

Syntheses of Dibenzo[*c,e*][1,2]diselenin and Related Novel Chalcogenide Heterocyclic Compounds

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Received August 13, 1990

Reaction of 2,2'-dilithio-1,1'-binaphthyl with selenium followed by air oxidation gives a mixture of dinaphthoselenophene and dimer and oligomers of 2,2'-diseleno-1,1'-binaphthyl. 2,2'-Dilithio-1,1'-biphenyl reacts with selenium to afford dibenzo[*c,e*][1,2]diselenin. Structures of the dimeric 2,2'-diseleno-1,1'-binaphthyl and dibenzo[*c,e*][1,2]diselenin have been confirmed by X-ray crystallographic analyses. Similar reaction of 2,2'-dilithio-1,1'-binaphthyl with sulfur or tellurium gives a mixture of dinaphthothiophene and dinaphtho[2,1-*c*:1',2'-*e*][1,2]dithiin or a mixture of dinaphthotellurophene and oligomer of 2,2'-ditelluro-1,1'-binaphthyl, respectively. Dibenzotellurophene and oligomer of 2,2'-ditelluro-1,1'-biphenyl are obtained from reaction of 2,2'-dilithio-1,1'-biphenyl with tellurium.

J. Heterocyclic Chem., **28**, 433 (1991).

Unsaturated heterocyclic compounds containing group VIB elements (sulfur, selenium, and tellurium) have received much attention in fields of physical chemistry and material science, because some cyclic diselenides and ditellurides such as TTN (1,4,5,8-tetrathionaphthalene) and TSeT (5,6,11,12-tetraselenotetracene) afford highly conductive charge-transfer complexes [3-13]. Many kinds of analogues which are planer molecules have been synthesized, but only a few compounds with nonplaner structure have been reported. We have been interested in the chemistry of the compounds with C_2 symmetry. Recently, some unique relationship between molecular chirality and the character of nematic liquid crystals has been reported for C_2 symmetrical dinaphtho[2,1-*c*:1',2'-*e*][1,2]dithiin [14-15]. The reported synthetic methods for sulfur-containing molecules [14-18] were sometimes inapplicable to syntheses of selenium or tellurium analogues, and only two examples have been prepared [19,20]. Since insertion reaction of a group VIB atom into carbon-metal is effective for carbon-chalcogen bond formation, reactions of 2,2'-dilithio-1,1'-binaphthyl and 2,2'-dilithio-1,1'-biphenyl with sulfur, selenium, and tellurium and their application to synthesis of novel organoselenium and -tellurium compounds were studied.

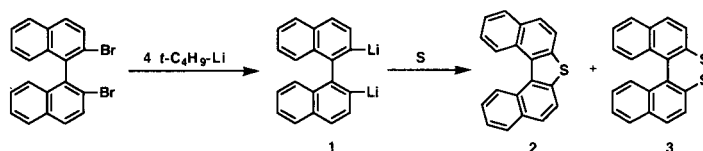
Reaction of 2 equivalents of sulfur with 2,2'-dilithio-1,1'-binaphthyl (**1**), which was prepared *in situ* from 2,2'-dibromo-1,1'-binaphthyl by the treatment with *t*-butyllith-

ium, [21-24] proceeded at $-78 - -20^\circ$ in THF to give dinaphthothiophene (**2**) and dinaphtho[2,1-*c*:1',2'-*e*][1,2]dithiin (**3**) [16-18] in 19 and 27% yields, respectively.

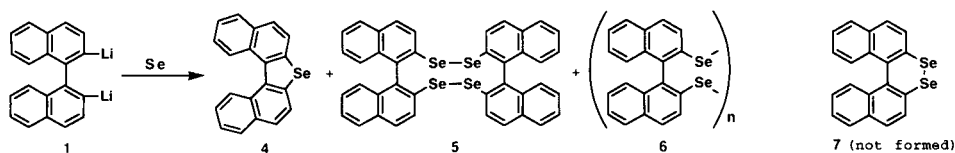
When the reaction mixture of **1** with 2 equivalents of selenium was oxidized by air, three new organoselenium compounds **4**, **5**, and **6** were obtained in 6%, 19%, and 53% yields, respectively. The structure of **4** was determined by spectroscopic analyses. However, it was difficult to determine the structure of **5**, because the ^{13}C -nmr and ms data of **5** were consistent with dinaphthodiselenin **7**, which is a selenium analogue of **3**. Finally, the structure of **5** was confirmed by single crystallographic X-ray analysis. The oligomeric structure of **6** was determined by the following evidence: ^{13}C -nmr showed 10 broad signals; the result of elemental analysis was consistent with $(\text{C}_{20}\text{H}_{12}\text{Se}_2)_n$ formula; observed molecular weight was 2820 ± 20 . The oligomer **6** was converted to **5** in 20% yield by the treatment with potassium in boiling THF followed by air oxidation.

Reaction of 2,2'-dilithio-1,1'-biphenyl (**8**) with selenium proceeded under the same conditions to give dibenzo[*c,e*][1,2]diselenin **9** [19] in 63% yield as an exclusive product. The structure of **9** was also determined by X-ray crystallographic analysis. Oxidative Se-Se bond cleavage of **9** was performed by bromination to give 2,2'-bis(bromoseleno)-1,1'-biphenyl (**10**). The compound **10** was easily converted

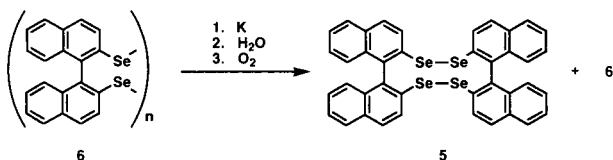
Scheme 1



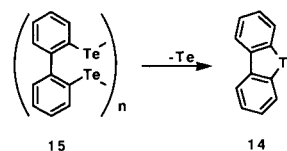
Scheme 2



Scheme 3

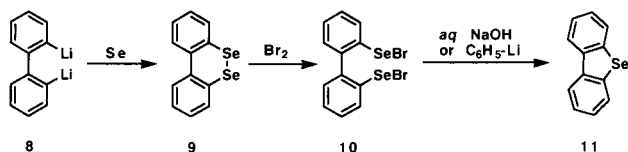


Scheme 6



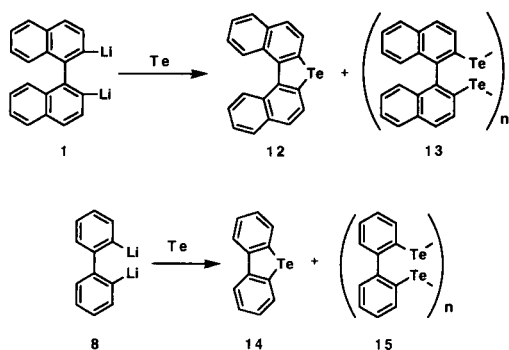
to dibenzoselenophene (**11**) by treatment with aqueous sodium hydroxide or phenyllithium.

Scheme 4



Reaction of **1** with tellurium under the same conditions gave dinaphthotellurophene (**12**) and the oligomer of 2,2'-ditelluro-1,1'-binaphthyl **13** in 19% and 24% yields, respectively. Reaction of **8** with tellurium gave a mixture of dibenzotellurophene (**14**, 32% yield) and an unstable compound, the structure of which seemed to be the reported oligomer of 2,2'-ditelluro-1,1'-biphenyl (**15**) [25], in 27% yield. Oligomeric structures of **13** and **15** were speculated by signal broadening of ^{13}C -nmr spectra and ms spectra. The compound **15** gradually decomposed to a mixture of **14** and tellurium metal upon exposure to air. The decomposition of **15** seemed to be carried out by oxygen initiated homolytic Te-Te bond fission [26,27].

Scheme 5



Molecular structures and atomic numbering of **5** and **9** are illustrated in Figure 1 and Figure 2, respectively, where hydrogen atoms are omitted. Crystal data and data collection details of **5** and **9** are shown in Table 1 and Table 2, respectively [28]. Selected interatomic distances and angles except hydrogen atoms of **5** and **9** are summarized in Table 3 and Table 4, respectively.

Table 1
Crystallographic Data for **5** and **9**

	5	9
molecular formula	$\text{C}_{40}\text{H}_{24}\text{Se}_4$	$\text{C}_{12}\text{H}_8\text{Se}_2$
molecular weight	820.46	310.12
crystal size/mm ³	0.35x0.20x0.13	0.20x0.10x0.10
space group	$P2_1/n$	$P4_12_12$
cells dimens		
$a/\text{Å}$	12.911(1)	14.151(3)
$b/\text{Å}$	24.409(2)	14.146(2)
$c/\text{Å}$	11.861(1)	21.651(7)
α/deg	89.99(1)	89.96(2)
β/deg	97.04(1)	90.11(2)
γ/deg	90.00(1)	90.02(1)
vol./Å ³	3709.6(6)	4334.2(17)
Z	4	16
$\rho_{\text{measd.}}/\text{g cm}^{-3}$	1.487	1.908
$\rho_{\text{calcd.}}/\text{g cm}^{-3}$	1.470	1.902

Characteristic other structural data of **5** and **9** in comparison to the reported data of **3**, dibenzo[*c,e*]dithiin (**16**), diphenyl disulfide, and diphenyl diselenide are shown in Table 5. Oxidation potentials of **5** and **9** obtained by cyclic voltammetry method are also cited in Table 5.

Structures 1

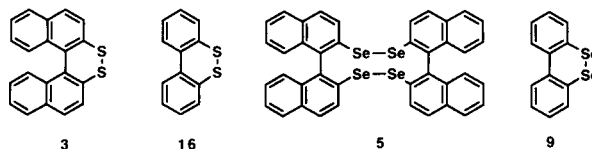


Table 2
Data Collection and Refinement Details for 5 and 9

	5	9
diffractometer		Rigaku automated four-circles diffractometer, AFC-5
radiation		CuK α (1.54051 Å)
monochromator		graphite crystal
scan type		θ - 2θ
scan speed, deg min ⁻¹		0° ≤ 2 θ ≤ 76° 8(2 θ) 76° ≤ 2 θ 102° 4(2 θ) 102° ≤ 2 θ 126° 2(2 θ)
background		0° ≤ 2 θ ≤ 76° 3s 76° ≤ 2 θ ≤ 126° 7s
2 θ scan limit, deg		126
"standard" reflections		3 every 100 reflections
indices	(-2,15,2), (7,-8,1), (-4,-13,3)	(0,7,-6), (0,7,6), (-6,-1,-4)
crystal stability	4.9-6.1% anisotropic decay	1.9-2.2% anisotropic decay
unique reflections with $I > \sigma(I)$	5661	1241
R factor	0.164	0.107
R_w	0.153	0.104

Table 3
Selected Bond Lengths and Angles of 5

bond length/Å					
C(1)-C(2)	1.39	C(1)-C(10)	1.41	C(2)-C(3)	1.39
C(3)-C(8)	1.54	C(4)-C(5)	1.57	C(5)-C(6)	1.53
C(7)-C(8)	1.47	C(8)-C(9)	1.43	C(9)-C(10)	1.41
C(10)-Se(42)	1.90	Se(41)-Se(42)	2.32	C(3)-C(4)	1.41
				C(6)-C(7)	1.42
				C(9)-C(12)	1.50
bond angle/deg					
C(2)-C(1)-C(10)	120	C(1)-C(2)-C(3)	121	C(2)-C(3)-C(4)	120
C(2)-C(3)-C(8)	120	C(4)-C(3)-C(8)	120	C(3)-C(4)-C(5)	115
C(4)-C(5)-C(6)	128	C(5)-C(6)-C(7)	108	C(6)-C(7)-C(8)	130
C(3)-C(8)-C(7)	118	C(3)-C(8)-C(9)	117	C(7)-C(8)-C(9)	125
C(8)-C(9)-C(10)	120	C(8)-C(9)-C(12)	118	C(10)-C(9)-C(12)	122
C(1)-C(10)-C(9)	123	C(1)-C(10)-Se(42)	122	C(9)-C(10)-Se(42)	116
C(10)-Se(42)-Se(41)	103				

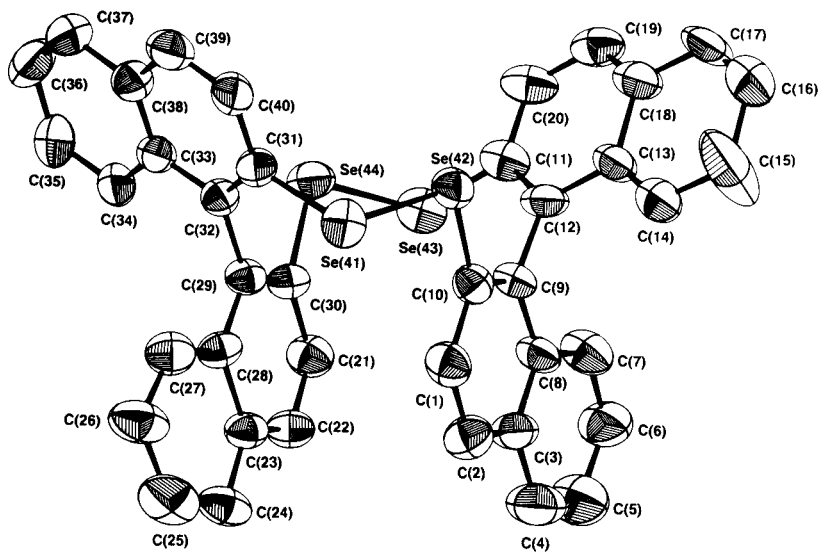
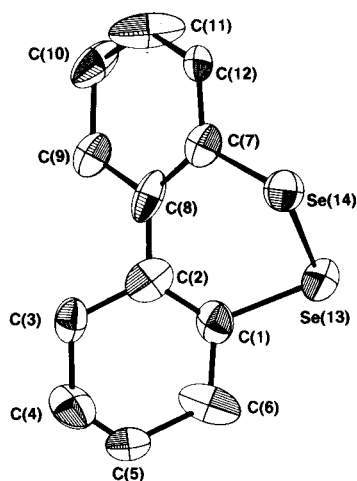


Figure 1. ORTEP Drawing of the Molecular Structure of 5.

Figure 2. ORTEP Drawing of the Molecular Structure of **9**.Table 4
Selected Bond Lengths and Bond Angles of **9**

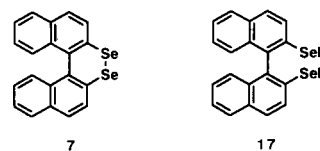
bond length/Å					
C(1)-C(2)	1.45	C(1)-C(6)	1.40	C(1)-Se(13)	1.93
C(2)-C(8)	1.47	C(3)-C(4)	1.55	C(4)-C(5)	1.29
C(7)-C(8)	1.32	C(7)-Se(14)	1.91	Se(13)-Se(14)	2.35
C(2)-C(3)	1.43	C(5)-C(6)	1.32		

bond angle/deg					
C(2)-C(1)-Se(13)	118	C(2)-C(1)-C(6)	125	C(6)-C(1)-Se(13)	117
C(1)-C(2)-C(3)	113	C(1)-C(2)-C(8)	123	C(2)-C(3)-C(4)	121
C(3)-C(4)-C(5)	116	C(4)-C(5)-C(6)	128	C(1)-C(6)-C(5)	118
C(8)-C(7)-Se(14)	124	C(2)-C(8)-C(7)	124	C(1)-Se(13)-Se(14)	92
C(7)-Se(14)-Se(13)	92				

It has been described that strong strain exists in the non-planer structures of dithiins **3** and **16** [29]. The magnitude of the strain could be estimated by dihedral angle around the S-S bond (C-S-S-C) or Se-Se bond (C-Se-Se-C) [29-32]. The dihedral angle of non-strained diphenyl disulfide and diphenyl diselenide are 96° and 97°, respectively. The observed structure of **5** and **9** showed that strong

strain existed in these molecules. The strain might be the major reason why the oxidative Se-Se bond formation of the bisselenol **17** did not afford the diselenin **7** but dimeric and oligomeric diselenides. In the case of tellurium analogues, intermolecular Te-Te bond formation proceeded to give the oligomers.

Structures 2



The strong molecular distortion of diselenides **5** and **9** does not affect their oxidation potentials to any great extent, and first oxidation potential peaks of **5** and **9**, 1.28 and 1.13 V (*vs* Ag/AgCl) respectively, are almost same as diphenyl diselenide (1.32 V).

EXPERIMENTAL

Melting points were uncorrected. The ir and uv spectra were determined on JASCO A-102 and Hitachi A-220 spectrometers, respectively. Both ¹H-nmr (90 MHz) and ¹³C-nmr (22.5 MHz) spectra were taken on a JEOL JNM FX-90Q instrument in deuteriochloroform and chemical shifts are reported in δ value (ppm) relative to internal tetramethylsilane (δ = 0). The ⁷⁷Se-nmr spectra were recorded on a JEOL JNM FX-90Q instrument by using resonance frequency of 17.04 MHz. The chemical shift is reported in δ value (ppm) relative to external dimethyl selenide (δ = 0). Molecular weight was observed by depression of vapor pressure method on a Hitachi 105 instrument in benzene solutions. Mass spectra were determined by EI method (ionization energy of 70 eV) on a JEOL JMS D-300 spectrometer. Oxidation potential were observed on a Yanagimoto polarographic analyzer P-1100 by cyclic voltammetry method in the following conditions: supporting electrolyte, 0.1M tetrabutylammonium fluoroborate; scan rate, 100 mV/s; electrode, glassy carbon electrode. Elemental microanalyses were performed at Elemental Analytical Center of Faculty of Agriculture, Nagoya University.

2,2'-Dibromo-1,1'-biphenyl [36] and 2,2'-dibromo-1,1'-binaph-

Table 5
Observed and Reported Bond Length, Bond Angles, and Oxidation Potential Peak of **3**, **5**, **9**, and Related Compounds

Compound	Bond length/Å		Bond angle/degree		Dihedral angle/degree		Oxidation potential peak (E _p /V vs Ag/AgCl electrode)
	S-S or Se-Se	C-S or C-Se [a]	S-S-C or Se-Se-C [a]	C-C-C arene	Ar-Ar [b]	C-S-S-C or C-Se-Se-C	
3 [c]	2.06	1.78	98.0	117-123	56	62	
16 [d]	2.05	1.76	98.2	118-123	34	69	
Ph-S-S-Ph [e]	2.03	1.81	106.2			96	
5	2.32 [a]	1.90	102.5	115-129	107	74.5 [a]	1.28, 1.47 [f]
9	2.35	1.92	92	112-128	46	59.3	1.13, 1.25 [g]
Ph-Se-Se-Ph [e]	2.29	1.93	106.1			97	1.32 [g]

[a] Mean value. [b] Between mean planes of two aromatic rings. [c] See ref [18] refs [33,34]. [e] See ref [35]. [f] In dichloromethane. [g] In acetonitrile.

thyl [22] were synthesized by procedures cited in the references. Sulfur, selenium, and tellurium powder their purity over 99.99% obtained from Aldrich Chemical Co. or Janssen Chimia Co. were employed to reactions without further purifications. A pentane solution of *t*-butyllithium obtained from Aldrich Chemical Co. was used as received. Tetrahydrofuran was distilled over a mixture of benzophenone and sodium before use. All reactions except oxidation process were carried out under nitrogen (>99.99% purity) atmosphere.

Reaction of 2,2'-Dilithio-1,1'-binaphthyl (**1**) with Sulfur.

A solution of 2,2'-dibromo-1,1'-binaphthyl (1.10 g, 2.67 mmoles) in THF (50 ml) was cooled in a dry ice/acetone bath and to this was added *t*-butyllithium (1.79 M, 5.3 ml, 10.7 mmoles). After the mixture was stirred for 4 hours, sulfur (0.205 g, 6.40 mmoles) was added in one portion and the cooling bath was removed. Then the mixture was stirred at 25° for 0.5 hour and to this was added a mixture of 1M ammonium chloride solution. The resulting mixture was extracted twice with benzene (100 ml). The extracts were dried over anhydrous magnesium sulfate and then concentrated. Column chromatography on silica gel eluting with 20% benzene in petroleum ether gave pure **2** (0.144 g, 19%) and **3** (0.226 g, 27%).

Compound **2** was obtained as colorless crystals, mp 204-205° (lit [37] mp 204°); uv (acetonitrile): max 353 nm (ϵ 10700), 338 (10700), 312 (11000), 275 (24000), 235 (30900), 212 (52500); ir (potassium bromide): 3050, 2970, 1510, 1508, 1260, 1090, 1025, 800, 761, 745 cm^{-1} ; $^1\text{H-nmr}$: 9.0-8.8 (m, 2H), 8.1-7.8 (m, 4H), 7.7-7.0 (m, 6H); $^{13}\text{C-nmr}$: 138.6, 132.3, 130.0, 128.7, 127.9, 127.4, 126.2, 125.3, 124.9, 120.9.

Anal. Calcd. for $\text{C}_{20}\text{H}_{12}\text{S}$: C, 84.47; H, 4.25. Found: C, 84.49; H, 4.36.

Compound **3** was obtained as yellow needles, mp 205-206° (lit [18] mp 213-214°); ir (potassium bromide): 3050, 2960, 1504, 1260, 1090, 1012, 810, 750 cm^{-1} ; $^1\text{H-nmr}$: 8.0-7.8 (m, 6H), 7.5-7.1 (m, 6H); $^{13}\text{C-nmr}$: 141.2, 135.9, 133.6, 132.2, 128.3, 127.9, 127.7, 127.0, 126.3, 126.0.

Anal. Calcd. for $\text{C}_{20}\text{H}_{12}\text{S}_2$: C, 75.91; H, 3.82. Found: C, 75.91; H, 3.87.

Reaction of **1** with Selenium. A General Procedure for the Reaction of 2,2'-Dilithio-1,1'-biaryl, **1** or **8**, with Selenium or Tellurium.

To a solution of 2,2'-dibromo-1,1'-binaphthyl (6.72 g, 16.3 mmoles) in THF (200 ml) was added *t*-butyllithium (36.4 ml, 65.2 mmoles) at -78°. After 4 hours stirring, to this was added selenium (2.58 g, 32.6 mmoles) and the temperature rose to 25°. Then to this was added a mixture of benzene (200 ml) and 1M ammonium chloride solution, and air was introduced into the mixture until the aqueous layer became colorless. The organic layer was separated, washed with saturated sodium chloride solution, dried over magnesium sulfate and concentrated *in vacuo*. Column chromatography on silica gel eluting with 20% benzene in petroleum ether gave **4** (0.324 g, 6%) as colorless crystals, **5** (1.26 g, 19%) as red crystals, and **6** (3.56 g, 53%) as a red powder.

Compound **4** had mp 206-207°; uv (acetonitrile): max 340 nm (ϵ 17000), 319 (15500), 284 (24500), 242 (46800), 216 (89100); ir (potassium bromide): 3055, 1608, 1580, 1510, 1362, 1136, 808, 770 cm^{-1} ; $^1\text{H-nmr}$: 7.9-7.8 (m, 4H), 7.6-7.1 (m, 8H); $^{13}\text{C-nmr}$: 138.6, 133.7, 133.0, 128.2, 127.9, 126.6, 126.0, 125.8, 125.3; ms: m/z

326-334 (M^+), 252 (M^+Se).

Anal. Calcd. for $\text{C}_{20}\text{H}_{12}\text{Se}$: C, 72.51; H, 3.65. Found: C, 72.35; H, 3.70.

Compound **5** had mp 215-216°; uv (dichloromethane): max 258 nm (ϵ 128800); ir (potassium bromide): 3070, 1582, 1508, 810, 750 cm^{-1} ; $^1\text{H-nmr}$: 8.1-7.9 (m, 4H), 7.7-7.0 (m, 20H); $^{13}\text{C-nmr}$: 138.2, 133.1, 133.0, 130.6, 129.2, 128.7, 128.1, 127.0, 126.3, 125.9; ms: m/z 406-412 ($\text{C}_{20}\text{H}_{12}\text{Se}_2$), 326-334 ($\text{C}_{20}\text{H}_{12}\text{Se}$), 252 ($\text{C}_{20}\text{H}_{12}$).

Anal. Calcd. for $\text{C}_{40}\text{H}_{24}\text{Se}_4$: C, 58.56; H, 2.95. Found: C, 58.33; H, 2.99.

Compound **6** had mp 192-198° dec; uv (4.25×10^{-3} g/l concentration in dichloromethane): max 335 nm (absorbance 0.0385, sh), 290 (0.232, sh), 255 (0.509, sh); ir (potassium bromide): 3050, 1582, 1507, 943, 813, 746 cm^{-1} ; $^1\text{H-nmr}$: 8.2-7.0 (broad m); $^{13}\text{C-nmr}$: broad signals, 134.4, 132.8, 132.6, 130.9, 129.9, 129.3, 127.6, 127.2, 126.0, 125.2; ms: m/z 563-572 ($\text{C}_{20}\text{H}_{12}\text{Se}_4$), 406-412 ($\text{C}_{20}\text{H}_{12}\text{Se}_2$), 326-334 ($\text{C}_{20}\text{H}_{12}\text{Se}$), 252 ($\text{C}_{20}\text{H}_{12}$).

Anal. Calcd. for ($\text{C}_{20}\text{H}_{12}\text{Se}_2$) $_n$: C, 58.56; H, 2.95. Found: C, 58.47; H, 3.33.

Reaction of **8** with Selenium.

Following the general procedure, pure **9** (6.46 g, 63% yield) was obtained from 2,2'-dibromo-1,1'-biphenyl (10.4 g, 33.2 mmoles) and selenium (5.77 g, 73.1 mmoles) as red crystals. Compound **9** had mp 110-111° (lit [19] mp 114-115°); uv (acetonitrile): max 290 nm (ϵ 13800), 212 (122000); ir (potassium bromide): 3070, 1568, 1460, 1420, 1240, 1040, 750 cm^{-1} ; $^1\text{H-nmr}$: 7.8-7.1 (m, 16H); $^{13}\text{C-nmr}$: 141.9, 131.7, 131.2, 129.4, 128.6, 127.4; $^{77}\text{Se-nmr}$ (deuteriochloroform): 353; ms: m/z 308-314 ($\text{C}_{12}\text{H}_8\text{Se}_2$), 229-236 ($\text{C}_{12}\text{H}_8\text{Se}$), 152 (C_{12}H_8).

Anal. Calcd. for $\text{C}_{12}\text{H}_8\text{Se}_2$: C, 46.48; H, 2.60. Found: C, 46.97; H, 2.59.

Reaction of **1** with Tellurium.

From 2,2'-dibromo-1,1'-binaphthyl (3.08 g, 7.48 mmoles) and tellurium (1.91 g, 14.9 mmoles) pure **12** (0.548 g, 19%) and **13** (0.906 g, 24%) were obtained.

Compound **12** was obtained as yellow crystals, mp 212-213°; uv (acetonitrile): max 355 nm (ϵ 30900), 330 (29500), 290 (66100), 241 (87100), 218 (218800); ir (potassium bromide): 3050, 1570, 1502, 1200, 1121, 952, 800, 763, 740 cm^{-1} ; $^1\text{H-nmr}$: 8.4-8.2 (m, 2H), 8.0-7.2 (m, 10H); $^{13}\text{C-nmr}$: 133.0, 132.8, 130.9, 129.1, 128.3, 127.2, 126.7, 125.3, 124.2; ms: m/z 372-383 (M^+), 252 (M-Te).

Anal. Calcd. for $\text{C}_{20}\text{H}_{12}\text{Te}$: C, 63.23; H, 3.18. Found: C, 63.16; H, 3.25.

Compound **13** was obtained as dark red powder; $^1\text{H-nmr}$: 8.3-7.0 (broad); $^{13}\text{C-nmr}$: broad signals, 141.6, 134.6, 132.2, 129.9, 129.0, 126.8, 126.3, 126.0, 125.6, 112.6; ms: m/z 762 and 763 ($\text{C}_{20}\text{H}_{12}\text{Te}_4$), 630-638 ($\text{C}_{20}\text{H}_{12}\text{Te}_3$), 506-510 ($\text{C}_{20}\text{H}_{12}\text{Te}_2$), 374-383 ($\text{C}_{20}\text{H}_{12}\text{Te}$), 252 ($\text{C}_{20}\text{H}_{12}$).

Anal. Calcd. for ($\text{C}_{20}\text{H}_{12}\text{Te}_2$) $_n$: C, 47.33; H, 2.38. Found: C, 47.30; H, 2.62.

Reaction of **8** with Tellurium.

From 2,2'-dibromo-1,1'-biphenyl (1.05 g, 3.37 mmoles) and tellurium (0.859 g, 6.73 mmoles) pure **14** (0.301 g, 32%) and **15** (0.376 g, 27%) were obtained.

Compound **14** was obtained as pale yellow crystals, mp 92-93° (lit [38-40] mp 94.5°); ir (potassium bromide): 3050, 1437, 1418, 1237, 1030, 1009, 836, 740 cm^{-1} ; $^1\text{H-nmr}$: 8.1-7.7 (m, 4H), 7.5-7.1 (m, 4H); $^{13}\text{C-nmr}$: 143.8, 132.4, 128.6, 126.7, 125.5, 124.5; ms: m/z

277-284 (M⁺), 152 (M⁺-Te).

Compound **15** was obtained as a dark brown powder; ¹H-nmr: 8.2-7.8 (m), 7.6-7.0 (m); ¹³C-nmr: 150.3, 138.2, 130.3, 129.1, 112.2; ms: (ei) m/z 406-412 (C₁₂H₈Te₂), 274-283 (C₁₂H₈Te), 152 (C₁₂H₈).

Reaction of **6** with Potassium.

Under a nitrogen atmosphere, to a solution of **6** (3.15 g, 7.68 mmoles) in THF (100 ml) was added small pieces of potassium (0.55 g, 0.014 g-atoms) and the mixture was refluxed for 2 hours. Then the mixture was cooled to 0° and isopropyl alcohol (5 ml) was added slowly. After the remaining potassium was dissolved completely, to this was added a mixture of 1M ammonium chloride (150 ml) and benzene (150 ml). Air was bubbled into the mixture until the water layer became colorless. Pure **5** (0.158 g, 5%) and **6** (2.32 g, 74%) were obtained from the organic layer by silica-gel column chromatography.

Reaction of **9** with Bromine.

To a solution of **9** (0.504 g, 0.813 mmoles) in dry carbon tetrachloride (20 ml) was added a solution of bromine in carbon tetrachloride (1.95 M, 3 ml, 5.9 mmoles) at 0°. Pure **10** (0.763 g, 100%) was precipitated as deep red crystals, mp 110° dec; ¹H-nmr: 8.3-7.3 (m, 8H).

Anal. Calcd. for C₁₂H₈Br₂Se₂: C, 30.67; H, 1.72. Found: C, 30.68; H, 1.73.

Dibenzoselenophene (**11**).

A mixture of a solution of **10** (0.500 g, 0.86 mmole) in benzene (50 ml) and 10% sodium hydroxide solution was shaken until the organic layer turned colorless. The organic layer was separated and dried over magnesium sulfate. Concentration gave pure **11** (0.446 g, 78%) as colorless crystals, mp 72.5-73° (lit [41-43] mp 71°); ir (potassium bromide): 3050, 1580, 1460, 1424, 1417, 1304, 1230, 1020, 740 cm⁻¹; ¹H-nmr: 8.2-8.0 (m, 2H), 7.9-7.8 (m, 2H), 7.5-7.3 (m, 4H); ¹³C-nmr: 139.3, 138.3, 126.8, 126.0, 124.8, 122.8; ms: m/z 228-234 (M⁺), 152 (M⁺-Se).

Anal. Calcd. for C₁₂H₈Se: C, 62.35; H, 3.49. Found: C, 62.20; H, 3.50.

Reaction of **10** with Phenyllithium.

A solution of phenyllithium (2.0 M in cyclohexane and ether, 3 ml, 6.0 mmoles) was added to a THF (4 ml) solution of **10** (0.071 g, 0.152 mmole) at -78°. The temperature was raised to 25° and the reaction was quenched by addition of water and the mixture was extracted 3 times with benzene. The combined extracts were dried over magnesium sulfate and concentrated *in vacuo*. Column chromatography on silica gel eluting with 10% benzene in petroleum ether gave pure **11** (0.035 g, 100%).

Acknowledgment.

Authors wish to thank Professor R. Noyori for encouragement of this research. Authors A. Y. and S. S. are grateful to Dr. C. Katayama and Dr. A. Kawamoto for their suggestion and help on correction and calculation of X-ray diffraction data. This research was partly supported by the Grant-in-Aids for Scientific Research, No. 60740270, 63740283, and 01740304 from the Ministry of Education, Science and Culture, Japan.

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