Protecting Groups for Organoselenium Compounds

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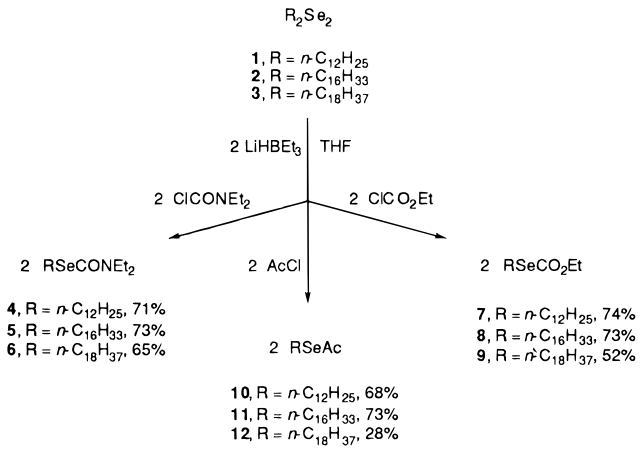
Introduction

In the course of our investigations on self-assembled monolayers (SAMs) of organoselenium compounds on gold,[1] we desired a protecting group for selenium that was stable to a variety of reaction conditions yet was easily removed under the conditions used for monolayer formation. We have previously reported a method for the in situ deprotection of aryl thioacetates using NH_4OH.[2] The thiols that were generated in situ served as molecular scale "alligator clips" (wire-to-surface binding units) for adhesion of molecular wires to metallic probes. With a desire to change the nature of the alligator clip to a more metallic element, and taking a lead from our sulfur chemistry, we decided to investigate the use of selenocarbamates, selenocarbonates, and selenoacetates as end groups for the molecular wires. We have also examined their deprotection and their stability with respect to Pd/Cu-catalyzed coupling reactions.

Utilization of organoselenium compounds often requires use of a protected selenol since, under ambient conditions, selenols readily oxidize to diselenides.[3] Selenols are usually protected as the symmetrical diselenide (RSeSeR) or as the selenocyanate (RSeCN); however, there are serious drawbacks and limitations to these approaches. For example, diselenides require strongly reducing conditions, such as Na/NH_3 or $NaBH_4$, to cleave the Se−Se bond. Additionally, the diselenide approach is incompatible for use with α,ω-diselenols since the protected material would consist of insoluble poly(diselenides), and diselenides are likely not stable toward Pd-catalyzed cross-coupling conditions as the Se−Se bond will oxidatively add to the Pd(0) catalyst and interrupt the catalytic cycle.[4] While selenocyanates can be deprotected under various conditions, their syntheses usually require the use of potassium selenocyanate (KSeCN) or selenocyanogen [$(SeCN)_2$] and their deprotection often releases HCN.[5] Although potassium selenocyanate is strongly nucleophilic and readily reacts with alkyl halides and aryldiazonium salts to form alkyl and aryl selenocyanates,[6] KSeCN requires an unappealing preparation (stirring a molten mixture of KCN and elemental Se)[7] and is extremely hygroscopic, decomposing slowly on contact with the common laboratory atmosphere. Selenocyanogen is prepared from KSeCN at low temperatures and is extremely toxic. All three of the protecting groups described here offer significant advantages over diselenides and selenocyanates.

Scheme 1



Ever since Sharpless and Lauer converted epoxides to allylic alcohols using diphenyl diselenide,[8] the use of selenium compounds in organic synthesis has been an area of intense study.[9] In recent years, a number of researchers have employed selenocarbamates, selenocarbonates, and selenoacetates as efficient sources of acyl radicals.[10] Among other applications, they have been used in ring-closing reactions to form lactones[10c] and substituted tetrahydrofurans,[10d] for the radical deoxygenation of alcohols,[11] and for the conversion of carboxylic acids to isonitriles.[10e] The many examples of the homolytic cleavage of the acyl C−Se bond to give the corresponding selenyl radical are contrasted by a surprising paucity of examples of selenolate anions derived from selenoacyl compounds. Vinyl selenoacetates have been cleaved by Na/HMPA in DMF to give vinyl selenolates that were oxidized with iodine to yield divinyl diselenides.[12] Also, aryl selenoesters have been deprotected

(1) There are only two reports of SAM formation by organoselenium compounds on gold: (a) Samant, M. G.; Brown, C. A.; Gordon, J. G., II. *Langmuir* **1992**, *8*, 1615. (b) Dishner, M. H.; Hemminger, J. C.; Feher, F. J. *Langmuir* **1997**, *13*, 4788.

(2) (a) Tour, J. M.; Jones, L., II; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. V. *J. Am. Chem. Soc.* **1995**, *117*, 9529. (b) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L., II; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705.

(3) *Organic Selenium Compounds: Their Chemistry and Biology*; Klayman, D. L., Günther, W. H. H., Eds.; The Chemistry of Organometallic Compounds; John Wiley & Sons: New York, 1973; p 73.

(4) While, to our knowledge, no accounts exist in the literature demonstrating addition of a diselenide to a Pd(0) complex, the corresponding reaction has been reported for disulfides (Zanella, R.; Ros, R.; Graziani, M. *Inorg. Chem.* **1973**, *12*, 2736) and ditellurides (Chia, L.-Y.; McWhinnie, W. R. *J. Organomet. Chem.* **1978**, *148*, 165).

(5) *Organic Selenium Compounds: Their Chemistry and Biology*; Klayman, D. L., Günther, W. H. H., Eds.; The Chemistry of Organometallic Compounds; John Wiley & Sons: New York, 1973; pp 42−44.

(6) *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; The Chemistry of Functional Groups; John Wiley & Sons: New York, 1987; Vol. 2, pp 541−574.

(7) Waitkins, G. R.; Shutt, R. *Inorg. Synth.* **1946**, *2*, 186.

(8) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 2697.

(9) *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; The Chemistry of Functional Groups; John Wiley & Sons: New York, 1987; Vol. 2, Chapters 3, 16, and 17.

(10) (a) Pfenninger, J.; Heuberger, C.; Graf, W. *Helv. Chim. Acta* **1980**, *63*, 2328. (b) Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* **1992**, *57*, 1429. (c) Bachi, M. D.; Bosch, E. *J. Org. Chem.* **1992**, *57*, 4696. (d) Clive, D. L. J.; Yang, W. *Chem. Commun.* **1996**, 1605. (e) Barrett, A. G. M.; Kwon, H.; Wallace, E. M. *J. Chem. Soc., Chem. Commun.* **1993**, 1760. (f) Haraguchi, K. Tanaka, H.; Miyasaka, T. *Tetrahedron Lett.* **1990**, *31*, 227. (g) Ryu, I.; Kusano, K.; Masumi, N.; Yamazaki, H.; Ogawa, A.; Sonoda, N. *Tetrahedron Lett.* **1990**, *31*, 6887.

(11) Hartwig, W. *Tetrahedron* **1983**, *39*, 2609.

(12) Testaferri, L.; Tiecco, M.; Tingoli, M.; Chianelli, D. *Tetrahedron* **1986**, *42*, 4577.

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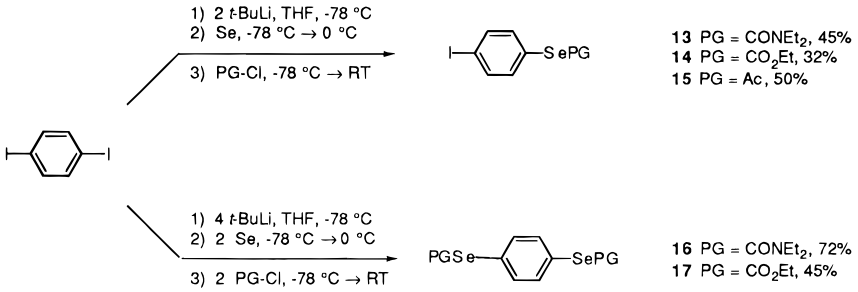
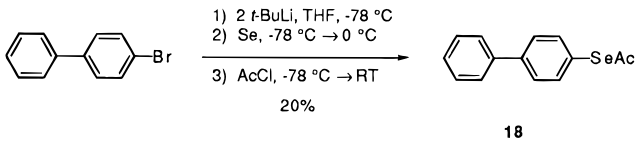
Scheme 2



Scheme 3



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with K_2CO_3 in THF/H_2O to give selenolates that add to phenylpropionitrile to give selenocinnamonitriles.[13] Therefore, further developments on the formation and hydrolysis of protected selenols is warranted.

Results and Discussion

Protected Selenol Syntheses. Utilizing the method of Gladysz,[14] lithium triethylborohydride reduction of elemental selenium followed by quenching with alkyl halides leads to formation of the dialkyl diselenides **1**−**3**. Unfortunately, a significant amount (5−15%) of the corresponding dialkyl selenide (R_2Se) is also produced in this reaction; however, this does not interfere in the subsequent reductive cleavage of the dialkyl diselenides since the selenides are unreactive toward $LiHBEt_3$. Therefore, treatment of crude **1**−**3** with $LiHBEt_3$ followed by reaction with diethylcarbamyl chloride, ethyl chloroformate, or acetyl chloride yields the corresponding alkyl selenocarbamates (**4**−**6**), selenocarbonates (**7**−**9**), and selenoacetates (**10**−**12**), respectively (Scheme 1). Protected arylselenols can also be readily prepared by employing the method outlined in Schemes 2 and 3. Lithium−halogen exchange from an aryl halide, followed by selenium insertion and finally quenching with the protecting group chloride affords compounds **13**−**18**. All yields are unoptimized. All of the compounds synthesized have been characterized by ^1H, ^{13}C, and ^{77}Se NMR, FTIR, and HRMS. Selected data for the protected alkyl and aryl selenols are listed in Table 1.

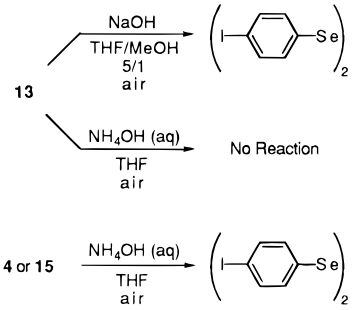
Protecting Group Stability. All three of the protecting groups studied were quite stable to both air and water. As expected, the selenocarbamates are significantly more robust than the selenocarbonates and selenoacetates. For example, compound **13** is unaffected by NH_4OH, hydrazine sulfate, sodium borohydride, tetrabutylammonium borohydride, tetrabutylammonium fluoride, tetrabutylammonium hydroxide, sodium azide, and *N*,*N*-(dimethylamino)pyridine. Only sodium hydroxide effected removal of the diethylcarbamyl group with concomitant formation of the corresponding diselenide. In contrast, compounds **14** and **15** are smoothly deprotected by treatment with aqueous NH_4OH in THF (Scheme 4). It has previously been reported that selenoesters can be cleaved using *n*-$BuNH_2$ in EtOH.[15]

Table 1. Selected Data for Protected Alkyl- and Arylselenols

compd	$^{13}C^a$	$^{77}Se^b$	IR[c]
4	163.80	390.63	1656, 1662
5	163.95	390.66	1655, 1663
6	163.92	390.77	1656, 1662
7	167.63	393.66	1717
8	167.54	393.63	1718
9	167.65	393.69	1718
10	198.09	559.72	1715
11	198.12	559.76	1715
12	197.85	559.47	1717
13	162.32	519.90	1665
14	166.09	509.54	1727
15	195.71	667.00	1709
16	162.62	519.82	1669
17	166.14	510.43	1726
18	196.90	664.12	1715

[a] Chemical shift of carbonyl carbon in ppm relative to TMS. [b] Chemical shift in ppm relative to Me_2Se in $CDCl_3$ (60% v/v). [c] Stretching frequency in cm^{-1} of carbonyl group (KBr pellet).

Scheme 4



Attempted Pd/Cu-Catalyzed Coupling of Protected Aryl Selenols. Despite their air and water stability, **13**−**15** do not undergo Pd/Cu-catalyzed cross coupling. Repeated attempts at coupling **13**, **14**, or **15** with (trimethylsilyl)acetylene under typical Sonogashira coupling conditions[16] were unsuccessful. Employing a number of catalysts, including $(Ph_3P)_2PdCl_2$, $Pd(dba)_2$, $(PhCN)_2PdCl_2$, and $(NMDPP)_2PdCl_2$,[17] all in the presence of CuI, at concentrations up to 10 mol % in a variety of solvents (C_6H_6, THF, CH_3CN) or in neat base (NEt_3, *i*-Pr_2NEt) gave only unreacted starting material with some unidentifiable impurities.

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(14) Gladysz, J. A.; Hornby, J. L.; Garbe, J. E. *J. Org. Chem.* **1978**, *43*, 1204.
(15) Mautner, H. G.; Chu, S.-H.; Günther, W. H. H. *J. Am. Chem. Soc.* **1963**, *85*, 3458.
(16) Sonogashira, K.; Tohda, H.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.
(17) NMDPP = (+)-neomenthyldiphenylphosphine.

Summary

We have prepared a series of alkyl and aryl selenocarbamates, selenocarbonates, and selenoacetates by either reductive cleavage of the corresponding diselenide or lithium−halogen exchange from an aryl halide and selenium insertion, followed by capping with the appropriate protecting group. Deprotection of these protected selenols was investigated, and the selenocarbamates were found to be significantly more robust than the other protecting groups. The selenocarbamates were stable to a variety of reducing agents and nucleophiles but were efficiently deprotected by NaOH. The selenocarbonates and selenoacetates were smoothly deprotected by treatment with aqueous NH_4OH. Unfortunately, Pd/Cu-catalyzed coupling reactions employing these protecting groups were unsuccessful. Despite this drawback, these protecting groups offer advantages over diselenides and selenocyanates in their ease of synthesis and removal, as well as their applicability to a wide variety of compounds such as α,ω-diselenols.

Experimental Procedures

General Methods. All reactions were performed under a dry, nitrogen atmosphere using standard air-sensitive techniques unless otherwise stated. Anhydrous diethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Hexanes were distilled prior to use. Silica gel was grade 60 (230−400 mesh, EM Science), and silica gel plates were 250 μm thick K6F grade (Whatman) and were used as received. Gray selenium powder (99.5+%, 200 mesh, Acros) was used as received. Didodecyl diselenide, dihexadecyl diselenide, and dioctadecyl diselenide were prepared by the method of Gladysz[14] and contained 5−15% of the corresponding selenide. A number of the products were highly viscous liquids or oils so the IR spectra were obtained by dissolving the material in a minimal amount of a suitable solvent, adding the solution to KBr, evaporating the solvent, and then forming a pellet.

General Procedure for the Synthesis of Protected Alkylselenols. Lithium triethylborohydride (2 equiv) was added dropwise to a stirred solution of the diselenide in THF at room temperature. Gas was evolved, and the solution changed from yellow to colorless. After the solution was stirred for at least 15 min, the protecting group chloride was added dropwise. After being stirred for at least 1 h at room temperature, the solution was poured into water and extracted with hexanes and ether. Purification was achieved by flash chromatography on silica gel eluting with hexanes.

***Se*-*n*-Dodecyl-*N*,*N*-diethylselenocarbamate (4).** Lithium triethylborohydride (2.0 mL of a 1.0 M solution in THF, 2.0 mmol), didodecyl diselenide (0.497 g, 1.0 mmol), THF (10 mL), and *N*,*N*-diethylcarbamyl chloride (0.28 mL, 2.2 mmol) afforded 0.492 g (71%) of **4** as a colorless liquid: IR (KBr) 2923, 2853, 1662, 1656, 1401, 1384, 1244, 1218, 1110, 846 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.386 (br q, J = 6.4 Hz, 2 H), 3.262 (br q, J = 6.4 Hz, 2 H), 2.794 (t, J = 7.4 Hz, 2 H), 1.657 (pent, J = 7.4 Hz, 2 H), 1.210 (broad overlapping multiplets, 24 H), 0.838 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 163.80, 43.14, 41.93, 32.01, 31.03, 30.20, 29.73, 29.70, 29.65, 29.45, 29.27, 26.87, 22.80, 14.24, 14.12, 13.33; ^{77}Se NMR ($CDCl_3$) δ 390.63; HRMS (EI) calcd for $C_{17}H_{35}NOSe$ *m*/*e* 349.1884, found 349.1886 (M^+).

***Se*-*n*-Hexadecyl-*N*,*N*-diethylselenocarbamate (5).** Lithium triethylborohydride (2.0 mL of a 1.0 M solution in THF, 2.0 mmol), dihexadecyl diselenide (0.609 g, 1.0 mmol), THF (10 mL), and *N*,*N*-diethylcarbamyl chloride (0.26 mL, 2.05 mmol) afforded 0.588 g (73%) of **5** as a yellow liquid: IR (KBr) 2923, 2851, 1663, 1655, 1400, 1244, 1215, 1110, 846 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.385 (q, J = 6.9 Hz, 2 H), 3.259 (q, J = 6.9 Hz, 2 H), 2.875 (t, J = 7.4 Hz, 2 H), 1.655 (pent, J = 7.4 Hz, 2 H), 1.333 (m, 2 H), 1.210 (br s, 24 H), 1.164 (br t, J = 6.8 Hz, 3 H), 1.108 (br t, J = 7.0 Hz, 3 H), 0.837 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 163.95, 43.07, 41.87, 31.93, 30.95, 30.12, 29.70, 29.66, 29.61, 29.56, 29.37, 29.18, 26.77, 22.70, 14.12, 14.01, 13.23; ^{77}Se NMR ($CDCl_3$) δ 390.66; HRMS (EI) calcd for $C_{21}H_{43}NOSe$ *m*/*e* 405.2510, found 405.2523 (M^+).

***Se*-*n*-Octadecyl-*N*,*N*-diethylselenocarbamate (6).** Lithium triethylborohydride (1.0 mL of a 1.0 M solution in THF, 1.0 mmol), dioctadecyl diselenide (0.332 g, 0.5 mmol), THF (15 mL), and *N*,*N*-diethylcarbamyl chloride (0.15 mL, 1.2 mmol) afforded 0.281 g (65%) of **6** as a pale yellow liquid: IR (KBr) 2923, 2851, 1662, 1656, 1401, 1383, 1244, 1217, 1110, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.395 (br q, J = 6.8 Hz, 2 H), 3.270 (br q, J = 6.6 Hz, 2 H), 2.884 (t, J = 7.4 Hz, 2 H), 1.664 (pent, J = 7.4 Hz, 2 H), 1.221 (br overlapping m, 36 H), 0.845 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 163.92, 43.07, 41.87, 31.94, 30.96, 30.12, 29.71, 29.67, 29.62, 29.57, 29.38, 29.18, 26.77, 22.70, 14.13, 14.01, 13.23; ^{77}Se NMR ($CDCl_3$) δ 390.77; HRMS (EI) calcd for $C_{23}H_{47}NOSe$ *m*/*e* 433.2823, found 433.2817 (M^+).

***Se*-*n*-Dodecyl-*O*-ethylselenocarbonate (7).** Lithium triethylborohydride (2.0 mL of a 1.0 M solution in THF, 2.0 mmol), didodecyl diselenide (0.497 g, 1.0 mmol), THF (10 mL), and ethyl chloroformate (0.21 mL, 2.2 mmol) afforded 0.474 g (74%) of **7** as a colorless liquid: IR (KBr) 2923, 2854, 1717, 1384, 1124, 1014, 835 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.271 (q, J = 7.1 Hz, 2 H), 2.863 (t, J = 7.4 Hz, 2 H), 1.702 (pent, J = 7.4 Hz, 2 H), 1.348 (br m, 2 H), 1.286 (t, J = 7.1 Hz, 3 H), 1.232 (br s, 16 H), 0.855 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 167.63, 63.69, 31.92, 30.59, 29.81, 29.64, 29.63, 29.59, 29.50, 29.35, 29.08, 27.20, 22.69, 14.34, 14.11; ^{77}Se NMR ($CDCl_3$) δ 393.66; HRMS (EI) calcd for $C_{15}H_{30}O_2Se$ *m*/*e* 322.1411, found 322.1404 (M^+).

***Se*-*n*-Hexadecyl-*O*-ethylselenocarbonate (8).** Lithium triethylborohydride (1.0 mL of a 1.0 M solution in THF, 1.0 mmol), dihexadecyl diselenide (0.304 g, 0.5 mmol), THF (15 mL), and ethyl chloroformate (0.12 mL, 1.26 mmol) afforded 0.274 g (73%) of **8** as a colorless liquid: IR (KBr) 2923, 2851, 1718, 1383, 1124, 1015, 835 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.273 (q, J = 7.2 Hz, 2 H), 2.865 (t, J = 7.4 Hz, 2 H), 1.704 (pent, J = 7.4 Hz, 2 H), 1.349 (br m, 2 H), 1.288 (t, J = 7.1 Hz, 3 H), 1.231 (br s, 24 H), 0.855 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 167.54, 63.76, 32.02, 30.67, 29.90, 29.76, 29.68, 29.59, 29.46, 29.18, 27.32, 22.81, 14.46, 14.24; ^{77}Se NMR ($CDCl_3$) δ 393.63; HRMS (EI) calcd for $C_{19}H_{38}O_2Se$ *m*/*e* 378.2037, found 378.2045 (M^+).

***Se*-*n*-Octadecyl-*O*-ethylselenocarbonate (9).** Lithium triethylborohydride (1.0 mL of a 1.0 M solution in THF, 1.0 mmol), dioctadecyl diselenide (0.332 g, 0.50 mmol), THF (15 mL), and ethyl chloroformate (0.12 mL, 1.26 mmol) afforded 0.212 g (52%) of **9** as a colorless liquid: IR (KBr) 2924, 2853, 1718, 1385, 1124, 1014, 835 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.269 (q, J = 7.1 Hz, 2 H), 2.861 (t, J = 7.4 Hz, 2 H), 1.702 (pent, J = 7.4 Hz, 2 H), 1.347 (br m, 2 H), 1.285 (t, J = 7.1 Hz, 3 H), 1.229 (br s, 24 H), 0.855 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 167.65, 63.71, 31.94, 30.59, 29.82, 29.71, 29.68, 29.65, 29.60, 29.51, 29.38, 29.09, 27.22, 22.71, 14.35, 14.13; ^{77}Se NMR ($CDCl_3$) δ 393.69; HRMS (EI) calcd for $C_{21}H_{42}O_2{}^{76}Se$ *m*/*e* 402.2377, found 402.2378 (M^+).

***n*-Dodecylselenoacetate (10).** Lithium triethylborohydride (8.0 mL of a 1.0 M solution in THF, 8.0 mmol), didodecyl diselenide (1.99 g, 4.0 mmol), THF (50 mL), and acetyl chloride (0.64 mL, 9.0 mmol) afforded 1.59 g (68%) of **10** as a colorless liquid: IR (KBr) 2923, 2851, 1715, 1383, 1105, 942, 721 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.874 (t, J = 7.4 Hz, 2 H), 2.372 (t, J_{Se-H} = 4.0 Hz, 3 H), 1.633 (pent, J = 7.4 Hz, 2 H), 1.229 (br s, 18 H), 0.853 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 198.09, 34.85, 31.92, 30.45, 29.95, 29.64, 29.59, 29.50, 29.35, 29.10, 26.03, 22.70, 14.12; ^{77}Se NMR ($CDCl_3$) δ 559.72; HRMS (EI) calcd for $C_{14}H_{28}OSe$ *m*/*e* 292.1305, found 292.1307 (M^+).

***n*-Hexadecylselenoacetate (11).** Lithium triethylborohydride (5.0 mL of a 1.0 M solution in THF, 5.0 mmol), dihexadecyl diselenide (1.52 g, 2.5 mmol), THF (20 mL), and acetyl chloride (0.43 mL, 6.0 mmol) afforded 1.27 g (73%) of **11** as a colorless liquid that solidified upon standing: IR (KBr) 2923, 2851, 1715, 1383, 1105, 942, 722 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.877 (t, J = 7.4 Hz, 2 H), 2.376 (t, J_{Se-H} = 4.0 Hz, 3 H), 1.636 (pent, J = 7.2 Hz, 2 H), 1.231 (br s, 26 H), 0.857 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 198.12, 34.86, 31.94, 30.46, 29.96, 29.71, 29.68, 29.61, 29.51, 29.38, 29.11, 26.04, 22.71, 14.14; ^{77}Se NMR ($CDCl_3$) δ 559.76; HRMS (EI) calcd for $C_{18}H_{36}OSe$ *m*/*e* 348.1931, found 348.1932 (M^+).

***n*-Octadecylselenoacetate (12).** Lithium triethylborohydride (5.0 mL of a 1.0 M solution in THF, 5.0 mmol), dioctadecyl

diselenide (1.66 g, 2.5 mmol), THF (25 mL), and acetyl chloride (0.43 mL, 6.0 mmol) afforded 0.531 g (28%) of **12** as a white, crystalline solid: IR (KBr) 2923, 2853, 1717, 1384, 1105, 942, 722 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.861 (t, J = 7.4 Hz, 2 H), 2.355 (t, J_{Se-H} = 4.0 Hz, 3 H), 1.623 (pent, J = 7.2 Hz, 2 H), 1.221 (br s, 30 H), 0.845 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 197.85, 34.79, 31.95, 30.48, 29.97, 29.73, 29.70, 29.67, 29.62, 29.53, 29.40, 29.13, 25.99, 22.71, 14.13; ^{77}Se NMR ($CDCl_3$) δ 559.47; HRMS (EI) calcd for $C_{20}H_{40}OSe$ *m/e* 376.2244, found 376.2236 (M^+).

General Procedure for the Synthesis of Protected Arylselenols. *tert*-Butyllithium (2 equiv/halide) was added dropwise to a stirred solution of the aryl halide in THF at −78 °C. After the solution was stirred for at least 15 min, gray selenium powder was added in one portion. After being stirred for at least 5 min at −78 °C, the solution was allowed to warm to 0 °C and then, if necessary, to room temperature until all of the selenium was consumed. The solution was cooled to −78 °C, and the protecting group chloride was added dropwise. The reaction mixture was warmed to room temperature. After being stirred for at least 1 h at room temperature, the solution was poured into water and extracted with ether or CH_2Cl_2.

1-(*N*,*N*-Diethylselenocarbamyl)-4-iodobenzene (13). *tert*-Butyllithium (9.6 mL of a 1.65 M solution in pentane, 15.8 mmol), 1,4-diiodobenzene (2.64 g, 8.0 mmol), THF (25 mL), selenium powder (0.633 g, 8.0 mmol), and *N*,*N*-diethylcarbamyl chloride (1.1 mL, 8.7 mmol) afforded 1.37 g (45%) of **13** as a yellow solid after flash column chromatography, first eluting with hexanes and then with ethyl acetate and finally with acetone: IR (KBr) 2972, 2931, 1665, 1403, 1239, 1210, 1110, 997, 839, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.597 (d, J = 8.3 Hz, 2 H), 7.257 (d, J = 8.3 Hz, 2 H), 3.50−3.15 (m, 4 H), 1.35−1.00 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 162.32, 138.40, 138.07, 126.61, 95.42, 43.30, 42.57, 14.21, 13.19; ^{77}Se NMR ($CDCl_3$) δ 519.90; HRMS (EI) calcd for $C_{11}H_{14}INO^{76}Se$ *m/e* 378.9312, found 378.9301 (M^+).

1-(*O*-Ethylselenocarbanoyl)-4-iodobenzene (14). *tert*-Butyllithium (12.5 mL of a 1.28 M solution in pentane, 16.0 mmol), 1,4-diiodobenzene (2.64 g, 8.0 mmol), THF (25 mL), selenium powder (0.633 g, 8.0 mmol), and ethyl chloroformate (0.91 mL, 9.5 mmol) afforded 0.916 g (32%) of **14** as a yellow oil following purification by flash column chromatography, eluting with 1:1 hexane/CH_2Cl_2: IR (KBr) 2980, 1727, 1472, 1123, 1001, 805 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.667 (d, J = 8.4 Hz, 2 H), 7.319 (d, J = 8.4 Hz, 2 H), 4.310 (q, J = 7.1 Hz, 2 H), 1.308 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.09, 138.40, 137.33, 125.84, 95.67, 64.76, 14.37; ^{77}Se NMR ($CDCl_3$) δ 509.54; HRMS (EI) calcd for $C_9H_9IO_2{}^{76}Se$ *m/e*351.8839, found 351.8847 (M^+).

1-(Selenoacetyl)-4-iodobenzene (15). *tert*-Butyllithium (8.4 mL of a 1.92 M solution in pentane, 16.1 mmol), 1,4-diiodobenzene (2.64 g, 8.0 mmol), THF (25 mL), selenium powder (0.633 g, 8.0 mmol), and acetyl chloride (0.68 mL, 9.6 mmol) afforded 1.28 g (50%) of **15** following purification by flash column chromatography, eluting first with hexane and then with CH_2Cl_2: IR (KBr) 1709, 1468, 1384, 1376, 1105, 1003, 947, 805 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.676 (d, J = 8.1 Hz, 2 H), 7.201 (d, J = 8.4 Hz, 2 H), 2.450 (t, J_{Se-H} = 4.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 195.71, 138.51, 137.36, 126.31, 95.63, 34.19; ^{77}Se NMR ($CDCl_3$) δ 667.00; HRMS (EI) calcd for $C_8H_7IO^{76}Se$ *m/e* 321.8734, found 321.8723 (M^+).

1,4-[Bis(*N*,*N*-diethylselenocarbamyl)]benzene (16). *tert*-Butyllithium (19.4 mL of a 1.65 M solution in pentane, 32.0 mmol), 1,4-diiodobenzene (2.64 g, 8.0 mmol), THF (30 mL), selenium powder (1.27 g, 16.1 mmol), and *N*,*N*-diethylcarbamyl chloride (2.25 mL, 17.8 mmol) afforded 2.50 g (72%) of **16** as a golden yellow solid: IR (KBr) 2972, 2930, 1669, 1402, 1241, 1210, 1112, 1008, 837, 806 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.550 (s, 4 H), 3.50−3.25 (m, 8 H), 1.35−1.05 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 162.62, 136.98, 127.81, 43.29, 42.50, 14.22, 13.21; ^{77}Se NMR ($CDCl_3$) δ 519.82; HRMS (EI) calcd for $C_{16}H_{24}N_2O_2{}^{76}Se_2$ *m/e* 436.0168, found 436.0152 (M^+).

1,4-[Bis(*O*-ethylselenocarbanoyl)]benzene (17). *tert*-Butyllithium (20.0 mL of a 1.61 M solution in pentane, 32.2 mmol), 1,4-diiodobenzene (2.64 g, 8.0 mmol), THF (30 mL), selenium powder (1.27 g, 16.1 mmol), and ethyl chloroformate (1.80 mL, 19.0 mmol) afforded 1.37 g (45%) of **17** as white needles following recrystallization from CH_2Cl_2/hexane at −10 °C: IR (KBr) 2995, 1718, 1132, 1009, 846, 831, 632 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.584 (s, 4 H), 4.313 (q, J = 7.1 Hz, 4 H), 1.309 (t, J = 7.1 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 166.14, 136.09, 127.48, 64.68, 14.36; ^{77}Se NMR ($CDCl_3$) δ 510.43; HRMS (EI) calcd for $C_{12}H_{14}O_4{}^{76}Se_2$ *m/e* 375.9290, found 375.9281 (M^+).

4,4′-Biphenyl-1-selenoacetate (18). *tert*-Butyllithium (5.4 mL of a 1.92 M solution in pentane, 10.4 mmol), 4-bromobiphenyl (1.21 g, 5.2 mmol), THF (30 mL), selenium powder (0.411 g, 5.2 mmol), and acetyl chloride (0.44 mL, 6.2 mmol) afforded 0.280 g (20%) of **18** following purification by flash column chromatography, eluting with 1:1 hexane/CH_2Cl_2: IR (KBr) 1715, 1385, 1097, 945, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.573 (m, 6 H), 7.438 (m, 2 H), 7.364 (d, J = 7.2 Hz, 1 H), 2.483 (t, J_{Se-H} = 3.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 196.90, 141.95, 140.32, 136.09, 128.88, 128.14, 127.73, 127.21, 125.53, 34.13; ^{77}Se NMR ($CDCl_3$) δ 664.12; HRMS (EI) calcd for $C_{14}H_{12}O^{76}Se$ *m/e* 272.0080, found 272.0072 (M^+).

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Supporting Information Available: ^1H NMR spectra for compounds **4**−**12**, **14**, **15**, and **17** and ^{13}C NMR spectra for compounds **13**, **16**, and **18** (15 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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