Pergamon

Tetrahedron Letters, Vol. 38, No. 33, pp. 5821-5824, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)01331-2

Syntheses of 1,2,5-Benzotrichalcogenepins. Reactions of 1,3,2-Benzodichalcogenastannoles with Thiiranes

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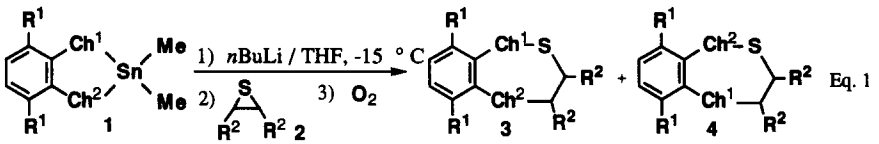
Abstract: Three types of 1,2,5-benzotrichalcogenepins (**3** and **4**) containing sulfur and selenium were synthesized by reactions of the corresponding 2,2-dimethyl-1,3,2-benzodichalcogenastannoles (**1**) with thiiranes (**2**) using *n*-butyllithium. © 1997 Elsevier Science Ltd.

Recently, heteroatom chemists have focussed much attention on the chemistry of cyclic benzopolychalcogenides containing sulfur, selenium, and tellurium such as benzotrithioles[1] and triselenoles,[2] benzopentathiepins,[3] and the related compounds[4] from the viewpoint of the chemical and biological properties of these compounds. At the present stage, it is, however, still difficult to introduce chalcogen atoms into the desired position in cyclic polychalcogenide. Our ongoing studies on the chemistry of cyclic benzopolysulfides led us to a successful one-pot synthesis of 1,2,5-benzotrithiepins from the corresponding benzenedithiols with thiiranes in satisfactory yields.[5] Moreover, we have also reported the structure and reactions of the 1,2,5-benzotrithiepin.[6] These results stimulated us to study further extension of the chemistry of 1,2,5-benzotrithiepin into one of the 1,2,5-benzotrichalcogenpins having an arbitrary chalcogen atom at the 1-, 2-, and/or 5-positions. Here, we wish to report a synthesis of some new 1,2,5-benzotrichalcogenepins **3** and **4** from the corresponding 2,2-dimethyl-1,3,2-benzodichalcogenastannoles **1**[2,7] and thiiranes **2** by treatment with *n*-butyllithium as a base followed by oxidation with oxygen (Eq. 1).



Eq. 1

Three types of trichalcogenepins, **3a-h** and **4a-c**, were generally synthesized as follows. A solution of *n*-butyllithium (2 equiv.) in hexane was added to a solution of 2,2-dimethyl-1,3,2-benzothiaselenastannole (**1**, 1 mmol) in THF (20 ml) and then thiirane **2** (1 mmol) in THF (20 mL) was also added dropwise for 1.5 hrs. To the solution, oxygen was bubbled for 8.5 hrs with stirring. After usual workup, chromatography on silica gel of the reaction mixture gave **3** and/or **4** as crystals (Table 1). The structures of the products were determined spectroscopically.[8] The chemical shifts for $^{77}Se\{^{1}H\}$NMR were observed at 363.6 (**3a**), 419.3 (**3b**), and 272.2 (**3c**) ppm to show selenide bonding, Ph-Se-CH-, whereas those of selenenyl sulfide bondings, Ph-Se-S-CH-, appeared at 497.3 (**4a**), 490.0 (**4b**), and 408.1 (**4c**) ppm, respectively.

In addition, the structures of products **3** and **4** were also confirmed chemically by reduction of **3a** and **4a**

Table 1. Reactions of 2,2-Dimethyl-1,3,2-benzodichalcogenastannoles **1** with Thiiranes **2**

Run[a]	Stannole **1**				Thiirane **2**			Additive		Yield of Products (%)			
	R^1	Ch^1	Ch^2	**1**	R^2	R^3	**2**		eq	**3**		**4**	
1	H	S	Se	**1a**	H	H	**2a**			15	**3a**	34	**4a**
2	H	S	Se	**1a**	H	H	**2a**	HCl	2	70	**3a**	2	**4a**
3	H	S	Se	**1a**	-$(CH_2)_4$-		**2b**			4	**3b**	40	**4b**
4	H	S	Se	**1a**	-$(CH_2)_4$-		**2b**	AcOH	2	40	**3b**	0	**4b**
5	H	S	Se	**1a**	-$(CH_2)_4$-		**2b**	H_2O	2.5	4	**3b**	86	**4b**
6	^{i}Pr	S	Se	**1b**	H	H	**2a**			16	**3c**	20	**4c**
7	^{i}Pr	S	Se	**1b**	H	H	**2a**	AcOH	2	82	**3c**	0	**4c**
8[b]	^{i}Pr	S	Se	**1b**	-$(CH_2)_4$-		**2b**			(8)	**3d** + **4d**		
9	H	Se	Se	**1c**	H	H	**2a**			-	**3e**		
10	H	Se	Se	**1c**	-$(CH_2)_4$-		**2b**			49	**3f**		
11	H	Se	Se	**1c**	-$(CH_2)_4$-		**2b**	AcOH	2	67	**3f**		
12	^{i}Pr	Se	Se	**1d**	H	H	**2a**			16	**3g**		
13	^{i}Pr	Se	Se	**1d**	H	H	**2a**	AcOH	2	92	**3g**		
14[b]	^{i}Pr	Se	Se	**1d**	-$(CH_2)_4$-		**2b**			12	**3h**		

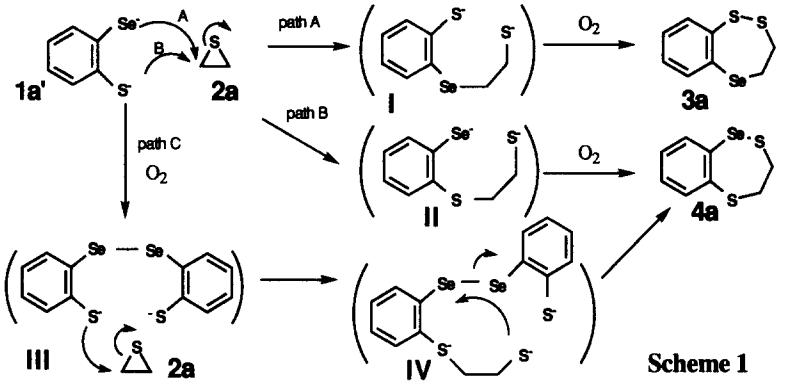
a) **1**: 0.5 mmol; **2**: 0.5 mmol; *n*BuLi: 1 mmol; THF: 20 mL; Temp: -15 °C. b) Temp: 0 °C

with $NaBH_4$ followed by methylation with methyl iodide to give the corresponding 2-(methylthio)ethyl 2-(methylthio)phenyl selenide (**5**) and 2-(methylthio)ethyl-2-(methylseleno)phenyl sulfide (**6**), respectively.[9]

The introduction of substituents such as an isopropyl group or a cyclohexane ring into the benzene or trichalcogenepin ring also led to similar results, to yield chalcogenepins **3b-c** and **4b-c** (Table 1, Runs 1-7). For improvement of the yield and selectivity to obtain the product **3** or **4**, addition of proton source such as acid and water was very effective. Thus, the dithiaselenepin **3a** was obtained mainly (70%) by addition of HCl (2 eq) to the reaction system. The product **3b** was formed in 40% yield upon addition of acetic acid(Run 4), whereas, **4b** was given preferentially in 86% yield (Run 5) by addition of water. Although the reaction of **1a** and **1b** having an isopropyl group with thiirane **2a** and **2b** also resulted in the formation of **3a-c** and **4a-c** in satisfactory yields (Table 1, Runs 1-7), we could not obtain 3,4-dihydro-2,1,3-benzothiadiselenepin (**3e**), which was labile and polymerized easily during the isolation (Run 9). The syntheses of benzothiadiselenepin **3f**, **3g**, and **3h** were performed by the reactions of benzodiselenastannoles **1c** and **1d** with thiiranes **2a** and **2b** in a similar manner as the synthesis of **3a-d** and **4a-d**. The new thiadiselenepins **3f-h** having substituents were also obtained in 12-92% yields (Runs 10-14).

We were interested in the formation of the product **4** having -Se-S- bonding in the trichalcogenepin ring, because it is well known that the nucleophilicity of the selenolate anion is much higher than that of the thiolate anion.[10] The formation of products **4** shows that the thiolate anion preferentially attacked the methylene carbon in the thiirane (**2a**) ring (Scheme 1). We tried to trap the intermediates, **I**, **II**, and **III**,

by methylation with methyl iodide. Consequently, we were able to trap three intermediates as methylated products; thus, the formation of selenide **5** from **I**, sulfide **6** from **II**, and bis[2-(methylthio)phenyl]-diselenide (**7**)[9] from **III**, respectively, was confirmed. Based on these results, the reaction pathways of the present reactions are shown in Scheme 1. The nucleophilic attack of the selenolate anion in dianion **1a'**, which was generated from **1a** by nucleophilic attack with 1-butanide anion, followed by oxidation accompanying with cyclization affords **3a** (path A), and competitive thiolate anion attack on the methylene carbon of **2a** gives also **4a** (path B). In addition, the formation of intermediate **III** suggests an alternative reaction path C involving initial oxidation of the selenolate anion to form diselenide **III** and following thiolate attack on methylene carbon of **2a** and cyclization via intermediate IV into **4a**. For the path C, the formation of **4a** was independently also confirmed by the reaction of **III**[11] with **2a**. The effect of addition of acids and water is interpreted in the light of protonation of thiolate or selenolate anion **1a'** to control the nucleophilicity.



Scheme 1

This work was partially supported by Grant-in Aid for Scientific Research (No. 09239204) from Ministry of Education, Science and Cultur, Japan.

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7. These benzodichalcogenastannoles **1** were recently developed as synthetic equivalent of labile and ill-smelling benzenedichalcogenols containing selenium. See ref. 2 and Satoh, S.; Yoshida, T.; Shimizu, T.; Sato, R. *Sulfur Lett.*, 1993, **16**, 5.
8. The spectral and analytical data for new compounds are in full agreement with the proposed structures. The selected examples for compounds **3** and **4** are shown as follows. Dithiaselenepin **3c**: Colorless crystals; mp 88.5-89.5 °C (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.22(6H, d, J=6.9 Hz, ^{i}Pr-Me), 1.23(6H, d, J=6.9 Hz, ^{i}Pr-Me), 3.20(2H, bs, CH_2), 3.37 (2H, bs, CH_2), 3.82 (1H, sept, J=6.9 Hz, ^{i}Pr-CH), 3.86 (1H, sept, J=6.9 Hz, ^{i}Pr-CH), 7.24 (1H, d, J = 8.2 Hz, ArH), 7.28 (1H, d, J=8.2 Hz, ArH); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 23.8, 24.0, 27.2, 32.6, 35.0, 36.4, 37.3, 126.0, 126.7, 140.8, 147.1, 150.0, 151.5; ^{77}Se{^{1}H} NMR (76 MHz,$CDCl_3$) δ = 272.2; IR (KBr) 2969, 1462,1241, 1108, 886, 631 cm^{-1}. MS (70 eV) m/z 332 (M^+). Anal. calcd for $C_{14}H_{20}S_2Se$: C, 50.74; H,6.08%. Found: C,50.56; H, 6.10%. Dithiaselenepin **4c**: Yellow crystals; mp 76.5-77.5 °C (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.23 (6H, d, J=6.9 Hz, ^{i}Pr-Me), 1.24 (6H, d, J=6.9 Hz, ^{i}Pr-Me), 3.34 (4H, bs, CH_2), 3.73 (1H, sept, J=6.9 Hz, ^{i}Pr-CH), 3.95 (1H, sept, J=6.9 Hz, ^{i}Pr-CH), 7.24 (1H, d, J=8.2 Hz, ArH), 7.28 (1H, d, J=8.2 Hz, ArH); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ = 24.5, 33.4, 35.4, 35.6, 37.8, 126.3, 127.4, 143.0, 148.3, 150.3, 152.5; ^{77}Se{^{1}H} NMR (76 MHz, $CDCl_3$) δ = 408.1. IR(KBr) 2960, 1462,1060, 830 cm^{-1}. MS (70 eV) m/z 248 (M^+). Anal. calcd for $C_{14}H_{20}S_2Se$: C, 50.74; H, 6.08%. Found: C, 50.35; H, 6.02%.
9. Selenide **5**: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.09 (3H, s, CH_2SCH_3), 2.44 (3H, s, $ArSCH_3$), 2.75-2.79 (2H, m, CH_2), 3.07-3.11 (2H, m, CH_2), 7.05 (1H, td, J=7.6, 1.4 Hz, ArH), 7.15 (1H, dd, J=7.6, 1.4 Hz, ArH), 7.24 (1H, td, J=7.6, 1.4 Hz, ArH), 7.45 (1H, dd, J=7.6, 1.4 Hz, ArH); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 15.1, 16.3, 25.9, 34.0, 125.5, 127.9, 128.6,133.1, 142.1; ^{77}Se{^{1}H} NMR (76 MHz, $CDCl_3$) δ 285.2 (t, $^2J_{Se-H}$= 13 Hz). IR (neat) 3051, 2978, 1569, 1268, 956, cm^{-1}. MS (70 eV) m/z 278 (M^+). Anal. calcd for $C_{10}H_{14}S_2Se$: C, 43.31; H, 5.09%. Found: C, 43.12; H, 5.03%. Sulfide **6**: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.10 (3H, s, CH_2SCH_3), 2.28 (3H, s, $ArSeCH_3$), 2.68-2.72 (2H, m, CH_2), 3.07-3.11 (2H, m, CH_2), 7.13 (1H, td, J = 7.5, 1.6 Hz, ArH), 7.19 (1H, td, J = 7.5, 1.6 Hz, ArH), 7.24 (1H, td, J=7.5, 1.6 Hz, ArH), 7.37 (1H, dd, J=7.5, 1.6 Hz, ArH); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 6.7, 15.4, 33.5, 34.2, 129.5, 128.0, 128.1, 132.2, 134.5, 137.6; ^{77}Se{^{1}H} NMR (76 MHz, $CDCl_3$) δ = 195.6 (q, $^2J_{Se-H}$= 13 Hz). IR (neat) 3051, 2970, 1426,1202, 959, cm^{-1}. MS (70 eV) m/z 278 (M^+). Anal. calcd for $C_{10}H_{14}S_2Se$: C, 43.31; H, 5.09%. Found: C, 42.91; H, 5.08%. Diselenide **7**: Orange crystals; mp 97.5-98.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.52 (6H, s, CH_3), 7.11 (2H, td, J = 7.6, 1.4 Hz, ArH), 7.19 (2H, td, J=7.6, 1.4 Hz, ArH), 7.32 (2H, dd, J = 7.6, 1.4 Hz, ArH), 7.63 (2H, dd, J=7.6, 1.4 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 18.7, 127.5, 127.8, 130.2, 130.3, 133.1, 137.3; ^{77}Se NMR (76 MHz, $CDCl_3$) δ = 404.3; IR (KBr) 3049, 2915, 1479 cm^{-1}. MS (70 eV) m/z 408 (M^+); Anal. calcd for $C_{14}H_{14}S_2Se_2$: C, 41.59; H, 3.49%. Found: C, 41.41; H, 3.44%.
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(*Received in Japan* 28 *May* 1997; *revised* 23 *June* 1997; *accepted* 27 *June* 1997)