ONE POT SYNTHESIS OF SELENIDES CONTAINING POLYARYLTHIOETHER MOIETY

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Abstract- The reactions of 5-arylthianthreniumyl perchlorates with sodium hydrogen selenide in ethanol and lithium *n*-butylselenolate in tetrahydrofuran under nitrogen at reflux afforded bis[2-(2-arylthiophenylthio)phenyl] selenides and 2-arylthio-2'-(*n*-butylseleno)diphenyl sulfides in 26 - 83% and 23 - 98% yields, respectively. A sulfurane mechanism is proposed.

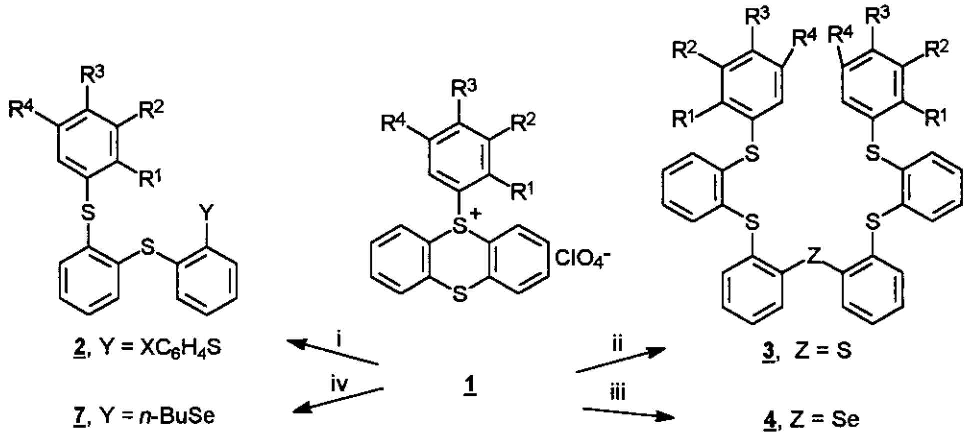
Most of the organoselenium compounds have been known for a long time.[1] They have been synthesized by a variety of methods. Among them, symmetrical diaryl selenides have generally been synthesized by treatment of arenediazonium salts with sodium selenides.[2] Treatment of diaryl diselenides with Raney Ni[3] and Friedel-Crafts reaction using selenium tetrachloride[4] as an electrophilic reagent are used for the synthesis of symmetrical diaryl selenides. The nucleophilic displacement reactions on halobenzenes bearing an electron withdrawing group by nucleophilic selenium species are also utilized for the symmetrical ones.[5] Photochemical reactions of haloarenes in the presence of areneselenolate give rise to diaryl selenides *via* $S_{RN}1$ mechanism.[6] Recently we developed an efficient method for the synthesis of bis(2-arylthiophenyl) sulfides (2)[7] and bis[2-(2-arylthiophenylthio)phenyl] sulfide (3)[8] (Z = S) by the reactions of 5-arylthianthreniumyl perchlorates (1) with various thiolates and sodium hydrogen sulfide, respectively (Scheme 1).

The results suggest that selenium containing analogues of compounds (2) and (3), i.e. 2-(arylseleno)-2′-(arylthio)diphenyl sulfides or 2-alkaneseleno-2′-(arylthio)diphenyl sulfides and bis[2-(2-arylthiophenylthio)-phenyl] selenides, would be synthesized by the reactions of 1 with arene- or alkaneselenolates and sodium hydrogen selenide, respectively. We have studied these possibilities. The results are described herein.

RESULTS AND DISCUSSION

We have found that compounds (1) react with sodium hydrogen selenide, *in situ* prepared by treatment of selenium metal with $NaBH_4$ in EtOH,[9] to give bis[2-(2-arylthiophenylthio)phenyl] selenides (4) (Z = Se) yields of which depend on the substituents. The quantities of the reactants, reaction times, and yields of compounds (**4**) are summarized in Table 1 and their analytical, IR, and ^{1}H NMR data are summarized in Table 2.

Scheme 1



Reagents and conditions : i, $XC_6H_4S^-Na^+$,THF, △. ii, $NaSH{\cdot}xH_2O$, THF/H_2O (10:1), C_6H_6/H_2O (1:1), or MeCN, △. iii, NaSeH, EtOH, △. iv, *n*-BuSeLi, THF, N_2, △.

Table 1. Reaction conditions and yields of bis[2-(2-arylthiophenylthio)phenyl] selenides (**4**) (Z = Se)

Compound	R^1	R^2	R^3	R^4	mmol	Se (mmol)	$NaBH_4$ (mmol)	EtOH (mL)	Time (h)	Yield[a] (%)	
1a	H	H	MeO	H	0.590	3.85	4.31	40	17	**4a**	83
1b	H	H	EtO	H	0.475	3.90	4.34	20	24	**4b**	77[b]
1c	H	H	*n*-BuO	H	0.467	3.85	4.35	20	27	**4c**	71
1d	H	MeO	MeO	H	0.531	3.89	4.36	30	36	**4d**	50[b]
1e	H	O- CH_2-O		H	0.497	3.89	4.72	40	36	**4e**	53[b]
1f	H	H	Me	H	0.704	3.89	4.30	20	23	**4f**	73[b]
1g	MeO	H	H	*t*-Bu	0.458	3.88	4.64	30	23	**4g**	50[b]
1h	H	H	MeCONH	H	0.540	4.00	5.30	50	16	**4h**	26
1i	H	H	*p*-$MeC_6H_4SO_2NH$	H	0.385	3.85	4.48	40	15	**4i**	42

[a] Isolated yield. [b] From the reactions of **1b**, **1d**, **1e**, **1f**, and **1g** were isolated thianthrene in 12%, 21%, 18%, 6%, and 10% yields, respectively.

The structures of compounds (**4**) were determined on the basis of the spectroscopic and mass spectral data and elemental analyses. Synthesis of symmetrical diaryl selenide (**4j**) ($R^1 = R^2 = R^3 = R^4$ = H, Z = Se)[2] was tried according to the slightly modified literature procedures[10] because of the solubility of 2-amino-2'-

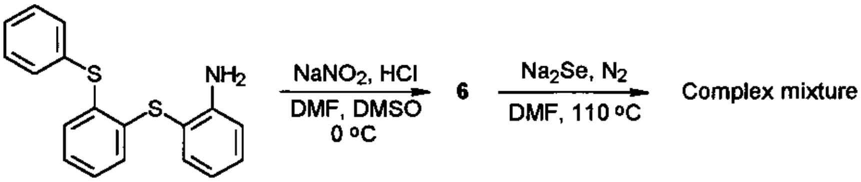
Table 2. Analytical, IR, and ^{1}H NMR data of bis[2-(2-arylthiophenylthio)phenyl] selenides (4) (Z = Se)

Compound	mp (°C)	IR (ν, cm^{-1})	^{1}H NMR (δ, ppm)	Molecular Formula	Calcd/Found %			
					C	H	N	S
4a	Sticky liquid	1491, 1443, 1249, 1032	3.75 (6H, s, 2MeO), 6.79 - 7.68 (24H, m, ArH)	$C_{38}H_{30}O_2S_4Se$	62.88 62.75	4.17 4.03		17.67 17.62
4b	126-126.5 (*n*-hexane -CHCl$_3$)	1491, 1441, 1286, 1440	1.39 (6H, t, J = 6.5 Hz, 2Me), 4.00 (4H, q, J = 8.0 Hz, 2CH$_2$), 6.88 - 7.69 (24H, m, ArH)	$C_{40}H_{34}O_2S_4Se$	63.73 63.59	4.55 4.46		17.01 17.04
4c	Sticky liquid	2960, 1491, 1441, 1246, 1023	0.91 (6H, t, J = 6.5 Hz, 2Me), 1.28 - 1.74 (8H, m, 2CH$_2$CH$_2$), 3.90 (4H, J = 8.0 Hz, 2OCH$_2$), 6.79 - 7.44 (24H, m, ArH)	$C_{44}H_{42}O_2S_4Se$	65.24 65.16	5.23 5.08		15.83 15.79
4d	109 - 110 (*n*-hexane -CHCl$_3$)	1503, 1440, 1252, 1136, 1024	3.86 (6H, s, 2MeO), 3.88 (6H, s, 2MeO), 6.86 - 7.69 (22H, m, ArH)	$C_{40}H_{34}O_4S_4Se$	61.13 61.05	4.36 4.27		16.31 16.23
4e	Sticky liquid	1491, 1475, 1443, 1235, 1036	5.97 (4H, s, 2-OCH$_2$O-), 6.79 - 7.28 (22H, m, ArH)	$C_{38}H_{26}O_4S_4Se$	60.55 60.39	3.48 3.51		17.01 17.06
4f	112 - 113 (*n*-hexane -CHCl$_3$)	1489, 1440, 1035, 1020, 739	2.28 (6H, s, 2Me), 6.83 - 7.59 (24H, m, ArH)	$C_{38}H_{30}S_4Se$	65.78 65.74	4.36 4.29		18.48 18.31
4g	Sticky liquid	2960, 1570, 1488, 1438, 1289, 1120, 732	1.17 (18H, s, 2*t*-Bu), 3.81 (6H, s, 2MeO), 6.87 - 7.64 (22H, m, ArH)	$C_{44}H_{46}O_2S_4Se$	65.92 65.77	5.53 5.68		15.30 15.41
4h	Sticky liquid	3301, 1667, 1595, 1477, 1442, 752	2.12 (6H, s, 2Me), 7.05 - 7.44 (24H, m, ArH), 7.57 (2H, s, 2NH)	$C_{40}H_{32}N_2O_2S_4Se$	61.60 61.48	4.14 4.06	3.59 3.55	16.44 16.39
4i	Sticky liquid	3255, 1595, 1490, 1442, 1387, 1185	2.29 (6H, s, 2Me), 6.69 - 7.59 (32H, m, ArH), 7.71 (2H, s, 2NH)	$C_{50}H_{40}N_2O_4S_6Se$	59.80 59.78	4.01 3.86	2.79 2.69	19.15 19.18

(phenylthio)diphenyl sulfide (5).[11] That is, compound (5) was treated with sodium nitrite in the presence of concentrated HCl in DMF containing DMSO at 0 °C to give its diazonium salt (6), which then reacted with *in situ* generated sodium selenide in DMF at 100 °C under nitrogen atmosphere[12] (Scheme 2). However, the reaction mixture gave many spots on TLC. Structural identification of the products failed.

On the other hand the reaction of 4-ethylaniline under the same conditions gave bis(4-ethylphenyl) selenide in 13% yield. The result indicates that synthesis of symmetrical diaryl selenides (4) by the conventional method involving diazonium ions would not be a promising method.

Scheme 2



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In the meantime, the reactions of 1 with lithium *n*-butylselenolate, prepared by treatment of *n*-butyllithium with selenium metal gave 2-arylthio-2'-(*n*-butylseleno)diphenyl sulfides (7) in good to moderate yields. The quantities of the reactants, reaction times, and yields of compounds (7) are summarized in Table 3 and their analytical, IR, and ^{1}H NMR data are summarized in Table 4.

Table 3. Reaction conditions and yields of 2-arylthio-2'-(*n*-butylseleno)diphenyl sulfides (7)

Compound	mmol	Se (mmol)	*n*-BuLi (mmol)	THF (mL)	Time (h)	Yield[a] (%)	
1a	0.554	3.94	3.75	40	19	**7a**	98
1b	0.469	2.56	2.75	50	21	**7b**	38[b]
1c	0.409	2.63	3.00	40	22	**7c**	59[c]
1d	0.539	2.90	3.00	30	4.5	**7d**	76
1e	0.523	2.42	2.50	40	18	**7e**	47[d]
1f	0.409	2.62	3.00	30	20	**7f**	59[e]
1i	0.306	2.54	3.00	40	14	**7g**	23
1j[f]	0.337	2.62	3.00	30	4.5	**7h**	76
1k[g]	0.406	2.55	3.00	40	7	**7i**	81

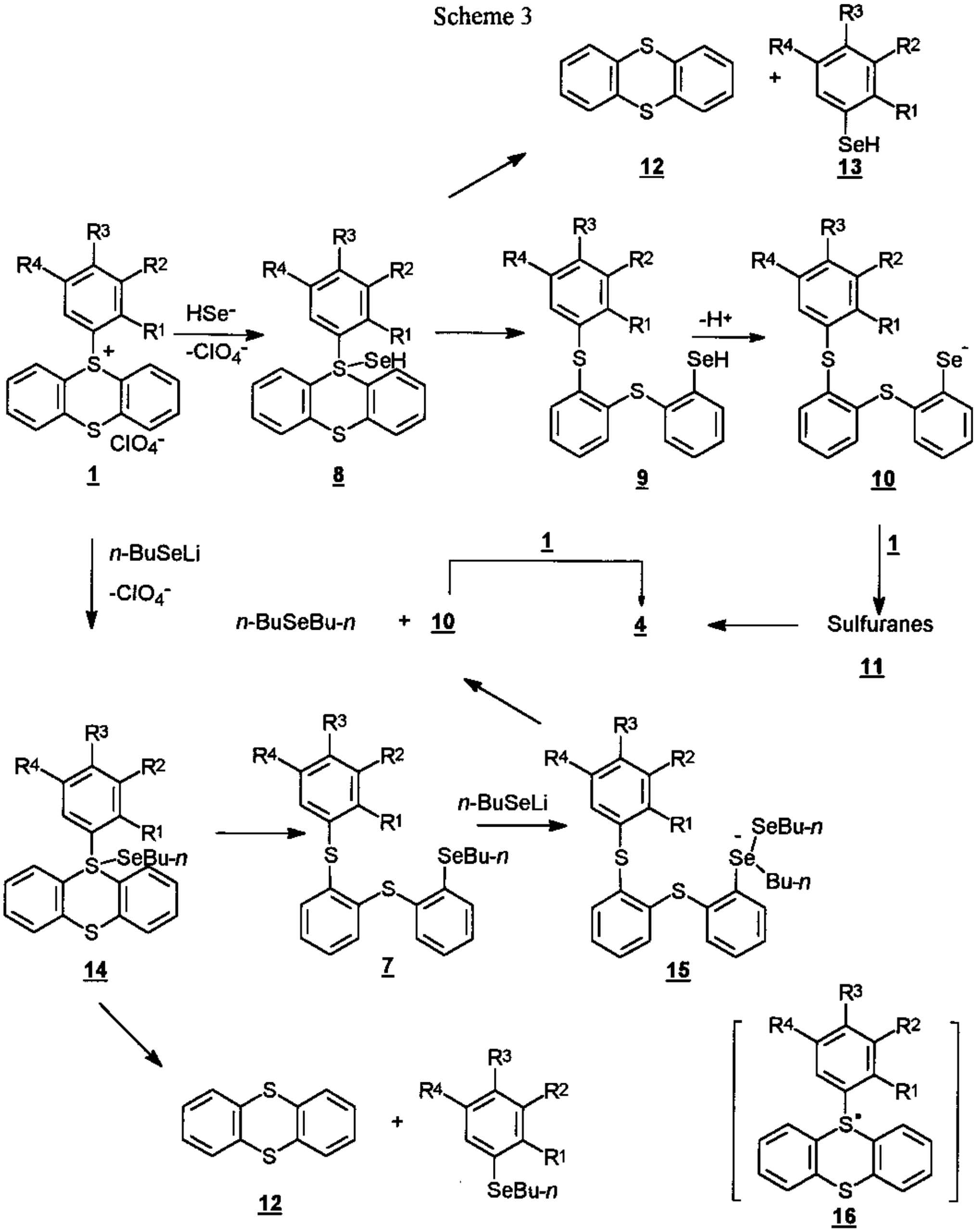
[a] Isolated yield. [b] Compound (4b) was isolated in 34% yield. [c] Compound (4c) was isolated in 35% yield. [d] Compound (4e) was isolated in 51% yield. [e] Compound (4f) was isolated in 35% yield. [f] 1j: $R^1 = R^3 = MeO$, $R^2 = R^4 = H$. [g] 1k: $R^1 = MeO$, $R^2 = R^4 = H$, $R^3 = t\text{-Bu}$.

The mechanism of the formation of compounds (4) and (7) might be explained on the basis of sulfuranes[14] (Scheme 3). The reactions of sulfonium salts (1) with hydrogen selenide give sulfuranes which undergo a bond reorganization leading to either selenols (9) or thianthrene (12) and areneselenols (13). Since

Table 4. Analytical, IR, and ^{1}H NMR data of 2-arylthio-2'-(*n*-butylseleno)diphenyl sulfides (7)

Compound	IR (ν, cm^{-1})	^{1}H NMR ($CDCl_3$) (δ, ppm)	Molecular formula	Calcd/Found % C	H	S
7a	2956, 1492, 1442, 1248	0.85 (3H, t, J = 6.0 Hz, Me), 1.47 (4H, m, CH_2CH_2), 2.94 (2H, t, J = 7.0 Hz, $SeCH_2$), 3.78 (3H, s, MeO), 6.93 - 7.91 (12H, m, ArH)	$C_{23}H_{24}OS_2Se$	60.12 60.01	5.26 5.18	13.95 13.84
7b	2956, 2925, 1492, 1441, 1246	0.88 (6H, t, J = 6 Hz, 2Me), 1.41 (4H, m, CH_2CH_2), 2.97 (2H, t, J = 7 Hz, $SeCH_2$), 4.02 (2H, q, J = 6 Hz, OCH_2), 6.79 - 7.97 (12H, m, ArH)	$C_{24}H_{26}OS_2Se$	60.87 60.82	5.53 5.62	13.54 13.49
7c	2956, 1492, 1440, 1245	0.95 (6H, m, 2Me), 1.50 (8H, m, $2CH_2CH_2$), 2.96 (2H, t, J = 7.0 Hz, $SeCH_2$), 3.95 (2H, t, J = 6 Hz, OCH_2), 6.81 - 7.97 (12H, m, ArH)	$C_{26}H_{30}OS_2Se$	62.26 62.31	6.03 6.17	12.78 12.70
7d	2956, 1503, 1441, 1253, 1025	0.80 (3H, t, J = 6.0 Hz, Me), 1.61 (4H, m, CH_2CH_2), 2.95 (2H, t, J = 7.0 Hz, $SeCH_2$), 3.74 (3H, s, MeO), 3. 79 (3H, s, MeO), 6.48 - 7.46 (11H, m, ArH)	$C_{24}H_{26}O_2S_2Se$	58.28 58.22	5.35 5.31	13.10 13.20
7e	2956, 1476, 1442, 1234, 1038	0.84 (3H, t, J = 6.0 Hz, Me), 1.50 (4H, m, CH_2CH_2), 2.94 (2H, t, J = 7.0 Hz, $SeCH_2$), 5.96 (2H, s, $-OCH_2O-$), 6.87 - 7.04 (11H, m, ArH)	$C_{23}H_{22}O_2S_2Se$	38.34 38.27	4.68 4.55	13.54 13.49
7f	2956, 1490, 1439	0.82 (3H, t, J = 6.0 Hz, Me), 1.61 (4H, m, CH_2CH_2), 2.26 (3H, s, Me), 2.95 (2H, t, J = 7.0 Hz, $SeCH_2$), 7.09 - 7.61 (12H, m ,ArH)	$C_{23}H_{24}S_2Se$	62.29 62.18	5.45 5.41	14.46 14.40
7g	3245, 2962, 1491, 1441, 1226, 1105	0.82 (3H, t, J = 6.0 Hz, Me), 1.54 (4H, m, CH_2CH_2), 2.32 (3H, s, Me), 2.92 (2H, t, J = 7.0 Hz, $SeCH_2$), 7.04 - 7.69 (16H, m, ArH), 7.72 (1H, s, NH)	$C_{29}H_{29}NO_2S_3Se$	58.18 58.24 (For N, 2.34) (For N, 2.29)	4.88 4.95	16.04 16.07
7h	2823, 1490, 1452, 1248, 1240, 759	0.80 (3H, t, J = 6.0 Hz, Me), 1.61 (4H, m, CH_2CH_2), 2.95 (2H, t, J = 7.0 Hz, $SeCH_2$), 3.74 (3H, s, MeO), 3.79 (3H, s, MeO), 6.48 - 7.36 (11H, m, ArH)	$C_{24}H_{26}O_2S_2Se$	58.88 58.94	5.35 5.43	13.10 13.17
7i	2962, 2956, 1460, 1442, 1233	0.89 (3H, t, J = 6.0 Hz, Me), 1.31 (9H, s, *t*-Bu), 1.50 (4H, m, CH_2CH_2), 2.92 (2H, t, J = 7.0 Hz, $SeCH_2$), 3.82 (3H, s, MeO), 6.94 - 7.46 (11H, m, ArH)	$C_{27}H_{32}OS_2Se$	62.89 62.82	6.26 6.20	12.44 12.36

Scheme 3



areneselenols are known to be more acidic than the corresponding sulfur analogs,[15] selenolate anions (<u>10</u>), which reacted with unreacted <u>1</u> in the same fashion as in the formation of sulfuranes (<u>8</u>) to give compounds (<u>4</u>) *via* new sulfuranes (<u>11</u>). However, more work has to be done to delineate the relationship between the variation of the yields of compound (<u>12</u>) and the nature of the substituents on the phenyl ring bonded to a trivalent sulfur atom of compound (<u>12</u>).

The formation of compounds (<u>7</u>) can be explained by the same mechanism as in the formation of compounds (<u>4</u>) by assuming the formation of sulfuranes (<u>14</u>). The formation of compounds (<u>4</u>) as minor products might be rationalized on the basis of the formation of selenurane anion (15) in the presence of excess amount of lithium *n*-butylselenolate. The chemoselective formation of selenurane anion (15) instead of sulfurane anion seems to be reasonable in view of the formation of selenurane anion by treatment of mixed thioselenoacetals with *n*-BuLi in THF at -78 °C.[16] The selenurane anion (15) would be decomposed to give di-*n*-butyl selenide and selenolates (10), which react with unreacted 1 to give compounds (4). This view is supported by the observation in which methyl phenyl selenide reacts with lithium methylselenolate to give lithium phenylselenolate.[14] In addition, it has been confirmed that treatment of compound (7a) with lithium *n*-butylselenolate gives compound (**4a**) in 68% yield. One might conceive of the formation of sulfuranyl radical (16) by either homolysis of sulfurane (8) or direct electron transfer between 1 and HSe$^-$.[18] However the mechanism involving sulfuranyl radical (16) is highly unlikely because it has been known that seleno radical undergoes rapidly dimerization to give diselenide,[19] which is incompatible with the high yields of compounds (**4a-c**) and (**4f**). By the same token, sulfurane rather than sulfuranyl radical mechanism is more likely involved for the formation of compounds (7a-d) and (7h-i).

EXPERIMENTAL

5-Arylthianthreniumyl perchlorates (1) were prepared by the literature methods.[7] Selenium metal and *n*-butyllithium were purchased from Aldrich. Tetrahydrofuran was purchased from Merck, and dried on sodium at reflux. Ethanol was purchased form Hayman Limited. IR spectra were obtained on a Shimadzu 540 spectrophotometer. ^{1}H NMR spectra were determined on a Brucker 80 MHz spectrometer using tetramethylsilane as an internal standard. Mass spectra were obtained by electron impact at 70 eV on a Varian Mat 711. Elemental analyses were determined by Korea Basic Science Center. Melting points were measured on a Fisher-Johns melting point apparatus and are uncorrected. Column chromatography was performed on a silica gel (Merck 230 - 400 mesh, ASTM).

General Procedures for the Synthesis of Bis[2-(2-arylthiophenylthio)phenyl] Selenides (4) (Z = Se): To a stirred solution of selenium metal (304 mg, 3.85 mmol) in absolute ethanol (40 mL) cooled to 0 °C was added sodium borohydride (4.31 mmol). The mixture was stirred for 15 min, followed by raising the temperature to room temperature. To the nearly colorless solution of sodium hydrogen selenide in EtOH was added compound (1) (0.590 mmol). The mixture was vigorously stirred for an appropriate time at reflux to give brown solution, which was poured into water (10 mL), followed by extracting with CH_2Cl_2 (3 × 50 mL). The extract was dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel column (8 × 3 cm). Elution with a mixture of *n*-hexane and chloroform (4:1, 100 mL) gave thianthrene (12). Elution with a mixture of *n*-hexane and ethyl acetate (5:1, 100 mL) gave compounds (4). In each case consult Table 1 for quantities of reactants, reaction times, and yields and Table 2 for analytical and spectroscopic data of 4.

General Procedure for the Synthesis of 2-Arylthio-2'-(*n*-butylseleno)diphenyl Sulfides (7): Selenium metals were placed in a septum capped two-necked flask equipped with a condenser under nitrogen atmosphere. Dried tetrahydrofuran and *n*-butyllithium (2.5 M in hexane) in a series were added into the flask at room temperature. The mixture was stirred for 40 min. To this was added compound (1), which was heated for an appropriate time at reflux. The reaction mixture was cooled to room temperature, followed by addition of water (3 mL). After evaporation of the solvent, water (100 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The extract was dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on a silica gel column (8 × 3 cm). Elution with a mixture of *n*-hexane and chloroform (3:1, 100 mL) gave di-*n*-butyl selenide and (12). Elution with a mixture of *n*-hexane and ethyl acetate (2:1, 100 mL) gave compounds (7). In each case consult Table 3 for quantities of reactants, reaction times, and yields and Table 4 for analytical and spectroscopic data of 7.

Attempted Preparation of Bis[2-(2-phenylthiophenylthio)phenyl] Selenide (4j): (a) Preparation of Sodium Selenide: A mixture of sodium (64 mg, 2.78 mmol), selenium metal (80 mg, 1.01 mmol), and naphthalene (33 mg, 0.26 mmol) was stirred for 1 h at 110 °C under nitrogen atmosphere. (b) To a solution of 2-amino-2'-(phenylthio)diphenyl sulfide (5) (110 mg, 0.36 mmol) in DMF (20 mL) at 0 °C was added concentrated HCl (0.5 mL), followed by addition of a solution of sodium nitrite (75 mg, 1.09 mmol) in a mixture of DMF and DMSO (1:1, 30 mL) by maintaining the temperature of the solution at 0 °C. To the solution at 0 °C was added dropwisely the *in situ* generated sodium selenide at 110 °C for 1 h, which was stirred for 24 h. After removal of the solvent *in vacuo*, the water (50 mL) was added to the residue which was extracted with CH_2Cl_2 (3 × 50 mL). The extract was dried over $MgSO_4$. Evaporation of the solvent gave a residue, which was chromatographed on a silica gel (10 × 3 cm). Elution with a mixture of *n*-hexane and CH_2Cl_2 (2:1, 100 mL) gave 3 mg of a mixture of unknown compounds.

Preparation of Bis(4-ethylphenyl) Selenide: To a solution of 4-ethylaniline (1.234 g, 10.18 mmol) in a mixture of concentrated hydrochloric acid (1.5 mL) and DMF (20 mL) at 0 °C was added a solution of sodium nitrite (1.500 g, 21.74 mmol) in a mixture of DMF and DMSO (1:1, 30 mL) by maintaining the temperature of the solution below 4 °C. This solution was dropwisely added to the *in situ* prepared sodium selenide at 110 °C for 1 h. The mixture was worked up as described for the attempted preparation of **4j**. Chromatography (12 × 1 cm) of the residue using *n*-hexane (300 mL) gave naphthalene (41 mg, 0.318 mmol) and bis(4-ethylphenyl) selenide (121 mg, 13%). IR (KBr, cm^{-1}): 2964, 2929, 1489, 1457, 1012, 820; ^{1}H NMR ($CDCl_3$): δ 1.19 (t, 6H, J = 6.0 Hz), 2.61 (q, 4H, J = 6.0 Hz), 7.06 (d, 4H, J = 8.0 Hz), 7.38 (d, 4H, J = 8.0 Hz); MS (EI, m/z, %): 290 (M$^+$, 40), 288 (20), 210 (52), 195 (100): Anal. Calcd for $C_{16}H_{18}Se$: C, 66.43; H, 6.27. Found: C, 66.31; H, 6.21. Elution with a mixture of *n*-hexane and CH_2Cl_2 (1:1, 300 mL) gave unknown mixtures (93 mg). Elution with a mixture of *n*-hexane and ethyl acetate (2:1, 150 mL) gave unreacted 4-ethylaniline (273 mg, 22%)

Reaction of 2-(4-Anisylthio)-2'-(*n*-butylseleno)diphenyl Sulfide (7a) with Lithium *n*-butylselenolate in the Presence of 5-(4-Anisyl)thianthreniumyl Perchlorate (1a): Selenium metal (42 mg, 0.532 mmol) was placed in a septum capped two-necked flask equipped with a condenser under nitrogen atmosphere. Dried THF (10 mL) and *n*-butyllithium (0.2 mL, 2.5 M in hexane) were added in a series by using a hypodermic syringe at room temperature. The mixture was stirred for 15 min, followed by addition of 7a (45 mg, 0.0979 mmol) in THF (30 mL) by using a hypodermic syringe, which was stirred for 2.5h at room temperature. To the solution was added 1a (42 mg, 0.100 mmol), which was heated at reflux for 15 h. The mixture was cooled to room temperature, followed by addition of water (2 mL). Evaporation of the solvent gave a residue to which water (50 mL) was added and then the mixture was extracted with CH_2Cl_2

(3 × 50 mL). The extract was dried over $MgSO_4$. Evaporation of the solvent gave a residue, which was chromatographed on silica gel column (8 × 3 cm). Elution with *n*-hexane (100 mL) gave 12 (6 mg, 0.0277 mmol). Elution with a mixture of *n*-hexane and CH_2Cl_2 (4:1, 100 mL) gave unreacted 7a (3 mg, 7%). Elution with the same solvent mixture (2:1, 100 mL) gave 4a (38 mg, 68%).

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