dried over sodium sulfate and evaporated. Recrystallization of the residue from hexane–benzene gave indole 14 (0.25 g).

3-Acetyl-2-[(phenylsulfonyl)methyl]indole (20). A solution of 14 (0.16 g) in acetic anhydride (8 mL) was treated with anhydrous aluminum chloride and stirred at 100 °C for 72 h. The mixture was poured into ice and extracted with chloroform. The organic layer was washed with aqueous sodium hydrogen carbonate and dried over sodium sulfate. The solvent was removed, and the residue was taken up with diisopropyl ether to afford **20** (0.12 g): mp 175–177 °C (from hexane–benzene); IR (Nujol) 3320, 1665 cm^{-1}; NMR (CD_3SOCD_3) δ 2.40 (s, 3 H), 5.27 (s, 2 H), 7.1–8.0 (m, 9 H), 12.2 (br s, 1 H); MS, *m/e* 313 (M^+). Anal. Calcd for $C_{17}H_{15}NO_3S$: C, 65.16; H, 4.81; N, 4.47. Found: C, 65.23; H, 4.97; N, 4.59.

1-Methyl-2-[(phenylsulfonyl)methyl]indole (19). To a solution of 14 (0.15 g) in dry acetone (20 mL) were added potassium carbonate (4.0 g) a methyl iodide (4 mL). The mixture was stirred at room temperature for 5 days. The undissolved material was filtered off, the solvent was evaporated under reduced pressure, and the residue was recrystallized from hexane–benzene to give **19** (85 mg): mp 177 °C; NMR (CD_3COCD_3) δ 3.80 (s, 3 H), 4.89 (s, 2 H), 6.22 (s, 1 H), 6.8–7.9 (m, 9 H); MS, *m/e* 285 (M^+). Anal. Calcd for $C_{16}H_{15}NO_2S$: C, 67.35; H, 5.29; N, 4.91. Found: C, 67.13; H, 5.31; N, 5.01.

Conversion of 14 into 15. To a solution of **14** (0.30 g) in benzene (30 mL) were added 50% sodium hydroxide (15 mL), tetrabutylammonium hydrogen sulfate (0.15 g), and benzaldehyde (0.30 g). The mixture was stirred at room temperature for 2 h. The organic layer was separated, washed with water, dried over sodium sulfate, and evaporated. The residue was chromatographed on a silica gel column with light petroleum–dichloromethane–diethyl ether (3:2:1) as the eluent to afford **15** (0.12 g).

Acknowledgment. We are indebted to M.P.I. (Rome) for financial support.

Registry No. **1a**, 2525-41-9; **1b**, 5324-64-1; **2**, 1137-96-8; **3**, 107081-84-5; **4b**, 107081-87-8; **5b**, 107081-88-9; **6a**, 17375-64-3; **6b**, 26862-65-7; **7b**, 26821-93-2; **8**, 107081-86-7; **9**, 107081-85-6; **10**, 2525-42-0; **11**, 107081-90-3; **12**, 107081-89-0; **13**, 107081-93-6; **14**, 107081-91-4; **15**, 107081-92-5; **16**, 107081-94-7; **17**, 107081-95-8; **18**, 107081-96-9; **19**, 107081-98-1; **20**, 107081-97-0; PhNHOH, 100-65-2; $PhSO_2CH_2COMe$, 5000-44-2; PhCHO, 100-52-7; 2-$O_2NC_6H_4CH_2COCH_2Br$, 57662-22-3; $PhSO_2Na$, 873-55-2.

Synthesis of 2-, 3- and 4-(Phenylseleno)benzonitrile by Electrochemically Induced Aromatic Nucleophilic Substitution in Acetonitrile

Chantal Degrand

Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (UA 33), Faculté des Sciences Gabriel, 21000 Dijon, France

Received September 9, 1986

2-, 3- and 4-bromobenzonitrile have been electrolyzed in acetonitrile with sonication in the presence of an equivalent amount of benzeneselenate initially prepared by electrochemical reduction of diphenyl diselenide. Thus 2-, 3-, and 4-(phenylseleno)benzonitrile have been isolated in 36%, 42%, and 59% yields, respectively. The electrochemically generated aryl radical $NCC_6H_4\cdot$ which is involved in the $S_{RN}1$ mechanism is deactivated partially by its further reduction to the corresponding anion and so the yields remain moderate. These yields can be improved by electrolysis of chlorobenzonitrile. A yield of 70% has been thus achieved in the case of 4-(phenylseleno)benzonitrile. The two-electron cathodic reduction of the seleno derivatives is accompanied by the formation of cyanobenzeneselenate. Electrochemical reduction of 4-(phenylseleno)benzonitrile followed by chemical oxidation by air has given a mixture of 4,4′-dicyanodiphenyl diselenide and diphenyl diselenide, which have been isolated in 76% and 24% relative yields, respectively.

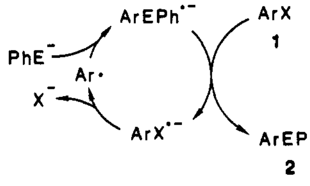
Benzenechalcogenates PhE^- (E = S, Se, Te) react with aromatic halides ArX under light stimulation by the $S_{RN}1$ aromatic nucleophilic substitution[1] (Scheme I) to give a large variety of unsymmetrical diaryl chalcogenides PhEAr.[1-6]

Liquid ammonia, which is a poor H atom donor, has mainly been used as solvent (SH) since the competitive reaction (1) is prevented.[1,3,7] However, satisfactory results can be also obtained in solvents such as dimethyl sulfoxide (Me_2SO).[3]

$$Ar^{\bullet} + SH \rightarrow ArH + S^{\bullet} \qquad (1)$$

Saveant et al. have shown that electrons supplied from a cathode can initiate $S_{RN}1$ reactions with benzenethiolate

Scheme I[a]



[a] E = S, Se, Te.

---

(1) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.

(2) (a) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3173. (b) Galli, C.; Bunnett, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 7140.

(3) Bunnett, J. F.; Scamehorn, R. G.; Traber, R. P. *J. Org. Chem.* **1976**, *41*, 3677.

(4) (a) Pierini, A. B.; Rossi, R. A. *J. Organomet. Chem.* **1978**, *144*, C12; (b) **1979**, *168*, 163. (c) Pierini, A. B.; Penenory, A. B.; Rossi, R. A. *J. Org. Chem.* **1984**, *49*, 486. (d) Penenory, A. B.; Pierini, A. B.; Rossi, R. A. *J. Org. Chem.* **1984**, *49*, 3834.

(5) (a) Pierini, A. B.; Rossi, R. A. *J. Org. Chem.* **1979**, *44*, 4667. (b) Rossi, R. A.; Palacios, S. M. *J. Org. Chem.* **1981**, *46*, 5300. (c) Rossi, R. A. *Acc. Chem. Res.* **1982**, *15*, 164.

(6) Palacios, S. M.; Alonso, R. A.; Rossi, R. A. *Tetrahedron* **1985**, *41*, 4147.

(7) (a) M'Halla, F.; Pinson, J.; Savéant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 4120. (b) Savéant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323. (c) Andrieux, C. P.; Savéant, J. M.; Zann, D. *Nouv. J. Chim.* **1984**, *8*, 107.

0022-3263/87/1952-1421$01.50/0

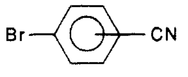
Table I. Large-Scale Electrochemical Reduction of 1 (2 mmol) in the Presence of an Equivalent Amount of Electrogenerated Benzeneselenate

electrolysis no.	compd	$-E$ (V)	charge consumed/ mmol electrons	n^a	product (yield, %)
1	**1a**	1.55–1.58	0.52	0.26	**2b** (58)
2	**1b**	1.45–1.82	1.00	0.50	**2d** (42)
3	**1c**	1.40–1.55	1.56	0.78	**2e** (36)

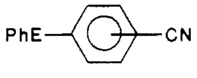
[a] Electron-equivalent consumed.

(Scheme I, where E = S).[7b,8,9] For instance, the electrochemical synthesis of 4-(phenylthio)benzonitrile (**2a**) in 80% yield (determination by GLC) has been carried out in acetonitrile from 4-bromobenzonitrile (**1a**) partially electrolyzed (0.2 electron equiv consumed) in the presence of a large excess of chemically prepared benzenethiolate.[8b] Very recently,[10] we have prepared 4-(phenylseleno)- (**2b**) and 4-(phenyltelluro)benzonitrile (**2c**) in 57% and 42% yields, respectively, by partial reduction of **1a** (0.2 electron equiv consumed), in the presence of an equivalent amount of benzeneselenate and benzenetellurate electrogenerated from diphenyl diselenide (**3a**) or ditelluride. The electrolyses have been carried out in acetonitrile with sonication in a H-type cell, the three compartments being separated by glass fritts.

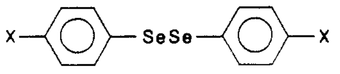
We now describe the electrochemical synthesis of the three seleno isomers **2b**, **2d**, and **2e** using slightly modified conditions. The electrolysis is not interrupted after partial reduction of bromobenzonitrile, but after its total depletion, in a cell equipped with ion-exchange membranes instead of glass fritts and so the anodic migration of benzeneselenate is avoided during electrolysis. The cathodic behavior of **2b**, **2d**, and **2e** has been examined and it is shown that the two-electron reductive cleavage of the C–Se bond occurs preferentially on the side of the unsubstituted phenyl group.



1a: *p*-CN
b: *m*-CN
c: *o*-CN



2a: E = S, *p*-CN
b: E = Se, *p*-CN
c: E = Te, *p*-CN
d: E = Se, *m*-CN
e: E = Se, *o*-CN



3a: X = H
b: X = CN

Results and Discussion

The electrochemical synthesis of **2b**, **2d**, and **2e** was carried out in a two-step process. In a first step, diphenyl diselenide (**3a**) (1 mmol) was reduced to benzeneselenate in acetonitrile with sonication, in a H-type cell of small capacity (the volume of the catholyte was 25 mL), equipped with ion-exchange membranes. Under such conditions, stirring was facilitated and anodic migration of $PhSe^-$ was avoided. In the second step, bromobenzonitrile (2 mmol) was added and the applied potential was moved toward negative values where **1** could be reduced (Table I). As already pointed out, sonication facilitates the electrochemical process.[11-13] In the case of **1a–c**, ultrasonically induced reduction starts at potentials 0.29–0.35 V positive to the corresponding half-wave potentials (compare the values of E in Table I to those of $E_{1/2}$ in Table II). The electrolysis was stopped after total depletion of **1a–c**.

Table II. Half-Wave Potential, $E_{1/2}$, and Limiting Current, i_L, of the Reduction Waves of 1 (2 mmol) and 2 (2 mmol) at a Glassy Carbon Rotating Disk Electrode in Acetonitrile

	first wave		second wave	
compd	I, $-E_{1/2}$ (V)	I, i_L (mA)	II, $-E_{1/2}$ (V)	I + II, i_L (mA)
1a	1.84[a]	0.47	2.38[b]	0.72
1b	1.80[a]	0.48	2.36[b]	0.68
1c	1.74[a]	0.51	2.36[b]	0.65
2b	2.00	0.29	2.46[c]	0.35
2d	2.10	0.28		
2e	2.03	0.30		

[a] Two-electron irreversible wave.[8b] [b] One-electron reversible reduction wave of benzonitrile.[8b] [c] Ill-defined wave.

The results presented in Table I show that the highest yield of isolated compound (58%) was obtained in the case of **2b**, from **1a** whose reduction consumed only 0.26 electron equiv. This yield is very close to the yield obtained when **1a** was partially reduced (57%, 0.20 electron equiv).[10] Furthermore, the lower the consumption of electricity, the higher the yield of isolated (phenylseleno)benzonitrile. As already pointed out by Pinson and Savéant,[8b] there is a definite relationship between the yield in substituted product **2** and the amount of electron equivalent consumed, when the $S_{RN}1$ mechanism (Scheme I) is involved: good yield is accompanied by a low consumption of electricity.

The electrochemical synthesis of **2b**, **2d**, and **2e** according to Scheme I is consistent with the cathodic behavior of these seleno ethers (Table II). They are reduced with half-wave potentials negative to those of the first wave of the corresponding bromobenzonitrile (Table II) and so, electron exchange between $ArEPh^{\bullet-}$ and **1** can take place. However, the reasonable to moderate yields of **2b,d,e** in Table I show the occurrence of competing reactions that deactivate the aryl radical $NCC_6H_4^\bullet$ and inhibit reaction 2.

$$NCC_6H_4^\bullet + PhSe^- \rightleftharpoons NCC_6H_4SePh^{\bullet-} \qquad (2)$$

Reactions 1 (where SH = CH_3CN), 3, and 4 are three possible modes for the deactivation of the aryl radical, which have been discussed in detail by Savéant et al. for the sulfur homologues.[7b,8,9] The hypothesis of a dimerization of the aryl radicals[14] can be ruled out since no dicyanobiphenyl was isolated. The three reactions correspond to a two-electron reduction of bromobenzonitrile to

$$NCC_6H_4^\bullet \overset{+e}{\rightleftharpoons} NCC_6H_4^- \qquad (3)$$

$$NCC_6H_4^\bullet \xrightarrow{+NCC_6H_4SePh^{\bullet-}} NCC_6H_4^- + NCC_6H_4SePh \qquad (4)$$

$$NCC_6H_4^- + SH \rightarrow PhCN + S^- \qquad (5)$$

---

(8) (a) Pinson, J.; Savéant, J. M. *J. Chem. Soc., Chem. Commun.* **1974**, 933; (b) *J. Am. Chem. Soc.* **1978**, *100*, 1506.

(9) (a) Amatore, C.; Chaussard, J.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1979**, *101*, 6012. (b) Amatore, C.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Electroanal. Chem.* **1980**, *107*, 75; (c) **1981**, *123*, 231. (d) Amatore, C.; Oturan, M. A.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1984**, *106*, 6318; (e) **1985**, *107*, 3451. (f) Amatore, C.; Combellas, C.; Pinson, J.; Oturan, M. A.; Robveille, S.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1985**, *107*, 4846.

(10) Degrand, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1113.

(11) (a) Gautheron, B.; Tainturier, G.; Degrand, C. *J. Am. Chem. Soc.* **1985**, *107*, 5579. (b) Degrand, C.; Nour, M. *J. Electroanal. Chem.* **1986**, *199*, 211. (c) Tainturier, G.; Gautheron, B.; Degrand, C. *Organometallics* **1986**, *5*, 942.

(12) Bard, A. J. *J. Anal. Chem.* **1963**, *35*, 1125.

(13) Connors, T. F.; Rusling, J. F. *Chemosphere* **1984**, *13*, 415.

(14) Rieger, P. H.; Bernal, I.; Reinmuth, W. H.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1963**, *85*, 683.

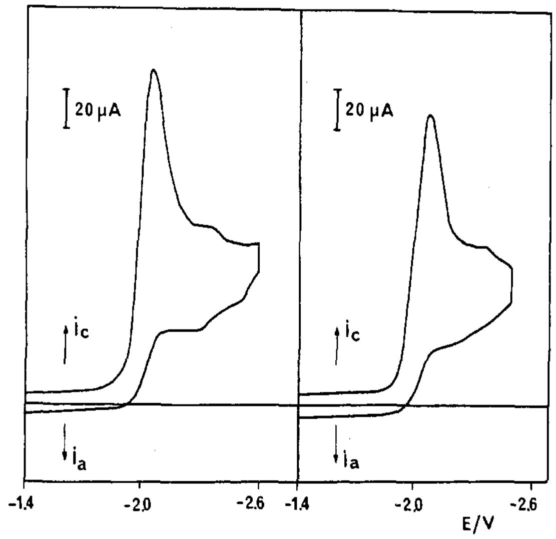


Figure 1. Cyclic voltammograms at a rotating disk electrode of 2 mM **2b** (left curve) and 2 mM **2e** (right curve). The scan rate is 0.1 V s^{-1}.

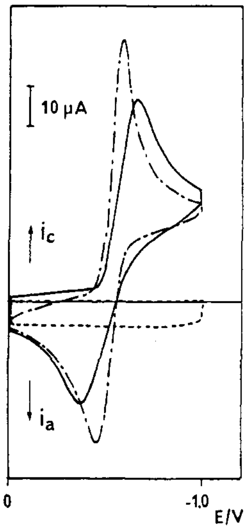


Figure 2. Cyclic voltammograms at a rotating disk electrode of 1 mM **3b**: (–) first scan; (-·) second and successive scans; 0.1 V s^{-1}.

benzonitrile, even in reaction (1) since the radical $\cdot CH_2CN$ generated in acetonitrile has been shown to be further reduced to the corresponding anion.[7,9e] A few complementary experiments which are described below show that the further reduction of the aryl radical according to the heterogeneous electron transfer (3) is the main competing reaction.

In usual organic solvents such as Me_2SO and MeCN, H-atom transfer from the solvent (1) may compete.[9,15] Since reactions 1 and 2 are second order in concentration, reaction 2 occurs more readily when benzeneselenate is present in excess or in high concentration. Under the experimental conditions of Table I, the initial concentration of $PhSe^-$ is not in excess but rather high (0.08 M) since the volume of the catholyte is very small (25 mL). We have repeated the electrolysis of **1a** in the presence of an equivalent of benzeneselenate, using an initial concentration of **1a** two times higher than in Table I. Under such conditions, 0.23 electron equiv has been consumed and the yield of **2b** (59%) was practically not improved. We can therefore conclude that reaction 1 does not interfere. Let us consider now the very fast[9e] heterogeneous and homogeneous electron transfers (3) and (4) which lead to the benzonitrile anions. The electron transfer occurs at the cathode according to (3) if the cleavage reaction following the first electron uptake by **1a–c** is rapid; otherwise, it occurs in the bulk of the catholyte according to (4).[9] Aryl bromides have been shown to cleave faster than the corresponding aryl chlorides.[8b,9e] For instance, in liquid ammonia, the rates are 2×10^9 and 9.3×10^8 s^{-1} for 4-bromo- and 4-chlorobenzonitrile, respectively.[9e] Therefore, reaction 3, whether it interferes, would hinder the coupling reaction 2 at a less extent if chlorobenzonitrile was used instead of bromobenzonitrile. Although the half-wave potential of 4-chlorobenzonitrile ($E_{1/2}$) is –1.96 V, it is only 40-mV positive to that of **2b** (cf. Table II) and consequently the electron exchange between $NCC_6H_4SePh^{\cdot -}$ and NCC_6H_4Cl is not very rapid, the large-scale electrolysis of 4-chlorobenzonitrile (4 mmol) in the presence of an equivalent of benzeneselenate provides **2b** in definitely higher yield (70%) than in the case of **1a**. A small amount of 4,4′-dicyanodiphenyl selenide (8%) is also isolated. It demonstrates that, in the case of bromobenzonitrile, the radical $NCC_6H_4^{\cdot}$ is further reduced to the corresponding anion at the surface of the electrode (reaction 3). This impedes the formation of **2b** and leads to benzonitrile (reaction 5), which remains in the aqueous phase during treatment of the cathodic solution.

A fourth mode of deactivation that has not been considered in the case of the sulfur homologues is, in the case of **2b**, **2d**, and **2e**, the decomposition reaction 6.

$$NCC_6H_4SePh^{\cdot -} \rightarrow NCC_6H_4Se^- + Ph^{\cdot} \qquad (6)$$

Whereas the radical anions of the corresponding thio ethers are stable,[8a] the radical anions of **2b**, **2d**, and **2e** are very unstable, as observed in cyclic voltammetry (Figure 1). The overall reduction process of **2b**, **2d**, and **2e** is totally irreversible since no anodic peak is observed on the reverse anodic sweep in cyclic voltammetry at a stationary electrode. In voltammetry at a rotating electrode, the reduction of **2b**, **2d**, and **2e** takes place in a single step, except in the case of **2b** where the main wave is followed by an ill-defined wave of small amplitude (Table II). A large-scale electrolysis of **2b** at potentials of the main wave consumed 2 electron equiv. After oxidation of the cathodic solution by air, 4,4′-dicyanodiphenyl diselenide (**3b**) was isolated as the main compound together with diphenyl diselenide as the minor compound (76% and 24% in relative yields). Se powder was observed to deposite, suggesting that electrochemically generated intermediates, such as $NCC_6H_4Se^-$, are not very stable in solution during electrolysis. It would explain the low yield of **3b** (27%). On repetitive cycling, the cyclic voltammograms of **3b** (Figure 2) tend to a pseudoreversible system corresponding to **3b**/4-$NCC_6H_4Se^-$. The coulometric results show that the fate of the phenyl radical generated in (6) is similar to that of benzonitrile radical (cf. reactions 1, 3, and/or 4). The formation of 4,4′-dicyanodiphenyl selenide in low yield during the electrochemical synthesis of **2b** is related to a fragmentation (6). Similarly the electrochemical synthesis of **2d** and **2e** was accompanied by the formation of minor compounds that have not yet been identified (see the Experimental Section) and that might arise in some cases from cleavages (6). Such bond fragmentations have been observed also by Bunnett[16] and Rossi.[5]

Sonication was introduced to facilitate stirring in the tiny cell during electrolysis. Its influence upon the different competing reactions and therefore on the yields of

---

[15] Swartz, J. E.; Stenzel, T. T. *J. Am. Chem. Soc.* **1984**, *106*, 2520.

[16] Bunnett, J. F.; Creary, Y. *J. Org. Chem.* **1975**, *40*, 3740.

2b, **2d**, and **2e** is difficult to predict. Increasing the stirring of the cathodic compartment may hinder the cathodic reaction (3) for the benefit of the bulk reaction (4). From a test to compare magnetic stirring and sonication, it has been concluded that sonication improves slightly the yields of substituted compounds in $S_{RN}1$ aromatic nucleophilic substitution.[17]

Experimental Section

Compounds **1a**–**c** and diphenyl diselenide are commercially available. Analytical grade acetonitrile (spectrosol SDS) was carefully dried on neutral alumina.

Elemental analyses were performed by Service Central d'Analyse, CNRS; Lyon. Spectra were recorded by means of the following instruments: infrared, Perkin-Elmer 580 B, ^1H NMR, JEOL FX 100.

Cyclic voltammograms at a stationary or rotating glassy carbon disk electrode (V 25 Carbone Lorraine; diameter = 3 mm) were obtained with a Tacussel UAP 4 unit and a GSTP function generator and were recorded on an Ifelec 2025 C x–y recorder. An Amel 552 potentiostat (output voltage ± 200 V at full load) and a Tacussel IG 5-N integrator were used in coulometry and preparative electrolysis. All the potentials referred to the aqueous saturated calomel electrode (SCE).

Large-scale electrolyses with sonication (Vat Bransonic B 32) were performed in a H-type cell, the three compartments of which were separated by ion-exchange membranes Ionac MA 3475 (anodic side) and MC 3470 (cathodic side) and filled with acetonitrile containing 0.1 M Bu_4NPF_6. The cathode was a graphite cloth of cylindric shape and the anode a Pt grid. The catholyte (25 mL) was deaerated with argon before and during electrolysis, and cooling of the cell by an ice bath was maintained during sonication.

Electrochemical Synthesis of 2b, 2d, and 2e (Table I). Diphenyl diselenide (1 mmol) was introduced and reduced to benzeneselenate. The potential had to be changed from −0.70 V to −1.20 V whereas the faradaic current dropped from 100 mA (initial value) to a negligible value after consumption of 193 C (2 mmol electrons). Bromobenzonitrile (2 mmol) was then added and the applied potential was moved to more negative values (see Table I) where the electrophile 1 could be reduced. This second electrolysis was stopped when the faradaic current became negligible. After electrolysis, sonication and an argon atmosphere were maintained for 10 min; then oxygen was introduced before treatment of the cathodic solution. This solution was diluted with water and the electrolysis products were extracted with diethyl ether. After the solution was dried, the ether was removed.

Electrochemical Synthesis of 2b (Electrolysis No. 1 of Table I). The crude product (418 mg) was separated by column chromatography with 1/9 acetone/hexane as eluent. The compounds were isolated in the order **3a** (traces), **2b** (300 mg, 58%), and 4,4′-dicyanodiphenyl selenide (19 mg, 7%).

4-(Phenylseleno)benzonitrile (2b): beige crystals; mp 52 °C (hexane) (lit.[18] mp 49 °C).

4,4′-Dicyanodiphenyl selenide: beige crystals; mp 143 °C (diethyl ether–hexane); IR (KBr) 2226 (C≡N stretching), 832, 825 (para substitution bands) cm^{-1}; ^1H NMR ($CDCl_3$) 7.55 (s, 8 H). Anal. Calcd for $C_{14}H_8N_2Se$: C, 59.38; H, 2.85; N, 8.89; Se, 27.88. Found: C, 59.42; H, 2.90; N, 9.43; Se, 27.85.

Electrochemical Synthesis of 2d (Electrolysis No. 2 of Table I). The crude product (323 mg) was separated by column chromatography with 2/8 acetone/hexane as eluent. The compounds were isolated in the order **2d** (215 mg, 42%) and three unidentified minor compounds (64 mg).

3-(Phenylseleno)benzonitrile (2d): oil; IR (neat) 2230 (C≡N stretching), 790 (meta substitution band), 740, 689, 681 (monosubstitution bands) cm^{-1}; ^1H NMR ($CDCl_3$) 7.26–7.61 (m, 9 H). Anal. Calcd for $C_{13}H_9NSe$: C, 60.48; H, 3.51; N, 5.42. Found: C, 60.64; H, 3.60; N, 5.49.

Electrochemical Synthesis of 2e (Electrolysis No. 3 of Table I). The crude product (345 mg) was separated by column chromatography with 2/8 acetone/hexane as eluent. The compounds were isolated in the order **3a** (18 mg, 6%), **2b** (185 mg, 36%), and five unidentified minor compounds (126 mg).

2-(Phenylseleno)benzonitrile (2e): beige powder; mp 69–70 °C (diethyl ether–hexane); IR (KBr) 2220 (C≡N stretching), 768 (ortho substitution band), 735, 685 (monosubstitution bands) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.17–7.39 (m, 3 H), 7.55–7.67 (m, 6 H). Anal. Calcd for $C_{13}H_9NSe$: C, 60.48; H, 3.51; N, 5.42; Se, 30.58. Found: C, 60.48; H, 3.41; N, 5.40; Se, 30.78.

Electrochemical Reduction of 4-Chlorobenzonitrile in the Presence of Benzeneselenate. Benzeneselenate (4 mmol) was electrochemically generated as above prior to the reduction of the substrate (0.550 g, 4 mmol) at −1.62 ± 0.03 V. The electrolysis was carried out as above. The crude product (880 mg) was separated by column chromatography with 2/8 acetone/hexane as eluent. The compounds were isolated in the order **3a** (21 mg, 3%), **2b** (723 mg, 70%), and 4,4′-dicyanodiphenyl selenide (45 mg, 8%).

Electrochemical Reduction of 4-(Phenylseleno)benzonitrile (2b). Substrate (0.258 g, 1 mmol) was reduced at 2.0 ± 0.2 V with sonication. The electrolysis was stopped after total depletion of the substrate and consumption of 193 C (2 mmol of electrons). After electrolysis, air was introduced and sonication was maintained for 10 min. Se powder was observed to deposit. The crude product (102 mg) was separated by column chromatography with 2/8 acetone/hexane as eluent. The compounds were isolated in the order **3a** (12 mg, 8.5%), **3b** (44 mg, 27%), and unidentified minor compound (12 mg). The relative yields of **3a** and **3b** are 24% and 76%, respectively.

4,4′-Dicyanodiphenyl diselenide (3b): yellow powder; mp 158 °C (diethyl ether–hexane) (lit.[19] mp 85 °C (ethanol)); IR (KBr) 2240 (C≡N stretching), 1590, 1480, 1020, 830, 822 (two para substitution bands). Anal. Calcd for $C_{14}H_8N_2Se_2$: C, 46.43; H, 2.23; N, 7.73; Se, 43.61. Found: C, 46.47; H, 2.17; N, 7.58; Se, 43.40.

Acknowledgment. The author is grateful to Mrs. Raveau-Fouquet for technical assistance and also appreciates the help of Mrs. Meunier and her students (Classe de Première S8, Lycée Montchapet; Contrat CNRS "1000 classes, 1000 chercheurs"). The financial support of the Centre National de la Recherche Scientifique and of the Agence Française pour la Maîtrise de l'Energie (PIRSEM Grant 06931) is greatly appreciated.

Registry No. **1a**, 623-00-7; **1b**, 6952-59-6; **1c**, 2042-37-7; **2b**, 94800-52-9; **2d**, 107037-19-4; **2e**, 107037-20-7; **3b**, 84019-98-7; $PhSe^-$, 65147-77-5; 4-chlorobenzonitrile, 623-03-0.

---

(17) Degrand, C., unpublished result.

(18) Cristau, H. J.; Chabaud, B.; Labaudinière, R.; Cristol, H. *Organometallics* **1985**, *4*, 657.

(19) Jeroschewski, P.; Ruth, W.; Struebing, B.; Berge, H. *J. Prakt. Chem.* **1982**, *324*, 787.