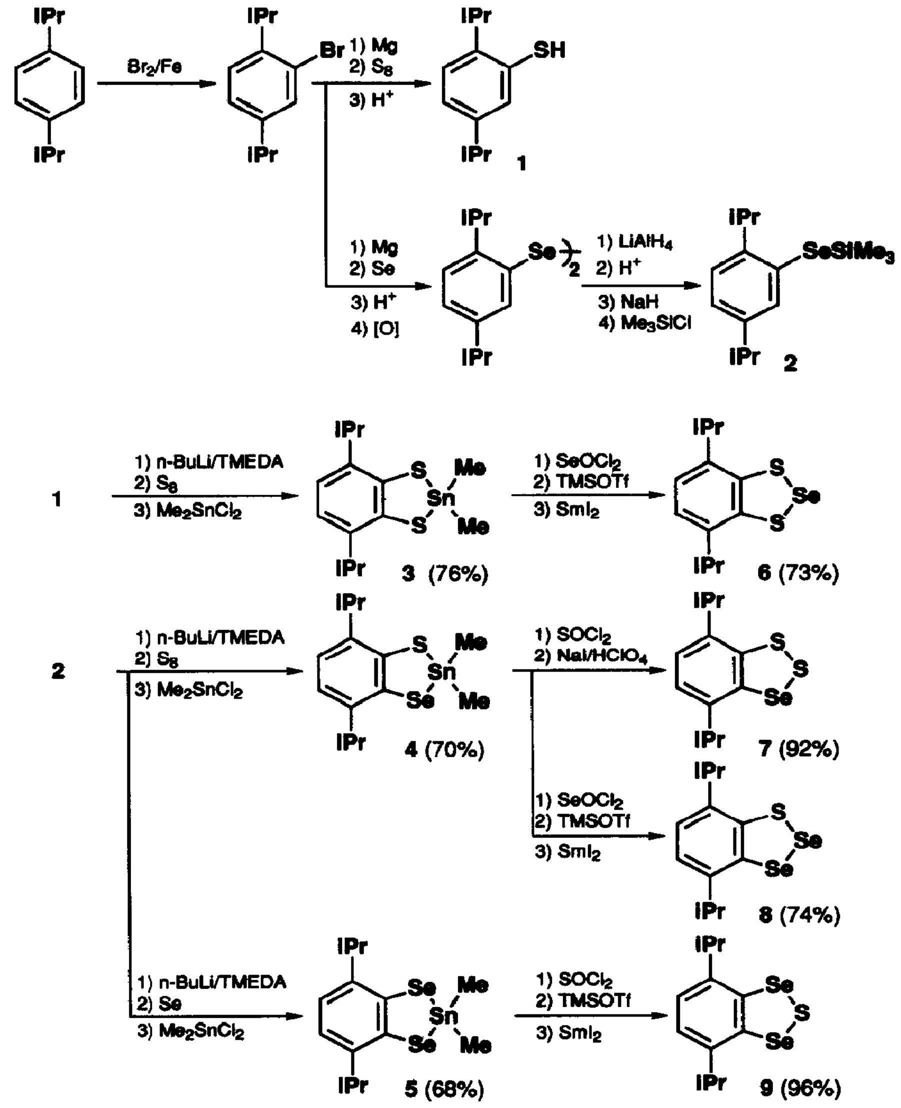
Abstract: Stable 4,7-disubstituted benzotrichalcogenoles containing both sulfur and selenium atoms in the five-membered ring were systematically and selectively prepared by the reactions of corresponding benzodichalcogenastannoles, synthetic equivalent of benzenedichalcogenols, with S_1 (thionyl chloride) or Se_1 (selenyl chloride) source in good yields. Characterization of these new trichalcogenole frameworks was performed by ^{77}Se NMR, and the cyclic voltammograms of the trichalcogenoles showed the reversible electrochemical oxidation with low oxidation potential.

There is considerable current interest in organic cyclic polychalcogenides because of their chemical reactivities,[1] synthetic utility,[2] and recent discovery in marine natural products.[3] Among such polychalcogenides, however, trichalcogenoles have received little attention due to their less stability. Indeed, there have been a few reports of trithioles,[4,5] triselenoles,[5,6] and only one example of trichalcogenole containing both sulfur and selenium atoms in the 5-membered ring.[5] Recently, we reported a new efficient method for the synthesis of benzotrithioles fused to benzene ring.[7] As a further advance of our research on the preparation and reactions of new stable benzotrichalcogenoles, we wish to report here the first systematic synthesis of four new benzotrichalcogenoles containing both sulfur and selenium atoms, which have the isopropyl groups at 4 and 7-positions of the benzene ring serving as efficient stabilization substituents for the 5-membered polychalcogenide ring.

4,7-Diisopropyl-2,2-dimethyl-1,3,2-benzodichalcogenastannoles **3**-**5**,[8] synthetic equivalent of unstable ortho benzenedichalcogenols, were prepared by the ortho lithiation[9] followed by stannylation[10] of thiol **1** and selenol equivalent **2**. A typical synthetic procedure for benzotrichalcogenole **6** is as follows (Scheme 1).[11] To a stirred solution of dithiastannole **3** (75 mg, 0.2 mmol) in THF (10 mL) was added selenyl chloride (0.014 mL, 0.2 mmol) in THF (5 mL) under an Ar atmosphere at -78 °C. After stirring for 15 min, the mixture was treated successively with trimethylsilyl trifluoromethanesulfonate (0.035 mL, 0.2 mmol) in THF (5 mL) and 0.1M samarium(II) iodide (4.0 mL, 0.4 mmol) in THF at -78 °C under an Ar atmosphere. The whole mixture was stirred at -78 °C for 15 min and then at room temperature for 30 min. After hydrolysis, treatment with aqueous sodium hydrogensulfite and extraction with hexane (3 x 10mL), the extract was dried with anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel; eluent, hexane) to give dithiaselenole **6** in 73% yield.

Selenium has one and tin has two NMR-active spin 1/2 nuclei of relatively high natural abundance; ^{77}Se, ^{119}Sn and ^{117}Sn. Therefore, the ^{77}Se and ^{119}Sn NMR spectra provided good information about the new 5-membered frameworks of dichalcogenastannoles **3**-**5** and trichalcogenoles **6**-**9** (Table 1). The ^{77}Se NMR spectra of **4** and **5** showed the signals with ^{119}Sn and ^{117}Sn satellites, which were in accordance with the



TMEDA: *N,N,N',N'*-tetramethylethylenediamine
TMSOTf: trimethylsilyl trifluoromethanesulfonate

Scheme 1

existence of selenium atom or atoms neighboring with a tin atom in the ring. The ^{119}Sn NMR spectra of **4** and **5** also showed ^{77}Se satellites. The ^{77}Se NMR spectra of **6**, **7** and **9** indicated that each 5-membered ring has a selenium atom at an appropriate position and the spectrum of **8** consisted of two equally intense signals, each with ^{77}Se satellites, which could be assigned to the selenium-selenium bonding in the ring.

Table 1. ^{77}Se and ^{119}Sn NMR of Dichalcogenastannoles **3-5** and Trichalcogenoles **6-9**$^{a)}$

Compd	^{77}Se$^{b)}$				^{119}Sn$^{c)}$	
	δ/ppm	*^1J/Hz*	*δ/ppm*	*^1J/Hz*	*δ/ppm*	*^1J/Hz*
3					174.3	
4	27.2	1089 (^{117}Sn) 1139 (^{119}Sn)			121.4	1139 (^{77}Se)
5	83.2	1061 (^{117}Sn) 1110 (^{119}Sn)			62.9	1110 (^{77}Se)
6	696.6					
7	628.0					
8	509.2	275 (^{77}Se)	575.1	275 (^{77}Se)		
9	653.9					

a) Measured in $CDCl_3$ at 298 K b) Relative to neat Me_2Se c) Relative to neat Me_4Sn

Table 2. Electrochemical Oxidation of Trichalcogenoles **6-9**$^{a)}$

Compd	**6**	**7**	**8**	**9**	Ph_2Se	Ph_2Se_2
Ep (V)	0.64	0.75	0.63	0.71	0.99$^{b)}$	1.11$^{b)}$
$E_{1/2}$ (V)	0.60	0.70	0.59	0.66	-	-

a) 2.0 mM sample in MeCN (supporting electrolyte 0.1M n-$Bu_4N^+ClO_4^-$; glassy carbon working electrode; scan rate 100 mVs^{-1}); Ep/V and $E_{1/2}$/V vs Ag/0.01M $AgNO_3$ b) Irreversible, see ref. 12

The solution redox properties of the trichalcogenoles **6-9** were studied by cyclic voltammetry technique, since little has been known about the electrochemical behavior of polychalcogenide ring systems. Cyclic voltammograms were measured in acetonitrile (MeCN) containing 0.1M n-$Bu_4N^+ClO_4^-$ as a supporting electrolyte using a glassy carbon working electrode and Ag/0.01M $AgNO_3$ couple in MeCN as a reference electrode. Interestingly, all thiaselenoles exhibited one reversible one-electron step with low oxidation potential. The peak potentials of the first oxidation peak (Ep) and half-wave ($E_{1/2}$) have been found to be governed by the atom present at 2-position of the chalcogen ring (Table 2). Recently, ring compounds containing three sulfur or three selenium atoms with a unusual 7π electron framework have been prepared.[13] Thus, the present results suggest that some stable one-electron oxidized species, 4,7-diisopropyl-1,2,3-benzotrichalcogenolium radical cations, may be generated during the electrochemical oxidation. Further studies on the oxidation of these mixed chalcogen ring systems are in progress.

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REFERENCES AND NOTES

1. Tokitoh, N. *J. Synth. Org. Chem. Jpn.* **1994**, *52*, 136-148; and references cited therein.
2. Sato, R.; Goto, T.; Saito, M. *J. Synth. Org. Chem. Jpn.* **1990**, 48, 797-805; and references cited therein
3. Davidson, B. S.; Molinski, T. F.; Barrows, L. R.; Ireland, C. M. *J. Am. Chem. Soc.* **1991**, *113*, 4709-4710; Litaudon, M.; Guyot, M. *Tetrahedron Lett.* **1991**, *32*, 911-994. Very recently, total syntheses of such cytotoxic metabolites have been reported; Behar, V; Danishefsky, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 7017-7018; Ford, P. W.; Davidson, B. S. *J. Org. Chem.* **1993**, *58*, 4522-4523.
4. Plater, M. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1991**, 317-321; Sato, R.; Kimura, T.; Goto, T.; Saito, M.; Kabuto, C. *Tetrahedron Lett.* **1989**, *30*, 3453-3456; Sato, R.; Kimura, T.; Goto, T.; Saito, M. *ibid.* **1988**, *29*, 6291-6294; Chenard, B. L.; Harlow, R. L.; Johnson, A. L.; Vladuchick, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 3871-3879; Rasheed, K.; Warkentin, J. D. *J. Org. Chem.* **1980**, *45*, 4806-4807.
5. Tokitoh, N.; Ishizuka, H.; Ando, W. *Chem. Lett.* **1988**, 657-660.
6. Earle, M. J.; Griffiths, K. R.; Massey, A. G. *Polyhedron* **1992**, *11*, 395; Humphries, R. E.; Massey, A. G. *Phosphorus and Sulfur* **1988**, *36*, 135-137.
7. Ogawa, S.; Yomoji, N.; Chida, S.; Sato, R. *Chem. Lett.* **1994**, 507-510.
8. 4,7-Disubstituted 2,2-dimethyl-1,3,2-benzodichalcogenastannoles **3-5** were characterized by physical and spectroscopic means. Full data will be reported in a future paper.
9. Figuly, G. D.; Loop, C. K.; Martin, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 654-658; Block, E; Eswarakrishnan, V.; Gernon, M.; Ofori-Okai, G.; Saha, C.; Tang, K.; Zubieta, J. *ibid.* **1989**, *111*, 658-665; Smith, K.; Lindsay, C. M.; Pritchard, G. J. *ibid.* **1989**, *111*, 665-669.
10. Grätz, K.; Huber, F.; Silvestri, A.; Alonzo, G.; Barbieri, R. *J. Organomet. Chem.* **1985**, *290*, 41-51; Poller, R. C.; Spillman, J. A. *J. Chem. Soc. (A)* **1966**, 958-960.
11. Dithiaselenole **6**: red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (d, 12H, *J* = 6.8 Hz, *Me*$_2$CH), 3.15 (sept, 2H, *J* = 6.8 Hz, Me$_2$C*H*), 6.94 (s, 2H, ArH); {^{1}H}^{13}C NMR (100 MHz, $CDCl_3$) δ 23.0, 35.4, 124.4, 141.1, 143.7; IR (neat) 2965, 2870, 1469, 1388, 1373, 1265, 1162, 1062, 896, 822, and 738 cm^{-1}; Exact mass calcd for $C_{12}H_{16}S_2Se$ (M^+, ^{80}Se), 303.9858. Found (M^+, ^{80}Se), 303.9822. Dithiaselenole **7**: dark red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (d, 6H, *J* = 6.8 Hz, *Me*$_2$CH), 1.25 (d, 6H, *J* = 6.8 Hz, *Me*$_2$CH), 2.79 (sept, 1H, *J* = 6.8 Hz, Me$_2$C*H*), 3.07 (sept, 1H, *J* = 6.8 Hz, Me$_2$C*H*), 7.04 (d, 1H, *J* = 6.9 Hz, ArH), 7.06 (d, 1H, *J* = 6.9 Hz, ArH); {^{1}H}^{13}C NMR (100 MHz, $CDCl_3$) δ 23.1, 23.2, 35.8, 38.8, 124.6, 124.8, 139.7, 141.1, 143.6, 144.6; IR (neat) 2960, 2867, 2358, 1887, 1642, 1467, 1386, and 819 cm^{-1}; Exact mass calcd for $C_{12}H_{16}S_2Se$ (M^+, ^{80}Se), 303.9858. Found (M^+, ^{80}Se), 303.9799. Thiadiselenole **8**: reddish brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (d, 6H, *J* =6.8 Hz, *Me*$_2$CH), 1.24 (d, 6H, *J* = 6.8 Hz, *Me*$_2$CH), 2.93 (sept, 1H, *J* = 6.8 Hz, Me$_2$C*H*), 3.21 (sept, 1H, *J* = 6.8 Hz, Me$_2$C*H*), 6.98 (d, 1H, *J* = 8.0 Hz, ArH), 7.00 (d, 1H, *J* = 8.0 Hz, ArH); {^{1}H}^{13}C NMR (100 MHz, $CDCl_3$) δ 23.1, 23.3, 35.6, 38.6, 124.6, 124.9, 140.4, 142.1, 144.7, 145.3; IR (neat) 2959, 2924, 2363, 1884, 1696, 1634, 1464, 1385, and 818 cm^{-1}; Exact mass calcd for $C_{12}H_{16}SSe_2$ (M^+, ^{80}Se), 351.9304. Found (M^+, ^{80}Se), 351.9270. Thiadiselenole **9**: reddish brown crystals; mp. 45.0-46.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (d, 12H, *J* = 6.8 Hz, *Me*$_2$CH), 2.88 (sept, 2H, *J* = 6.8 Hz, Me$_2$C*H*), 7.09 (s, 2H, ArH); {^{1}H}^{13}C NMR (100 MHz, $CDCl_3$) δ 23.4, 38.9, 125.0, 140.7, 141.3; IR (neat) 2959, 2925, 2865, 1631, 1582, 1457, 1363, 1316, 824, and 781 cm^{-1} ; Exact mass calcd for $C_{12}H_{16}SSe_2$ (M^+, ^{80}Se), 351.9304. Found (M^+, ^{80}Se), 351.9345.
12. Fujihara, H.; Higuchi, Y.; Mima, H.; Furukawa, N. *Chem. Lett.* **1994**, 619-622; Fujihara, H.; Akaishi, R.; Furukawa, N. *ibid.* **1990**, 549-550.
13. Wolmershäuser, G.; Heckmann, G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 779-780; Cameron, T. S.; Haddon, R. C.; Mattar, S. M.; Parsons, S.; Passmore, J.; Ramirez, A. P. *J. Chem. Soc., Chem. Commun.* **1991**, 358-360.

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