Generation of Selenabenzenes Bearing an Electron-Withdrawing Group at the 2-Position

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3,6-Dihydro-2*H*-selenopyrans 2 with an electron-withdrawing group at the 2-position were prepared by the Diels–Alder reaction of butadienes with selenoaldehydes generated *in situ* from selenocyanates 1 and triethylamine. Oxidation of the dihydroselenopyrans 2 with 1.5 eq of *m*-chloroperbenzoic acid provided 2*H*-selenopyrans 9 and 3,6-dihydro-2*H*-selenopyran-2-yl *m*-chlorobenzoates 10. The benzoates 10 were smoothly converted into the selenopyrans 9 using polyphosphoric acid trimethylsilyl ester. The selenopyrans 9 were methylated with methyl trifluoromethanesulfonate to give *Se*-methyl selenopyranium trifluoromethanesulfonates 12. Deprotonation of the selenonium salts 12 with sodium hydride or triethylamine generated the selenabenzene derivatives 13, but they were too unstable to be isolated. Therefore, we confirmed the generation of 13 by ^{1}H- and ^{13}C-NMR spectroscopy at −30 °C.

Keywords cyclic selenium ylide; selenabenzene; selenopyranium salt; selenopyran; dihydroselenopyran; Pummerer reaction

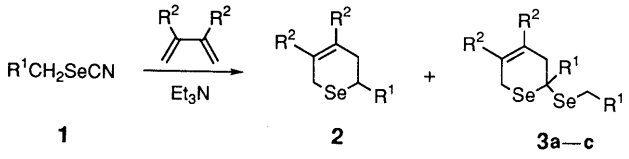
Selenabenzenes are cyclic selenium ylides involving four π-electrons of a diene moiety and two electrons of an adjacent carbanion, and are less stable than thiabenzenes.[1] We have already synthesized the cyano-stabilized selenanaphthalenes, 2-cyano-1-methyl-1-selenanaphthalene[2] and 1-cyano-2-methyl-2-selenanaphthalene,[3] and found interesting reactions different from those of the corresponding thiabenzenes.[4] However, these selenabenzene derivatives are benzo-condensed derivatives and synthesis of the monocyclic selenabenzenes is required in order to study the intrinsic properties of selenabenzenes.

This paper describes the generation of monocyclic selenabenzenes bearing an electron-withdrawing group such as a cyano, an ester or a benzoyl group at the 2-position.

Results and Discussion

Dihydroselenopyrans, key starting materials for the synthesis of selenabenzenes, have been synthesized by the Diels–Alder reaction of selenoaldehydes with dienes.[5,6] Kirby's method[6] using selenocyanates and triethylamine was selected among several possible synthetic methods for the selenoaldehydes bearing an electron-withdrawing group at the 2-position, because this method is applicable to a ten gram-scale experiment and to the preparation of selenoaldehydes bearing different kinds of electron-withdrawing groups. The known compound **2a**[6] and the unknown compounds **2b—f** were prepared by the methods shown in Chart 1.

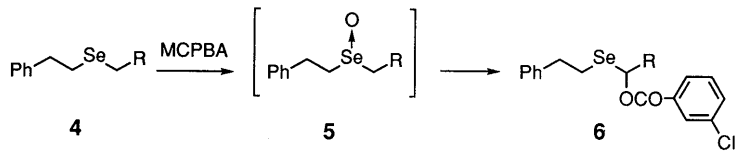
It has been reported that selenides with an α-electron-withdrawing group are oxidized with peracids to give not selenoxide, but the Pummerer reaction products, α-acyloxy selenides,[7] although oxidation of selenides with both an α-electron-withdrawing group and a β-hydrogen has not yet been reported. Therefore, we initially conducted oxidation of the acyclic selenides **4** with *m*-chloroperbenzoic acid (MCPBA). The Pummerer reaction products **6a, b** were obtained in yields of 44% and 57%, respectively, but **6c** was not obtained from the selenide **4c** lacking an α-electron-withdrawing group. These findings show that selenides **2** bearing an α-electron-withdrawing group undergo the Pummerer reaction in preference to the alkenation *via* C–Se bond fission



1a: R^1=CN; **1b**: R^1=$COC_6H_4Br(p\text{-})$; **1c**: R^1=$COC_6H_4NO_2(p\text{-})$

2,**3a**: R^1=CN; R^2=Me
b: R^1=CN; R^2=Ph
c: R^1=CN; R^2=$C_6H_4Cl(p\text{-})$
d: R^1=$COC_6H_4Br(p\text{-})$; R^2=Me
e: R^1=$COC_6H_4Br(p\text{-})$; R^2=Ph
f: R^1=$COC_6H_4NO_2(p\text{-})$; R^2=Me

Chart 1



a: R=CN; **b**: R= CO_2Et; **c**: R=H

Chart 2

(*β-syn*-elimination).

3,6-Dihydro-2*H*-selenopyrans **2** were oxidized with 1.5 eq of MCPBA in dichloromethane at room temperature. 2*H*-Selenopyrans **9** and 3,6-dihydro-2*H*-selenopyran-2-yl *m*-chlorobenzoates **10** were obtained as major products in the yields listed in Table I. The proton nuclear magnetic resonance (^{1}H-NMR) spectra of the selenopyrans showed the methylene protons in the region of δ 3.24—3.81 as singlets and the olefinic protons in the region of δ 6.80—7.22 as singlets. From these spectral data, the selenopyrans obtained are proved to be not 2-R^1-4,5-di(R^2)-2*H*-selenopyrans **11** but 6-R^1-2,3-di(R^2)-2*H*-selenopyrans **9**. It was shown that the *m*-chlorobenzoyloxy group of the other products **10** did not lie at the 6-position but lay at the 2-position on the basis of their ^{1}H-NMR spectra exhibiting two pairs of doublets in the region of δ 2.78—3.91. Deprotonation of the 2-position of selenoxides **7** with a base may assist the formation of selenonium ions **8** and we conducted the MCPBA oxidation in the presence of a base. However, the yield of selenopyrans **9** was not improved. When the MCPBA oxidation of **2f** was carried out in the presence of trifluoroacetic anhydride, which brings about the Pummerer reaction even at 0 °C,[8] a complex mixture was obtained. An unprecedented ring-contraction of dihydroselenopyrans into selenophenes occurred on the treatment of dihydroselenopyrans with 4 eq of MCPBA or with 4 eq of sodium periodate.[9] Reaction of **2a** with 1.5 eq of benzoyl peroxide in dichloromethane at 0 °C gave a selenopyran **9a** (12%) and 3,6-dihydro-2*H*-selenopyran-2-yl benzoate **10g** (46%).

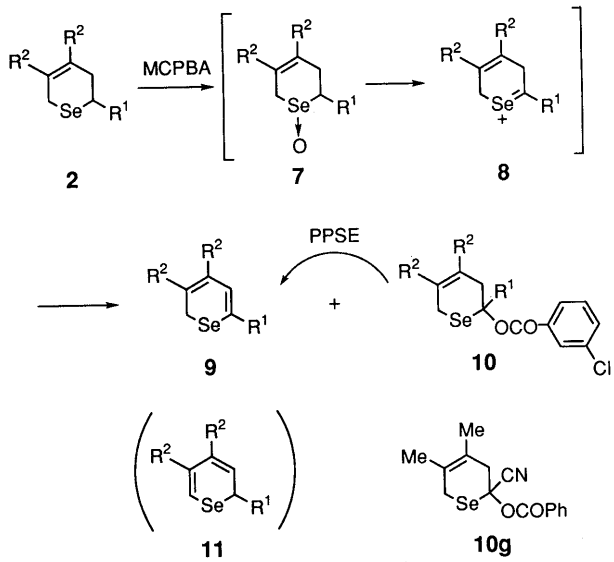
Next, we investigated the conversion of 3,6-dihydro-2*H*-selenopyran-2-yl *m*-chlorobenzoates **10** into selenopyrans **9**. The 2-cyano derivative **10a** was treated with sodium hydrogen carbonate in dichloromethane at 0 °C or with lithium diisopropylamide in tetrahydrofuran (THF) at −78 °C to remove the 3-proton of **10a** and to eliminate *m*-chlorobenzoic acid. However, the selenopyran **9a** was not obtained. Therefore, we selected polyphosphoric acid trimethylsilyl ester (PPSE)[10] from the viewpoint of activation of the ester group under neutral conditions. The benzoates **10** were refluxed with PPSE in 1,2-dichloroethane and the desired products **9** were obtained in high yields. A mixture of **9** and **10** could be similarly converted into **9**.

Methylation of 2*H*-selenopyrans **9** with methyl trifluoromethanesulfonate (triflate) gave *Se*-methylselenopyranium salts **12**. The ^{1}H-NMR spectrum of each selenonium salt showed a singlet due to the *Se*-methyl

TABLE I. Oxidation of Dihydroselenopyrans (**2**) with MCPBA

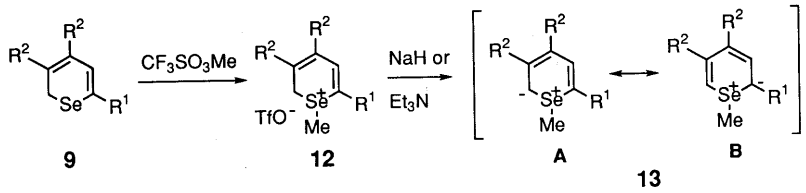
Entry	2	Base (eq)	Products (% yield)
1	**2a**	None	**9a** (41), **10a** (29)
2	**2a**	$NaHCO_3$ (1.5)	**9a** (24.5), **10a** (31)
3	**2a**	CH_3COONa (1.5)	**9a** (31.5), **10a** (27.5)
4	**2a**	K_2CO_3 (1.5)	**9a** (18.5), **10a** (22.5)
5	**2b**	None	**9b** (29.5), **10b** (35.5)
6	**2c**	None	**9c** (28), **10c** (43)
7	**2d**	None	**9d** (47.5), **10d** (21.5)
8	**2d**	$NaHCO_3$ (1.5)	**9d** (55.5), **10d** (20.5)
9	**2d**	CH_3COONa (1.5)	**9d** (54.5), **10d** (25.5)
10	**2d**	K_2CO_3 (1.5)	**9d** (42), **10d** (29.5)
11	**2d**	$NH(SiMe_3)_2$ (1.5)	**9d** (27.5), **10d** (17.5)
12	**2d**[a]	$NH(SiMe_3)_2$ (5)	**9d** (24.5), **10d** (24)
13	**2d**	Et_3N (10)	No reaction
14	**2d**	$(CF_3CO)_2O$ (2)	Complex mixture
15	**2e**[b]	$NaHCO_3$ (2)	**9a** and **10e** mixture
16	**2f**	None	**9f** (26), **10f** (7.5)
17	**2f**	$NaHCO_3$ (1.5)	**9f** (25), **10f** (31)

a) 3 eq MCPBA. *b*) 2 eq MCPBA.



7—10a: R^1=CN; R^2=Me
b: R^1=CN; R^2=Ph
c: R^1=CN; R^2=C$_6$H$_4$Cl(*p*-)
d: R^1=COC$_6$H$_4$Br(*p*-); R^2=Me
e: R^1=COC$_6$H$_4$Br(*p*-); R^2=Ph
f: R^1=COC$_6$H$_4$NO$_2$(*p*-); R^2=Me

Chart 3



TfO$^-$ =CF$_3$SO$_3^-$

12,13a: R^1=CN; R^2=Me
b: R^1=CN; R^2=Ph
c: R^1=CN; R^2=C$_6$H$_4$Cl(*p*-)
d: R^1=COC$_6$H$_4$Br(*p*-); R^2=Me
e: R^1=COC$_6$H$_4$NO$_2$(*p*-); R^2=Me

Chart 4

group and therefore it consists of a single isomer. The selenopyranium salt **12d** was deprotonated with triethylamine in ethanol at 0 °C or with sodium hydride in THF at 0 °C, but the selenabenzene **13d** thus generated was too labile to be isolated. All attempts to isolate the decomposed products were unsuccessful. Therefore, we confirmed the generation of selenabenzenes by NMR spectroscopy. Selenopyranium salts **12a, d** were treated with sodium hydride in acetonitrile-d_3 at −30 °C under an argon atmosphere and the ^{1}H- and carbon (^{13}C-) NMR spectra of the resultant selenabenzenes **13a, d** were measured. The H, C correlation spectroscopy (COSY) spectrum of the 2-(*p*-bromobenzoyl) derivative **13d** showed the correlation of the olefinic proton signals at δ 5.56 and 6.39 with the carbon signals at δ 89.6 and 127.6, respectively. The olefinic proton signal at δ 5.56 was accompanied with a pair of satellite peaks due to the coupling with the selenium atom (J=28 Hz). Nuclear Overhauser effect (NOE) enhancement was observed between the signal at δ 6.39 and the doublet signal at δ 7.41 due to 3′,5′-H of the benzoyl group. On the basis of these spectral data, the signals at δ 5.56, 6.39, 89.6 and 127.6 were assigned to 6-H, 3-H, 6-C and 3-C, respectively. The carbon signal at δ 85.1 did not correlate with any proton signal in the H, C COSY spectrum and was therefore assigned to 2-C. The ^{1}H- and ^{13}C-NMR signals of the cyano derivative **13a** were determined by comparison with those of the corresponding thiabenzene derivative[11] and **13d**. The proton signals at δ 5.01 and 6.45, and the carbon signals at δ 31.7, 78.2 and 130.2 were assignable to 6-H, 3-H, 2-C, 6-C and 3-C, respectively.

The 6-H signals of **13a, d** appeared at rather higher field than the olefinic 3-H signals in the ^{1}H-NMR spectra, and the 6-C signals of **13a, d** were observed considerably upfield from the 3-C signals in the ^{13}C-NMR spectra. This indicates that the selenabenzenes are the ylidic compounds and that not only the resonance form **13B** but also the resonance form **13A** contributes to the resonance structure of selenabenzenes **13**.

In conclusion, we attempted to synthesize monocyclic selenabenzenes bearing an electron-withdrawing group at the 2-position but they were fairly unstable compared with the isolable thiabenzenes.[11] The next step in our attempt to isolate stable monocyclic selenabenzene derivatives will be introduction of an additional electron-withdrawing group at the 6-position.

Experimental

Melting points were determined on Yanagimoto micro melting point apparatus and are uncorrected. Infrared (IR) spectra were determined on a JASCO IRA-100 spectrophotometer. ^{1}H-NMR spectra were recorded on JEOL JNM-GX-270 (270 MHz) and JEOL JNM-EX-400 (400 MHz) spectrometers. ^{13}C-NMR spectra were run on JEOL JNM-GX-270 (67.5 MHz) and JEOL JNM-EX-400 (100 MHz) spectrometers. Mass spectra (MS) were recorded with a JEOL JMS-D-300 spectrometer and high-resolution MS (HRMS) with the JMA 2000 on-line system.

***p*-Bromobenzoylmethyl Selenocyanate (1b)** a) A mixture of *p*-bromophenacyl bromide (10.4 g, 37.4 mmol), potassium selenocyanate (6.5 g, 45 mmol) and 18-crown-6 (200 mg) in THF (200 ml) was refluxed for 2 h, cooled to room temperature, and poured into a sodium hydrogen carbonate solution (300 ml). The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using hexane–dichloromethane (2:1) as an eluent and recrystallized from dichloromethane–hexane to give pale red leaflets (6.6 g, 58%), mp 159—162 °C (dec.). IR (KBr) cm^{-1}: 1655 (CO). ^{1}H-NMR ($CDCl_3$) δ: 4.88 (2H, s, $SeCH_2$), 7.68, 7.82 (each 2H, d, J=8.8 Hz, ArH). MS *m/z*: 303 (M^+), 183 (base). *Anal.* Calcd for $C_9H_6BrNOSe$: C, 35.67; H, 2.00; N, 4.62. Found: C, 35.60; H, 2.05; N, 4.72.

b) *p*-Bromophenacyl bromide (27.8 g, 0.1 mol) was added to a suspension of potassium selenocyanate (17.3 g, 0.12 mol) in dry ethanol (200 ml). The mixture was stirred for 5 h at room temperature and concentrated under reduced pressure. The residue was dissolved in dichloromethane and the insoluble material was removed by filtration. The filtrate was dried ($MgSO_4$) and concentrated. The residual solid was recrystallized from acetone to give **1b** (18.6 g, 61%). This was identical with the sample prepared by method a.

***p*-Nitrobenzoylmethyl Selenocyanate (1c)** This compound was prepared from potassium selenocyanate (17.3 g, 0.12 mol) and *p*-nitrophenacyl bromide (24.4 g, 0.1 mol) as described under method b for **1b**. Pale yellow leaflets (from acetone), mp 135—139 °C (dec.). Yield: 15.8 g (59%). IR (KBr) cm^{-1}: 2150 (CN), 1650 (CO), 1515, 1335 (NO_2). ^{1}H-NMR ($CDCl_3$) δ: 4.92 (2H, s, $SeCH_2$), 8.15, 8.40 (each 2H, d, J=9 Hz, ArH). *Anal.* Calcd for $C_9H_6N_2O_3Se$: C, 40.17; H, 2.25; N, 10.41. Found: C, 40.16; H, 2.26; N, 10.43.

2-Cyano-3,6-dihydro-4,5-diphenyl-2*H*-selenopyran (2b) and 2-Cyano-2-cyanomethylseleno-3,6-dihydro-4,5-diphenyl-2*H*-selenopyran (3b) A solution of triethylamine (2.1 ml, 15 mmol) in ethanol (50 ml) was added dropwise during 1.5 h to a suspension of cyanomethyl selenocyanate[6] **1a** (2.18 g, 15 mmol), 2,3-diphenyl-1,3-butadiene[12] (6.2 g, 30 mmol) and calcium chloride dihydrate (2.2 g, 15 mmol) in ethanol (150 ml) under reflux. The reaction mixture was refluxed for 2 h, cooled and concentrated under reduced pressure. The residue was dissolved in dichloromethane and the insoluble material was removed by filtration. The filtrate was washed with water, dried ($MgSO_4$) and concentrated to dryness. The residue was chromatographed on silica gel using hexane–ethyl acetate (20:1) as an eluent to give **2b** (1.1 g, 25%) and **3b** (2.0 g, 30%).

2b: Colorless prisms (dichloromethane–hexane), mp 146—147 °C. IR (KBr) cm^{-1}: 2215 (CN). ^{1}H-NMR ($CDCl_3$) δ: 3.05 (1H, dd, J=15.6, 4.9 Hz, H-3), 3.16 (1H, dd, J=15.6, 5.9 Hz, H-3), 3.68, 3.83 (each 1H, d, J=5.9, 4.9 Hz, H-2), 4.06, 4.07 (each 1H, d, J=5.9 Hz, 6-H), 7.05—7.15 (10H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 18.4 (d), 13.3 (t), 36.6 (t), 120.6 (s), 126.8 (d), 126.9 (d), 128.0 (d×2), 128.9 (d×2), 135.8 (s), 137.0 (s), 140.9 (s), 141.3 (s). MS *m/z*: 325 (M^+), 205 (base). *Anal.* Calcd for $C_{18}H_{15}NSe$: C, 66.67; H, 4.66; N, 4.32. Found: C, 66.67; H, 4.69; N, 4.35.

3b: Brown massive crystals (dichloromethane–hexane), mp 104—105 °C. IR (KBr) cm^{-1}: 2250, 2225 (CN). ^{1}H-NMR ($CDCl_3$) δ: 3.34, 3.48 (each 1H, d, J=15 Hz, H-3), 3.38, 3.67 (each 1H, d, J=15 Hz, H-6), 3.80, 3.89 (each 1H, d, J=13 Hz, $SeCH_2CN$), 7.07—7.16 (10H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 9.4 (t), 26.9 (s), 27.7 (t), 44.9 (t), 116.6 (s), 119.8 (s), 127.1 (d), 127.3 (d), 128.1 (d×2), 128.2 (d×2), 128.7 (d×2), 129.2 (d×2), 136.8 (s), 138.5 (s), 140.0 (s), 140.2 (s). MS *m/z*: 444 (M^+), 243 (base). *Anal.* Calcd for $C_{20}H_{16}N_2Se_2$: C, 54.31; H, 3.65; N, 6.33. Found: C, 54.18; H, 3.81; N, 6.17.

4,5-Di(*p*-chlorophenyl)-2-cyano-3,6-dihydro-2*H*-selenopyran (2c) and 2-Cyano-2-cyanomethylseleno-4,5-di(*p*-chlorophenyl)-3,6-dihydro-2*H*-selenopyran (3c) Reaction of **1a** (2.18 g, 15 mmol) with 2,3-di(*p*-chlorophenyl)-1,3-butadiene[12] (8.3 g, 30 mmol) was conducted in a way similar to that described for **2b**. The products were separated by column chromatography on silica gel using hexane–ethyl acetate (20:1) to give **2c** (1.5 g, 25%) and **3c** (0.7 g, 9%). **2c**: Pale yellow prisms (dichloromethane–hexane), mp 124—125 °C. IR (KBr) cm^{-1}: 2240 (CN). ^{1}H-NMR ($CDCl_3$) δ: 3.10, 3.27 (each 1H, dd, J=16, 5 Hz, H-3), 3.76, 3.87 (each 1H, d, J=14 Hz, H-6), 4.24 (1H, t, J=5 Hz, H-2), 7.10—7.27 (8H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 18.3 (d), 22.8 (t), 36.3 (t), 120.4 (s), 128.3 (d×2), 130.1 (d×2), 130.3 (d×2), 132.7 (s), 132.8 (s), 135.3 (s), 136.4 (s), 138.8 (s), 139.3 (s). MS *m/z*: 393 (M^+), 238 (base). *Anal.* Calcd for $C_{18}H_{13}Cl_2NSe$: C, 54.99; H, 3.33; N, 3.56. Found: C, 54.75; H, 3.31; N, 3.61.

3c: Yellow oil. IR (film) cm^{-1}: 2225, 2210 (CN). ^{1}H-NMR ($CDCl_3$) δ: 3.41, 3.74 (each 1H, d, J=15 Hz, H-3), 3.50, 3.64 (each 1H, d, J=16 Hz, H-6), 3.84, 3.95 (each 1H, d, J=13 Hz, $SeCH_2CN$), 7.09, 7.13, 7.25, 7.26 (each 2H, d, J=9 Hz, ArH). ^{13}C-NMR ($CDCl_3$) δ: 9.6 (t),

26.7 (s), 27.4 (t), 44.7 (t), 116.7 (s), 119.6 (s), 128.6 (d × 2), 130.0 (d × 2), 130.6 (d × 2), 133.3 (s), 133.4 (s), 136.4 (s), 138.1 (s), 138.3 (s). HRMS Calcd for $C_{20}H_{14}Cl_2N_2Se_2$ *m/z*: 511.8864. Found *m/z*: 511.8892.

2-(*p*-Bromobenzoyl)-3,6-dihydro-4,5-dimethyl-2*H*-selenopyran (2d) This compound was prepared from **1b** (6.1 g, 20 mmol) and 2,3-dimethyl-1,3-butadiene (11.3 ml, 0.1 mol) in a way similar to that described for **2b**. Purification by column chromatography on silica gel using hexane–dichloromethane (3 : 1) as an eluent gave colorless needles (dichloromethane–hexane) (3.6 g, 50%), mp 98—99 °C. IR (KBr) cm^{-1}: 1675 (CO). ^{1}H-NMR ($CDCl_3$) δ: 1.83, 1.85 (each 3H, s, Me), 2.47 (1H, dd, J=16, 4 Hz, H-3), 2.68 (1H, dd, J=16, 7 Hz, H-3), 3.03, 3.19 (each 1H, d, J=14 Hz, H-6), 4.61 (1H, dd, J=7, 4 Hz, H-2), 7.57, 7.80 (each 2H, d, J=8.8 Hz, ArH). ^{13}C-NMR ($CDCl_3$) δ: 19.4 (q), 20.3 (q), 23.5 (t), 32.9 (t), 38.5 (d), 125.9 (s), 128.0 (s), 129.5 (s), 129.7 (d × 2), 131.8 (d × 2), 134.8 (s), 195.2 (s). MS *m/z*: 358 (M^+), 183 (base). *Anal.* Calcd for $C_{14}H_{15}BrOSe$: C, 46.95; H, 4.22. Found: C, 47.06; H, 4.29.

2-(*p*-Bromobenzoyl)-3,6-dihydro-4,5-diphenyl-2*H*-selenopyran (2e) This compound was prepared from **1b** (4.6 g, 15 mmol) and 2,3-diphenyl-1,3-butadiene (6.2 g, 30 mmol) in a way similar to that described for **2b**. Purification by column chromatography on silica gel using hexane and then hexane–dichloromethane (17 : 3) as eluents gave yellow needles (dichloromethane–hexane) (2.6 g, 36%), mp 147—149 °C. IR (KBr) cm^{-1}: 1675 (CO). ^{1}H-NMR ($CDCl_3$) δ: 3.09 (1H, dd, J=15, 4 Hz, H-3), 3.21 (1H, dd, J=15, 9 Hz, H-3), 3.50, 3.79 (each 1H, d, J=13 Hz, H-6), 4.81 (1H, dd, J=9, 4 Hz, H-2), 7.06—7.15 (10H, m, ArH), 7.60, 7.83 (each 2H, d, J=9 Hz, ArH). ^{13}C-NMR ($CDCl_3$) δ: 25.0 (t), 34.2 (t), 40.7 (d), 126.5 (d), 126.6 (d), 127.9 (d × 2), 128.0 (d × 2), 128.4 (s), 128.8 (d × 2), 129.2 (d × 2), 129.8 (d × 2), 132.0 (d × 2), 135.2 (s), 136.4 (s), 138.1 (s), 141.4 (s), 142.2 (s), 195.2 (s). MS *m/z*: 482 (M^+), 183 (base). *Anal.* Calcd for $C_{24}H_{19}BrOSe$: C, 59.77; H, 3.97. Found: C, 59.54; H, 3.98.

3,6-Dihydro-4,5-dimethyl-2-(*p*-nitrobenzoyl)-2*H*-selenopyran (2f) This compound was prepared from **1c** (5.4 g, 20 mmol) and 2,3-dimethyl-1,3-butadiene (11.3 ml, 0.1 mol) in a way similar to that described for **2b**. Purification by column chromatography on silica gel using hexane–dichloromethane (1 : 1) as an eluent gave colorless needles (dichloromethane–hexane) (3.1 g, 48.5%), mp 104.5—105.5 °C. IR (KBr) cm^{-1}: 1685 (CO), 1525, 1340 (NO_2). ^{1}H-NMR ($CDCl_3$) δ: 1.84, 1.87 (each 3H, s, Me), 2.51—2.73 (2H, m, H-3), 3.04, 3.19 (each 1H, d, J=14 Hz, H-6), 4.66—4.70 (1H, m, H-2), 8.09, 8.29 (each 2H, d, J=8.8 Hz, ArH). ^{13}C-NMR ($CDCl_3$) δ: 19.5 (q), 20.3 (q), 23.4 (t), 32.5 (t), 38.5 (d), 123.7 (d × 2), 125.6 (s), 129.2 (d × 2), 140.8 (s), 150.0 (s), 194.1 (s). MS *m/z*: 325 (M^+), 150 (base). *Anal.* Calcd for $C_{14}H_{15}NO_3Se$: C, 51.86; H, 4.66; N, 4.32. Found: C, 51.64; H, 4.59; N, 4.31.

Bis(2-phenylethyl) Diselenide Ethanol (400 ml) was added to a mixture of selenium powder (21.2 g, 0.27 mol) and sodium borohydride (7.1 g, 0.19 mol) with cooling in an ice-bath during 1.5 h and then the mixture was refluxed for 1.5 h. 2-Phenylethyl bromide (55.5 g, 0.3 mol) was added dropwise at 0 °C to the sodium diselenide solution thus prepared. The whole was stirred overnight at room temperature, poured into water (300 ml) and extracted with ether. The extracts were washed with water, dried ($MgSO_4$) and concentrated. The residual oil was purified by column chromatography on silica gel using hexane–dichloromethane (15 : 1) as an eluent to give an orange oil (26.8 g, 54%). ^{1}H-NMR ($CDCl_3$) (60 MHz) δ: 3.00—3.25 (8H, m, CH_2 × 4), 7.10—7.55 (10H, m, ArH).

2-Phenylethylselenoacetonitrile (4a) A solution of bis(2-phenylethyl) diselenide (3.7 g, 10 mmol) in dry THF (7 ml) was added to a suspension of lithium aluminum hydride (0.22 g, 5.7 mmol) in dry THF (60 ml) under an argon atmosphere at −78 °C and the mixture was gradually warmed to −50 °C. Hexamethylphosphortriamide (HMPA) (2 ml) was added to the mixture and the whole was cooled to −78 °C. A solution of bromoacetonitrile (2.5 g, 20 mol) in dry THF (8 ml) was then added and the temperature was raised to room temperature. The reaction mixture was decomposed with a saturated ammonium chloride solution and extracted with ether. The extracts were washed with water, dried ($MgSO_4$) and concentrated to dryness. The residue was chromatographed on silica gel using hexane–dichloromethane (2 : 1) as an eluent to give **4a** (2.75 g, 64%) as a yellow oil. IR (film) cm^{-1}: 2240 (CN). ^{1}H-NMR ($CDCl_3$) δ: 2.96 (2H, br s, $SeCH_2CN$), 3.07 (4H, dd, J=6.4, 4.4 Hz, $ArCH_2CH_2$), 7.20—7.31 (5H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 2.1 (t), 26.9 (t), 36.2 (t), 117.4 (s), 126.6 (d), 128.4 (d × 2), 128.5 (d × 2), 139.8 (s). MS *m/z*: 225 (M^+), 105 (base). *Anal.* Calcd for $C_{10}H_{11}NSe$: C, 53.58; H, 4.95; N, 6.25. Found: C, 53.51; H, 4.39; N, 6.23.

Ethyl 2-Phenylethylselenoacetate (4b) Ethyl bromoacetate (3.3 g, 20 mmol) was allowed to react with 2-phenylethaneselenolate, prepared by reduction of bis(2-phenylethyl) diselenide (3.7 g, 10 mmol) with lithium aluminum hydride. The reaction mixture was worked up in a way similar to that described for **4a**. The oily crude product was purified by column chromatography on silica gel using hexane–dichloromethane (2 : 1) as an eluent to give **4b** as a pale yellow oil (4.1 g, 75%). IR (film) cm^{-1}: 1730, 1270 (ester). ^{1}H-NMR ($CDCl_3$) δ: 1.26 (3H, t, J=7 Hz, $CH_2\underline{CH}_3$), 2.99 (4H, br s, $ArCH_2CH_2$), 3.12 (2H, s, $SeCH_2CO$), 4.16 (2H, q, J=7 Hz, $C\underline{H}_2CH_3$), 7.18—7.31 (5H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 14.0 (q), 22.2 (t), 26.2 (t), 36.4 (t), 61.0 (t), 126.3 (d), 128.3 (d × 2), 128.4 (d × 2), 140.7 (s), 171.4 (s). MS *m/z*: 272 (M^+), 105 (base). *Anal.* Calcd for $C_{12}H_{16}O_2Se$: C, 53.14; H, 5.95. Found: C, 53.03; H, 5.91.

Methyl 2-Phenylethyl Selenide (4c) Bis(2-phenylethyl) diselenide (3.7 g, 10 mmol) was reduced with lithium aluminum hydride (0.22 g, 5.7 mmol) and methylated with methyl iodide (2.8 g, 20 mmol) in a way similar to that described for **4a**. The oily product was chromatographed on silica gel using hexane–dichloromethane (3 : 1) as an eluent to give **4c** as a yellow oil (1.9 g, 49%). ^{1}H-NMR ($CDCl_3$) (60 MHz) δ: 1.94 (3H, s, SeMe), 3.04—3.09 (4H, m, $ArCH_2CH_2$), 7.18—7.27 (5H, m, ArH). MS *m/z*: 200 (M^+), 105 (base).

Oxidation of 2-Phenylethylselenoacetonitrile (4a) with MCPBA MCPBA (0.19 g, 1.1 mmol) was added to a solution of **4a** (224 mg, 1 mmol) in dry dichloromethane (8 ml) with stirring at 0 °C. The mixture was stirred for 30 min, followed by addition of a saturated sodium hydrogen carbonate solution. After the whole had been stirred for 20 min, the organic layer was separated and the aqueous layer was extracted with dichloromethane. The organic layer and the extracts were combined, washed with water, dried ($MgSO_4$), and concentrated to dryness. The residue was fractionated by preparative layer chromatography (PLC) on silica gel using hexane–dichloromethane (2 : 1) as a developing solvent to give 1-cyano-1-(2-phenylethylseleno)methyl *m*-chlorobenzoate (**6a**), a pale yellow oil (167 mg, 44%). IR (film) cm^{-1}: 2250 (CN), 1740, 1250 (ester). ^{1}H-NMR ($CDCl_3$) δ: 3.12 (2H, t, J=8 Hz, $ArCH_2$), 3.32, 3.40 (each 1H, t, J=8 Hz, $SeCH_2$), 6.74 (1H, s, SeCH), 7.20—7.98 (9H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 27.7 (t), 36.6 (t), 72.9 (d), 114.5 (s), 126.8 (d), 128.0 (d), 128.3 (d × 2), 128.6 (d × 2), 129.5 (s), 129.9 (d), 130.0 (d), 134.2 (d), 134.8 (s), 139.6 (s), 162.7 (s). MS *m/z*: 379 (M^+), 105 (base). *Anal.* Calcd for $C_{17}H_{14}ClNO_2Se$: C, 53.92; H, 3.73; N, 3.70. Found: C, 53.91; H, 3.79; N, 3.74.

Oxidation of Ethyl 2-Phenylethylselenoacetate (4b) with MCPBA Compound **4b** (271 mg, 1 mmol) was oxidized with MCPBA (259 mg, 1.5 mmol) in a way similar to that described for **4a**. The oily product was purified by PLC on silica gel using hexane–dichloromethane (2 : 1) to give 1-ethoxycarbonyl-1-(2-phenylethylseleno)methyl *m*-chlorobenzoate (**6b**) (241 mg, 57%) as an orange oil. IR (film) cm^{-1}: 1740—1760, 1280, 1235 (ester). ^{1}H-NMR ($CDCl_3$) δ: 1.32 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 2.99—3.20 (4H, m, $ArCH_2CH_2$), 4.29 (2H, q, J=7 Hz, $C\underline{H}_2CH_3$), 6.43 (1H, s, SeCH), 7.19—7.57 (6H, m, ArH), 7.95—8.08 (2H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 14.0 (q), 25.7 (t), 36.9 (t), 62.0 (t), 66.9 (d), 126.5 (d), 128.0 (d), 128.3 (d × 2), 128.5 (d × 2), 129.8 (d), 129.9 (d), 130.6 (s), 133.7 (d), 134.6 (s), 140.4 (s), 164.2 (s), 167.5 (s). MS *m/z*: 426 (M^+), 139 (base). *Anal.* Calcd for $C_{19}H_{19}ClO_4Se$: C, 53.60; H, 4.50. Found: C, 53.54; H, 4.57.

General Procedure for Oxidation of 3,6-Dihydro-2*H*-selenopyrans 2 with MCPBA MCPBA was gradually added at 0 °C to a solution or a suspension of the 3,6-dihydro-2*H*-selenopyran **2** and a base cited in Table I in dichloromethane and the reaction mixture was stirred for 2 h. A saturated sodium hydrogen carbonate solution was added to the reaction mixture. The whole was stirred for 20 min and then extracted with dichloromethane. The extracts were washed with water, dried ($MgSO_4$) and concentrated to dryness. The residue was chromatographed on a silica gel column using hexane–dichloromethane (3 : 1) or hexane–ethyl acetate (5 : 1) for the products from **2a—c** or **2d—h**, respectively, to give 2*H*-selenopyran **9** and 3,6-dihydro-2*H*-selenopyran-2-yl *m*-chlorobenzoate **10**. Their yields are listed in Table I.

6-Cyano-3,4-dimethyl-2*H*-selenopyran (**9a**): A yellow oil. IR (film) cm^{-1}: 2215 (CN). ^{1}H-NMR ($CDCl_3$) δ: 1.86, 1.96 (each 3H, s, Me), 3.27 (2H, s, H-6), 6.84 (1H, s, H-3). ^{13}C-NMR ($CDCl_3$) δ: 18.1 (d), 20.3 (d), 25.1 (t), 95.8 (s), 117.5 (s), 127.0 (s), 128.7 (s), 142.7 (d). MS *m/z*: 199 (M^+), 184 (base). *Anal.* Calcd for C_8H_9NSe: C, 48.50; H, 4.58; N, 7.07. Found: C, 48.51; H, 4.67; N, 7.00.

2-Cyano-3,6-dihydro-4,5-dimethyl-2*H*-selenopyran-2-yl *m*-Chlorobenzoate (**10a**): Colorless prisms (dichloromethane–hexane), mp

112.5—113 °C. IR (KBr) cm^{-1}: 2240 (CN), 1730, 1250 (ester). ^{1}H-NMR ($CDCl_3$) δ: 1.92, 2.02 (each 3H, s, Me), 2.91, 3.13 (each 1H, d, J=14 Hz, H-3), 3.27, 3.33 (each 1H, d, J=13 Hz, H-6), 7.39—7.95 (4H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 18.7 (q), 20.6 (q), 26.1 (t), 43.2 (t), 72.4 (t), 118.3 (s), 126.2 (s), 128.0 (d), 129.9 (d), 130.0 (d), 130.5 (s), 133.1 (s), 134.0 (d), 134.7 (s), 163.6 (s). MS m/z: 355 (M^+), 139 (base). *Anal.* Calcd for $C_{15}H_{14}ClNO_2Se$: C, 50.79; H, 3.98; N, 3.95. Found: C, 50.89; H, 4.06; N, 4.00.

6-Cyano-3,4-diphenyl-2*H*-selenopyran (**9b**): Yellow prisms (dichloromethane–hexane), mp 138—139 °C. IR (KBr) cm^{-1}: 2210 (CN). ^{1}H-NMR ($CDCl_3$) δ: 3.81 (2H, s, H-6), 6.93—7.18 (10H, m, ArH), 7.19 (1H, s, H-3). ^{13}C-NMR ($CDCl_3$) δ: 26.7 (t), 100.0 (s), 117.3 (s), 127.4 (d), 127.8 (d), 128.2 (d×2), 129.4 (d×2), 129.5 (s), 129.7 (d×2), 136.2 (s), 139.1 (s), 139.5 (s), 142.1 (d). MS m/z: 323 (M^+), 243 (base). *Anal.* Calcd for $C_{18}H_{13}NSe$: C, 67.09; H, 4.07; N, 4.35. Found: C, 67.27; H, 4.04; N, 4.38.

2-Cyano-3,6-dihydro-4,5-diphenyl-2*H*-selenopyran-2-yl *m*-Chlorobenzoate (**10b**): Colorless prisms (dichloromethane–hexane), mp 191—192 °C. IR (KBr) cm^{-1}: 2220 (CN), 1725, 1250 (ester). ^{1}H-NMR ($CDCl_3$) δ: 3.33, 3.79 (each 1H, d, J=14 Hz, H-3), 3.74, 3.91 (each 1H, d, J=12 Hz, H-6), 7.08—7.24 (10H, m, ArH), 7.32—7.81 (4H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 27.0 (t), 44.0 (t), 72.5 (s), 118.1 (s), 127.2 (d), 127.3 (d), 128.2 (d), 128.3 (d×2), 128.6 (d×2), 129.2 (d×2), 129.8 (s), 129.9 (d), 133.5 (s), 134.1 (s), 134.8 (s), 139.9 (s), 140.4 (s), 140.7 (s), 163.6 (s). MS m/z: 479 (M^+), 139 (base). *Anal.* Calcd for $C_{25}H_{18}ClNO_2Se$: C, 62.71; H, 3.79; N, 2.93. Found: C, 62.75; H, 3.77; N, 3.05.

3,4-Di(*p*-chlorophenyl)-6-cyano-2*H*-selenopyran (**9c**): Yellow prisms (dichloromethane–hexane), mp 147—148 °C. IR (KBr) cm^{-1}: 2240 (CN). ^{1}H-NMR ($CDCl_3$) δ: 3.78 (2H, s, H-6), 6.89, 7.05 (each 2H, d, J=8 Hz, ArH), 7.13 (1H, s, H-3), 7.16, 7.17 (each 2H, d, J=8 Hz, ArH). ^{13}C-NMR ($CDCl_3$) δ: 26.5 (t), 101.2 (s), 116.9 (s), 128.4 (s), 128.6 (d×2), 128.7 (d×2), 130.7 (d×2), 130.9 (d×2), 133.7 (s), 133.9 (s), 135.5 (s), 137.2 (s), 137.5 (s), 141.3 (d). MS m/z: 390 (M^+), 311 (base). *Anal.* Calcd for $C_{18}H_{11}Cl_2NSe$: C, 55.27; H, 2.83; N, 3.58. Found: C, 55.18; H, 2.87; N, 3.67.

4,5-Di(*p*-chlorophenyl)-2-cyano-3,6-dihydro-2*H*-selenopyran-2-yl *m*-Chlorobenzoate (**10c**): Colorless prisms, mp 165—166 °C. IR (KBr) cm^{-1}: 2220 (CN), 1730, 1255 (ester). ^{1}H-NMR ($CDCl_3$) δ: 3.33, 3.72 (each 1H, d, J=14 Hz, H-3), 3.72, 3.87 (each 1H, d, J=13 Hz, H-6), 7.02, 7.10, 7.17, 7.23 (each 2H, d, J=8 Hz, ArH), 7.36—7.82 (4H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 26.8 (t), 43.9 (t), 72.4 (s), 117.9 (s), 128.1 (s), 128.7 (d×4), 129.6 (s), 129.9 (d), 129.9 (d×2), 130.1 (d), 130.5 (d×2), 133.0 (s), 133.5 (s), 134.3 (d), 134.9 (s), 137.9 (s), 138.8 (s), 140.2 (s), 163.6 (s). MS m/z: 547 (M^+), 139 (base). *Anal.* Calcd for $C_{25}H_{16}Cl_3NO_2Se$: C, 54.82; H, 2.94; N, 2.56. Found: C, 54.61; H, 2.98; N, 2.63.

6-(*p*-Bromobenzoyl)-3,4-dimethyl-2*H*-selenopyran (**9d**): Yellow needles (dichloromethane–hexane), mp 79—80 °C. IR (KBr) cm^{-1}: 1610 (CO). ^{1}H-NMR ($CDCl_3$) δ: 1.82, 2.00 (each 3H, s, Me), 3.24 (2H, s, H-6), 6.81 (1H, s, H-3), 7.55, 7.60 (each 2H, d, J=8.8 Hz, ArH). ^{13}C-NMR ($CDCl_3$) δ: 18.6 (q), 20.5 (q), 24.1 (t), 126.6 (s), 128.9 (s), 129.6 (s), 130.4 (d×2), 131.5 (d×2), 131.9 (s), 135.7 (s), 141.7 (d), 193.3 (s). MS m/z: 356 (M^+), 92 (base). *Anal.* Calcd for $C_{14}H_{13}BrOSe$: C, 47.22; H, 3.68. Found: C, 46.99; H, 3.83.

2-(*p*-Bromobenzoyl)-3,6-dihydro-4,5-dimethyl-2*H*-selenopyran-2-yl *m*-Chlorobenzoate (**10d**): Pale yellow prisms (dichloromethane–hexane), mp 141—143 °C. IR (KBr) cm^{-1}: 1680 (CO), 1720, 1260 (ester). ^{1}H-NMR ($CDCl_3$) δ: 1.80, 1.92 (each 3H, s, Me), 3.11, 3.19 (each 1H, d, J=15.1 Hz, H-3), 3.30, 3.38 (each 1H, d, J=13.2 Hz, H-6), 7.27—7.89 (4H, m, ArH), 7.49, 7.91 (each 2H, d, J=8.8 Hz, ArH). ^{13}C-NMR ($CDCl_3$) δ: 18.7 (q), 20.6 (q), 27.0 (t), 39.5 (t), 96.1 (s), 127.8 (d), 128.0 (s), 128.7 (s), 129.0 (s), 129.6 (d), 129.9 (d), 130.0 (d×2), 130.5 (s), 131.7 (d×2), 133.0 (s), 133.7 (d), 134.7 (s), 164.4 (s), 191.6 (s). MS m/z: 512 (M^+), 139 (base). *Anal.* Calcd for $C_{21}H_{18}BrClO_3Se$: C, 49.20; H, 3.54. Found: C, 49.24; H, 3.56.

3,4-Dimethyl-6-(*p*-nitrobenzoyl)-2*H*-selenopyran (**9f**): Yellow prisms (dichloromethane–hexane), mp 118—120 °C (dec.). IR (KBr) cm^{-1}: 1600 (CO), 1515, 1350 (NO_2). ^{1}H-NMR ($CDCl_3$) δ: 1.84, 2.03 (each 3H, s, Me), 3.29 (2H, s, H-6), 6.80 (1H, s, H-3), 7.81, 8.31 (each 2H, d, J=8.8 Hz, ArH). ^{13}C-NMR ($CDCl_3$) δ: 18.7 (q), 20.7 (q), 24.1 (t), 123.5 (d×2), 129.0 (s), 129.6 (d×2), 129.7 (s), 130.8 (s), 131.9 (s), 142.7 (s), 142.9 (d), 192.5 (s). MS m/z: 323 (M^+), 92 (base). *Anal.* Calcd for $C_{14}H_{13}NO_3Se$: C, 52.19; H, 4.07; N, 4.35. Found: C, 51.93; H, 4.06; N, 4.29.

3,6-Dihydro-4,5-dimethyl-2-(*p*-nitrobenzoyl)-2*H*-selenopyran-2-yl *m*-Chlorobenzoate (**10f**): Yellow prisms (dichloromethane–hexane), mp 137—138 °C. IR (KBr) cm^{-1}: 1715, 1255 (ester), 1690 (CO), 1520, 1340 (NO_2). ^{1}H-NMR ($CDCl_3$) δ: 1.81, 1.94 (each 3H, s, Me), 3.12, 3.19 (each 1H, d, J=15 Hz, H-3), 3.34, 3.42 (each 1H, d, J=13 Hz, H-6), 7.34—8.23 (8H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 18.8 (q), 20.7 (q), 27.3 (t), 39.5 (t), 96.0 (s), 123.7 (d×2), 127.9 (d), 128.9 (s), 129.1 (s), 129.5 (d×2), 129.8 (d), 130.0 (d), 130.2 (s), 134.1 (d), 134.9 (s), 139.4 (s), 149.9 (s), 164.7 (s), 191.4 (s). MS m/z: 479 (M^+), 139 (base). *Anal.* Calcd for $C_{21}H_{18}ClNO_5Se$: C, 52.68; H, 3.79; N, 2.93. Found: C, 52.64; H, 3.90; N, 3.04.

Oxidation of 2a with Benzoyl Peroxide Benzoyl peroxide (363 mg, 1.5 mmol) was gradually added to a solution of **2a** (200 mg, 1 mmol) in dry dichloromethane (10 ml) at 0 °C with stirring. The reaction mixture was stirred for 3 h at that temperature, followed by addition of a saturated sodium hydrogen carbonate solution. The whole was stirred for 20 min and extracted with dichloromethane. The extracts were washed with water, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was fractionated by PLC on silica gel using hexane–dichloromethane (3:1) to give a selenopyran **9a** (24 mg, 12%) and 2-cyano-3,6-dihydro-4,5-dimethyl-2*H*-selenopyran-2-yl benzoate (**10g**) (148 mg, 46%).

10g: Pale red prisms (dichloromethane–hexane), mp 109—110 °C. IR (KBr) cm^{-1}: 2220 (CN), 1730, 1270 (ester). ^{1}H-NMR ($CDCl_3$) δ: 1.90, 2.01 (each 3H, s, Me), 2.89, 3.12 (each 1H, d, J=14 Hz, H-3), 3.25, 3.32 (each 1H, d, J=13 Hz, H-6), 7.44—8.03 (5H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 18.6 (q), 20.5 (q), 25.9 (t), 43.1 (t), 71.9 (s), 118.5 (s), 126.2 (s), 128.1 (s), 128.5 (d×2), 129.8 (d×2), 132.9 (s), 134.0 (d), 164.6 (s). MS m/z: 321 (M^+), 105 (base). *Anal.* Calcd for $C_{15}H_{15}NO_2Se$: C, 56.26; H, 4.72; N, 4.37. Found: C, 56.18; H, 4.75; N, 4.25.

Reaction of 2-Cyano-3,6-dihydro-4,5-dimethyl-2*H*-selenopyran-2-yl *m*-Chlorobenzoate (10a) with PPSE PPSE was prepared by the procedure of Imamoto *et al.*[10] Hexamethyl disiloxane (9.2 ml) was added to a suspension of phosphorus pentoxide (4.33 g) in dry 1,2-dichloroethane (18 ml) under a nitrogen atmosphere and the mixture was refluxed for 1 h. The PPSE solution (5 ml) was added to a solution of **10a** (354 mg, 1 mmol) in dry 1,2-dichloroethane (5 ml) under a nitrogen atmosphere and the mixture was refluxed for 23 h. Water was added to the cooled reaction mixture, and the whole was extracted with dichloromethane. The extracts were washed with a saturated hydrogen carbonate solution and with water, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by PLC on silica gel using hexane–dichloromethane (3:1) to give 6-cyano-3,4-dimethyl-2*H*-selenopyran (**9a**) (190 mg, 96%). This was identical with the sample obtained by the MCPBA oxidation of **2a**.

Reaction of 2-Cyano-3,6-dihydro-4,5-diphenyl-2*H*-selenopyran-2-yl *m*-Chlorobenzoate (10b) with PPSE The PPSE solution (5 ml) prepared above was added to a solution of **10b** (479 mg, 1 mmol) in 1,2-dichloroethane (5 ml) under a nitrogen atmosphere and the mixture was refluxed for 40 h. Work-up similar to that described for **10a** gave 6-cyano-3,4-diphenyl-2*H*-selenopyran (**9b**) (205 mg, 64%). This was identical with the sample obtained by the MCPBA oxidation of **2b**.

Reaction of 3,4-Di(*p*-chlorophenyl)-2-cyano-3,6-dihydro-2*H*-selenopyran-2-yl *m*-Chlorobenzoate (10c) with PPSE Compound **10c** (548 mg, 1 mmol) was similarly treated with the PPSE solution prepared above and gave 3,4-di(*p*-chlorophenyl)-6-cyano-2*H*-selenopyran (**9c**) (293 mg, 75%).

6-(*p*-Bromobenzoyl)-3,4-diphenyl-2*H*-selenopyran (9e) from 3,6-Dihydro-2*H*-selenopyran 2e MCPBA (690 mg, 4 mmol) was gradually added to a solution of **2e** (965 mg, 2 mmol) in dry dichloromethane (20 ml) at 0 °C with stirring and the mixture was stirred for 3 h. A saturated sodium hydrogen carbonate solution was added to the mixture. The whole was stirred for 20 min and then extracted with dichloromethane. The extracts were washed with water, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was dissolved in dry 1,2-dichloroethane (10 ml) and treated with the PPSE solution (5 ml) prepared above. Work-up similar to that described for **10a** gave **9e** (297 mg, 31%) as colorless prisms (dichloromethane-hexane), mp 143 °C (dec.). IR (KBr) cm^{-1}: 1630 (CO). ^{1}H-NMR ($CDCl_3$) δ: 3.79 (2H, s, H-6), 6.94 (1H, s, H-3), 7.12—7.35 (10H, m, ArH), 7.58, 7.64 (each 2H, d, J=8.3 Hz, ArH). ^{13}C-NMR ($CDCl_3$) δ: 25.5 (t), 127.1 (d), 127.6 (d), 128.0 (d×2), 128.2 (d×2), 129.6 (d×2), 129.7 (d×2), 130.5 (d×2), 131.7 (d×2), 135.4 (s), 135.9 (s), 136.6 (s), 140.1 (s), 140.2 (s), 140.3 (d), 193.7 (s). MS m/z: 480 (M^+), 183 (base). *Anal.* Calcd for $C_{24}H_{17}BrOSe$: C, 60.02; H, 3.57. Found: C, 60.09; H, 3.73.

6-Cyano-1,3,4-trimethyl-2*H*-selenopyranium Triflate (12a) Methyl triflate (328 mg, 2 mmol) was added to a solution of the selenopyran **9a** (369 mg, 2 mmol) in dry dichloromethane (1 ml). The mixture was stirred for 12 h at room temperature and followed by addition of ether. The resulting precipitate was collected by filtration and recrystallized from acetonitrile–ether to give **12a** as slightly brown prisms (404 mg, 56%), mp 143—144 °C. IR (KBr) cm^{-1}: 2230 (CN), 1250, 1030 (SO_3^-). ^{1}H-NMR (CD_3CN) δ: 1.99, 2.09 (each 3H, s, Me), 2.79 (3H, s, SeMe), 3.90, 4.38 (each 1H, d, J=16.6 Hz, H-6), 7.39 (1H, s, H-3). ^{13}C-NMR (CD_3CN) δ: 18.2 (q), 18.4 (q), 21.2 (q), 36.8 (t), 89.4 (s), 114.5 (s), 128.7 (s), 132.0 (s), 152.6 (d). *Anal.* Calcd for $C_{10}H_{12}F_3NO_3SSe$: C, 33.16; H, 3.34; N, 3.87. Found: C, 32.88; H, 3.39; N, 3.81.

6-Cyano-1-methyl-4,5-diphenyl-2*H*-selenopyranium Triflate (12b) This compound was similarly prepared from **9b** (460 mg, 1.4 mmol) and methyl triflate (328 mg, 2 mmol). Yellow prisms (acetonitrile–ether) (205 mg, 30%), mp 128—130 °C. IR (KBr) cm^{-1}: 2210 (CN), 1240—1285, 1030 (SO_3^-). ^{1}H-NMR (CD_3CN) δ: 3.04 (3H, s, Me), 4.39, 4.88 (each 1H, d, J=16 Hz, H-6), 7.14—7.27 (10H, m, ArH), 7.75 (1H, s, H-3). ^{13}C-NMR (CD_3CN) δ: 18.7 (q), 37.1 (t), 92.4 (s), 113.9 (s), 128.3 (d), 128.5 (d×2), 129.0 (d), 129.2 (d×2), 134.1 (s), 135.1 (s), 137.0 (s), 137.9 (s), 151.7 (d). *Anal.* Calcd for $C_{20}H_{16}F_3NO_3SSe$: C, 49.39; H, 3.32; N, 2.88. Found: C, 49.43; H, 3.39; N, 2.98.

4,5-Di(*p*-chlorophenyl)-6-cyano-1-methyl-2*H*-selenopyranium Triflate (12c) This compound was prepared from **9c** (313 mg, 0.8 mmol) and methyl triflate (131 mg, 0.8 mmol). Yellow prisms (acetonitrile–ether) (139 mg, 37%), mp 152—153 °C. IR (KBr) cm^{-1}: 2210 (CN), 1240, 1030 (SO_3^-). ^{1}H-NMR (CD_3CN) δ: 4.37, 4.87 (each 1H, d, J=16 Hz, H-6), 7.12, 7.14, 7.28, 7.30 (each 2H, d, J=8 Hz, ArH), 7.72 (1H, s, H-3). ^{13}C-NMR (CD_3CN) δ: 19.1 (q), 36.9 (t), 93.1 (s), 113.8 (s), 128.7 (d×2), 128.8 (d×2), 130.8 (d×2), 131.1 (d×2), 133.5 (s), 134.0 (s), 134.5 (s), 134.9 (s), 135.5 (s), 136.3 (s), 151.1 (d). *Anal.* Calcd for $C_{20}H_{14}Cl_2F_3NO_3SSe$: C, 43.26; H, 2.54; N, 2.52. Found: C, 43.11; H, 2.63; N, 2.56.

6-(*p*-Bromobenzoyl)-1,3,4-trimethyl-2*H*-selenopyranium Triflate (12d) This compound was prepared from **9d** (256 mg, 0.7 mmol) and methyl triflate (164 mg, 1 mmol). Yellow powder (acetonitrile–ether) (352 mg, 94%), mp 162—163 °C (dec.). IR (KBr) cm^{-1}: 1615 (CO), 1240, 1025 (SO_3^-). ^{1}H-NMR ($CDCl_3$) δ: 1.98, 2.14 (each 3H, s, Me), 2.64 (3H, s, SeMe), 3.86, 4.26 (each 1H, d, J=17 Hz, H-6), 7.26 (1H, s, H-3), 7.69, 7.76 (each 2H, d, J=9 Hz, ArH). ^{13}C-NMR (CD_3CN) δ: 17.3 (q), 19.0 (q), 21.4 (q), 34.9 (t), 123.0 (s), 128.5 (s), 128.9 (s), 131.6 (d×2), 132.6 (d×2), 133.2 (s), 133.6 (s), 148.6 (d), 190.5 (s). *Anal.* Calcd for $C_{16}H_{16}BrF_3O_4SSe$: C, 36.94; H, 3.10. Found: C, 36.66; H, 3.05.

1,3,4-Trimethyl-6-(*p*-nitrobenzoyl)-2*H*-selenopyranium Triflate (12e) This compound was prepared from **9f** (190 mg, 0.6 mmol) and methyl triflate (164 mg, 1 mmol). Slightly brown powder (acetonitrile–ether) (232 mg, 81%), mp 172—173 °C. IR (KBr) cm^{-1}: 1640 (CO), 1520, 1350 (NO_2), 1255—1280, 1035 (SO_3^-). ^{1}H-NMR (CD_3CN) δ: 1.98, 2.16 (each 3H, s, Me), 2.67 (3H, s, SeMe), 3.91, 4.31 (each 1H, d, J=17 Hz, H-6), 7.26 (1H, s, H-3), 7.96, 8.36 (each 2H, d, J=8.8 Hz, ArH). ^{13}C-NMR (CD_3CN) δ: 17.3 (q), 19.0 (q), 21.5 (q), 35.0 (t), 122.8 (s), 124.4 (d×2), 128.9 (s), 131.0 (d×2), 134.1 (s), 140.0 (s), 149.5 (d), 190.2 (s). *Anal.* Calcd for $C_{16}H_{16}F_3NO_6SSe$: C, 39.52; H, 3.32; N, 2.88. Found: C, 39.44; H, 3.40; N, 2.92.

Generation of 2-Cyano-1,4,5-trimethylselenabenzene (13a) A solution of this compound in acetonitrile-d_3 was prepared in an NMR tube. Sodium hydride (15 mg) was added to a solution of the selenonium salt **12a** (100 mg, 0.3 mmol) in acetonitrile-d_3 (0.5 ml) under an argon stream at −30 °C. The mixture was shaken and the ^{1}H- and ^{13}C-NMR spectra were measured at −30 °C. ^{1}H-NMR (CD_3CN) δ: 1.86 (3H, s, 4-Me), 1.92 (3H, s, 5-Me), 2.04 (3H, s, Se-Me), 5.01 (1H, s, H-6), 6.45 (1H, s, H-3). ^{13}C-NMR (CD_3CN) δ: 19.3 (q, 4-Me), 21.4 (q, 5-Me), 23.0 (q, Se-Me), 31.7 (s, C-2), 78.2 (d, C-6), 112.5 (s, C-4), 124.0 (s, CN), 130.2 (d, C-3), 144.5 (s, C-5).

Generation of 2-(*p*-Bromobenzoyl)-1,4,5-trimethylselenabenzene (13d) A solution of this compound was prepared from **12d** (100 mg, 0.2 mmol) and sodium hydride (10 mg) in acetonitrile-d_3 in an NMR tube and the ^{1}H- and ^{13}C-NMR spectra were measured at −30 °C. ^{1}H-NMR (CD_3CN) δ: 1.82 (3H, s, 4-Me), 2.05 (3H, s, 5-Me), 2.14 (3H, s, Se-Me), 5.56 (1H, s, H-6), 6.39 (1H, s, H-3), 7.41, 7.56 (each 2H, d, J=8 Hz, ArH). ^{13}C-NMR (CD_3CN) δ: 20.1 (q, 4-Me), 22.2 (q, 5-Me), 25.6 (q, Se-Me), 85.1 (s, C-2), 89.6 (d, C-6), 113.1 (s, C-4), 123.1 (s), 127.6 (d, C-3), 130.7 (d×2, 3′,5′-Ph), 131.0 (d×2, 2′,6′-Ph), 138.2 (s), 147.2 (s, C-5), 179.4 (s, CO).

References

1) J. Stackhouse, G. H. Jr. Senkler, B. E. Maryanoff, K. Mislow, *J. Am. Chem. Soc.*, **96**, 7835 (1974).
2) M. Hori, T. Kataoka, H. Shimizu, K. Tsutsumi, S. Imaoka, *Heterocycles*, **26**, 2365 (1987).
3) M. Hori, T. Kataoka, H. Shimizu, K. Tsutsumi, M. Yoshimatsu, *Heterocycles*, **30**, 295 (1990); *idem*, *J. Org. Chem.*, **55**, 2458 (1990).
4) M. Hori, T. Kataoka, H. Shimizu, H. Aoki, *Heterocycles*, **5**, 413 (1976); *idem.*, *Chem. Pharm. Bull.*, **36**, 3816 (1988); M. Hori, T. Kataoka, H. Shimizu, K. Narita, S. Ohno, H. Aoki, *Chem. Lett.*, **1974**, 1101; M. Hori, T. Kataoka, H. Shimizu, S. Ohno, K. Narita, H. Takayanagi, Y. Iitaka, *Tetrahedron Lett.*, **1979**, 4315; M. Hori, T. Kataoka, H. Shimizu, S. Ohno, K. Narita, H. Koyama, *J. Chem. Soc., Chem. Commun.*, **1981**, 364; M. Hori, T. Kataoka, H. Shimizu, K. Narita, S. Ohno, H. Ogura, H. Takayanagi, Y. Iitaka, H. Koyama, *J. Chem. Soc., Perkin Trans. 1*, **1988**, 1885.
5) J. Nakayama, J. Nuijima, M. Hoshino, *Tetrahedron Lett.*, **28**, 4423 (1987); P. T. Meinke, G. A. Krafft, *J. Am. Chem. Soc.*, **110**, 8671 (1988).
6) G. W. Kirby, A. N. Trethwey, *J. Chem. Soc., Perkin Trans. 1*, **1988**, 1913.
7) G. Galambos, V. Simonidesz, *Tetrahedron Lett.*, **23**, 4371 (1982).
8) H. Shimizu, N. Ueda, T. Kataoka, M. Hori, *Chem. Pharm. Bull.*, **32**, 2571 (1984).
9) T. Kataoka, Y. Ohe, T. Iwamura, M. Yoshimatsu, H. Shimizu, *J. Chem. Soc., Chem. Commun.*, **1993**, 577.
10) T. Imamoto, H. Yokoyama, M. Yokoyama, *Tetrahedron Lett.*, **22**, 1803 (1981).
11) H. Shimizu, N. Kudo, T. Kataoka, M. Hori, *Tetrahedron Lett.*, **31**, 115 (1990).
12) Y. Ishino, I. Nishiguchi, F. Takihira, T. Hirashima, *Tetrahedron Lett.*, **21**, 1527 (1980).