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Cathodic Synthesis of Dicyanodiphenyl Diselenide From Phenylselenobenzonitrile

Chantal Degrand*, Christine Gautier and Mohamed Kharroubi

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

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Abstract The cathodic reduction of 2-, 3- and 4-(phenylseleno)benzonitrile has been carried out in N,N-dimethylformamide and acetonitrile, at mercury, Pt, and glassy carbon electrodes. The first reduction step is accompanied by C-Se bond breaking. In the presence of an acid (fluorene, phenol, Bu_4NSO_4H), cyanobenzeneselenolate anions are thus generated in high yields, together with a small amount of benzeneselenolate anions (about 85 % and 15 % yields, respectively). The former anions can be oxidised either anodically or chemically by air in alkaline aqueous solutions, and so 2,2'-, 3,3'- and 4,4'-dicyanodiphenyl diselenide are isolated in 59 %, 70 % and 75 % yields, respectively.

Aryl selenolate anions $ArSe^-$ which are important precursors of aromatic seleno derivatives are usually prepared by reaction of elemental selenium with Grignard reagents or aryl lithium (eq 1).[1]

$$ArM + Se \longrightarrow ArSeM \xrightarrow{H_2O,\,HO^-} ArSe^- \qquad (1)$$

(M = MgX, Li)

$$ArN_2^+X^- + KSeCN \text{ or } Se^{2-}_x \longrightarrow \longrightarrow ArSe^- \qquad (2)$$

When these methods fail, $ArSe^-$ anions can be synthesized from aromatic diazonium salts (eq 2). A few examples are given in refs 1-3. An alternative clean route to the synthesis of $ArSe^-$ is the electrochemical strategy proposed below (eq 3-5). These anions can be stored in their oxidised form ArSeSeAr (eq 6). The overall process (eq 7) corresponds to a reductive transfer of Se units from a readily available aliphatic or aromatic diselenide RSeSeR to ArSeSeAr which cannot be prepared from magnesium or lithium derivatives.

$$1/2\ RSeSeR + e \longrightarrow RSe^- \qquad (3)$$

$$ArX + RSe^- \xrightarrow{S_NAr \text{ or } S_{RN}1 \text{ (cathode)}} ArSeR + X^- \qquad (4)$$

$$ArSeR + 2e \longrightarrow ArSe^- + R^- \qquad (5)$$

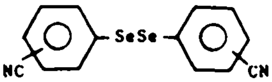
$$ArSe^- \underset{+\,e}{\overset{-\,e}{\rightleftharpoons}} 1/2\ ArSeSeAr \qquad (6)$$

$$1/2\ RSeSeR + ArX + 2e \longrightarrow 1/2\ ArSeSeAr + R^- + X^- \qquad (7)$$

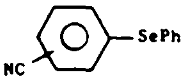
To illustrate the feasibility of the electrochemical method, we have carried out the synthesis of the diselenides 1a-c according to the overall reaction 8.

$$1/2\ PhSeSePh + NCC_6H_4Cl + 2e + H^+ \longrightarrow 1/2\ \underset{\underline{1a\text{-}c}}{NCC_6H_4SeSeC_6H_4CN} + C_6H_6 + Cl^- \qquad (8)$$

Although a "one-pot" electrochemical synthesis of 1a-c can be envisaged, we have performed two successive electrolyses. First the selenides 2a-c have been prepared in MeCN by $S_{RN}1$ substitution, using a redox mediator, and isolated in 61 %, 68 % and 70 % yields, respectively. This part of the work is described in ref. 4. The results presented below are concerned with the cathodic behavior of 2a-c and their large-scale electrolyses. We have found that, under appropriate conditions, the diselenides 1a-c could be isolated in 59 %, 70 % and 75 % yields, respectively. Prior to our work, this compound was claimed to be isolated in 15 % yield by cathodic polarisation of a Se electrode, in DMF, in the presence of p-chlorobenzonitrile.[5] However, the melting point was surprisingly low (85°C instead of 158°C), and so the nature of the isolated compound seems dubious.



1 { a : o,o' ; b : m,m' ; c : p,p' }



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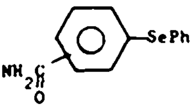


3 { a : o ; b : m }

Results and Discussion

Cathodic behavior of 2a-c. Compounds 2a-c were first examined in N,N-dimethylformamide (DMF) at Hg electrode, because polarographic waves with half-wave potentials $E_{1/2}$ as negative as - 2.7 V vs a saturated calomel electrode (SCE) were still well defined under such conditions. Three waves A, B and C were observed. The diffusion current of wave B was small compared to wave A whereas the most negative wave C was well-defined only in the case of 2b (Fig. 1). In acetonitrile, this wave was hidden by the electrolyte discharge. Waves B and C corresponded to reversible redox systems, as shown by cyclic voltammetry at a hanging mercury drop electrode (HMDE) (Fig. 2). Due to the small amplitude of wave B, the corresponding reversible peak system B/B' appeared as shoulders. When phenol was added in excess, a twofold increase of the diffusion current of waves B and C was observed (Fig. 1) together with a loss of reversibility. Furthermore, the characteristics of wave B were identical to those of the single wave of benzonitrile. Polarograms of diphenyl selenide were also recorded and used as references to determine the apparent number of electrons n_A, n_B and n_C involved in each reduction step, assuming that the diffusion coefficient of diphenyl selenide and 2a-c were identical. The reduction of PhSePh has been shown to consume two electrons.[6] The polarographic data which are summarized in Table I, show that less than two electrons were involved in the first reduction step (wave A). In the case of 2b, they indicate that the values of $n_B + n_C$ were 1 and the absence of phenol and 2 in its presence (Fig. 1). Similar results were observed at a glassy carbon electrode by voltammetry at a rotating disc electrode (RDE) or cyclic voltammetry at a stationary disc electrode (SDE), except for wave C which was again hidden by the discharge of the supporting electrolyte. Scheme I can account for the above results.

Table I. Polarographic data of PhSePh (2 mM) and 2a-c (2 mM) in DMF

Compound	wave A - $E_{1/2}$(V)	n_A	wave B - $E_{1/2}$(V)	n_B	wave C - $E_{1/2}$(V)	n_C
PhSePh	2.55	2.0				
2a	1.99	1.70	2.30	0.15	2.82	ill defined
2b	2.04	1.61	2.32	0.12	2.72	0.88
2b[a]	2.03	1.61	2.30	0.27	2.67	1.77
2c	1.93	1.60	2.32	0.17	2.77	ill defined

[a] Phenol (10 mM) was added.

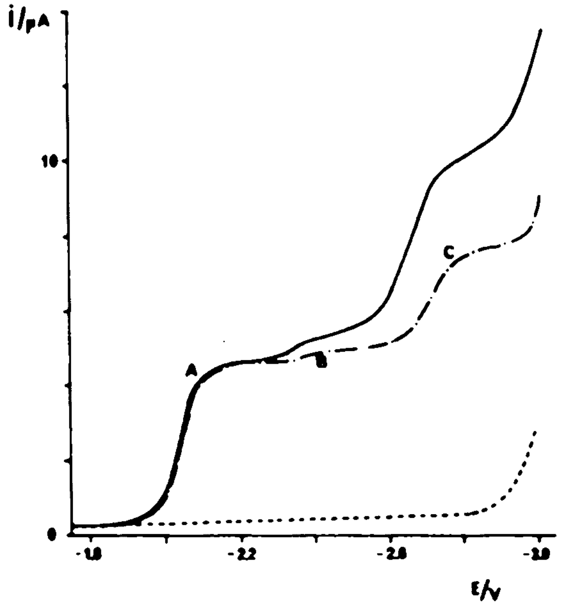
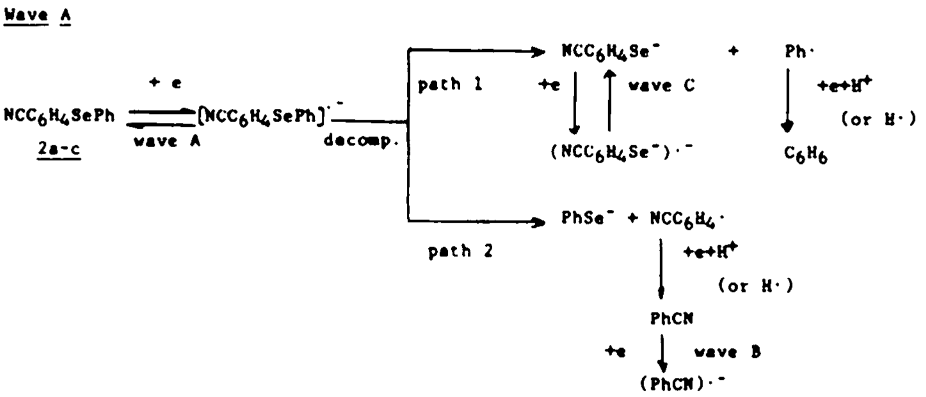


Fig. 1 Polarograms of 2b (2 mM) in DMF, in the absence (-·-) and presence (full line) of phenol (10 mM). The dotted curve corresponds to the background current.

Scheme I



The one-electron reduction of 2a-c gave unstable radical anions which diffused partially toward the solution where they cleaved competitively according to pathways 1 (main route) and 2. As shown by ROSSI[7] competition between bond breaking indicated that antibonding σ molecular orbitals (σ^*MO) of the C-Se bonds and π^*-MO had similar energy. A small amount of benzonitrile was generated through pathway 2, which was reversibly reduced at the potentials of wave B. Whereas the radicals Ph· and NCC_6H_4· generated close to the electrode were further reduced, those liberated in the solution were hydrogenated by solvent molecules.[8] Thus less than two electrons were involved in the first reduction step, due to a competition between reduction and hydrogenation. Reduction of PhSePh which was chosen as reference was a two-electron process because the reductive cleavage was faster than in the case of 2a-c and so all the Ph· radicals were generated close to the electrode and immediately reduced to $Ph^{\cdot -}$. If we consider again route 2, its involvement could be evaluated quantitatively from the n_B values since wave B corresponded to the reduction of benzonitrile (1 electron in the absence and 2 in the presence of phenol). Thus it was calculated that 15 ± 5 % of $PhSe^-$ anions and consequently 85 ± 5 % of $NCC_6H_4Se^-$ anions were generated.

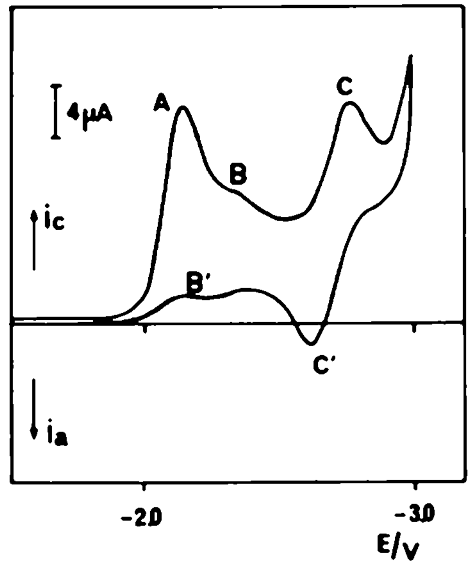


Fig. 2 Cyclic voltammogram of 2b (2.5 mM) in DMF at HMDE. The scan rate is 1 V s^{-1}.

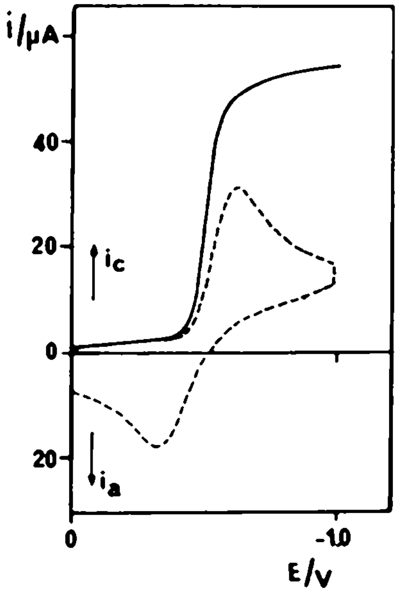


Fig. 3 Voltammograms of 1c (1 mM) in DMF at a glassy carbon RDE (full line) and SDE (dotted curve). The scan rate is 0.1 V s^{-1}.

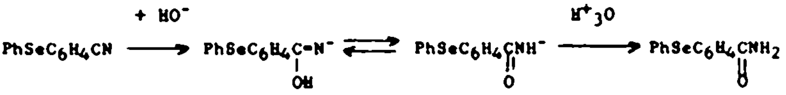
Large-scale electrolysis of 2a-c. The cathodic reduction of 2a-c was carried out in DMF and MeCN, at Hg, glassy carbon and Pt electrodes, at potentials corresponding to wave A (Table II). Selenolate anions were thus generated, requiring n_1 electrons molecule^{-1}, then oxidised either anodically, in a n_2 electron process (electrolyses no 1, 2 and 4) or chemically by air (electrolyses no 3, 5 and 6). In the anodic process, the formation of PhSeSePh preceded that of 1a-c (see the experimental section) and so no mixed diselenide

Table II. Large-scale electrochemical reduction of 2a-c (2 mmol) followed by oxidation (anode or air)

Electrolysis no	Compound	electrode	solvent	Added Acid(mmol)	n_1	oxidn	n_2	yields (%) of isolated compounds		
								PhSeSePh	1a-c	3a,b
1	2a	Pt^a	DMF	-	1.57	anod	1.04	9	42	16
2		C^b	MeCN	Bu_4NSO_4H(10)	3.04^c	anod	1.15	24^c	59^c	
3	2b	Hg^a	DMF	-	1.08	O_2	-	5	51.5	25
4		C^b	MeCN	PhOH(4)	3.06	anod	2.48	17	70	
5	2c	Hg^a	DMF	fluorene(2)	1.64	O_2	-	7	75	
6		Pt^a	DMF	PhOH(4)	3.34	O_2	-	12	60	

[a] Magnetic stirring. [b] Sonication. [c] Taking into account some 2a left (26 %).

$NCC_6H_4SeSePh$ was isolated. Similarly, when air was introduced in the cathodic solution, a rapid oxidation of $PhSe^-$ to PhSeSePh took place whereas very slow homogeneous electron exchanges occurred between the $NCC_6H_4Se^-$ anions and dioxygen because the oxidation potentials of these anions are positive to the reduction of O_2 (vide infra). Thus, these anions remained partially in the aqueous phase during treatment of the cathodic solution. They could be slowly oxidised later to the expected diselenide 1a-c in alkaline media (pH 12) (see the Experimental Section). In a previous publication,[9] 1c was isolated in low yield (27 %) by cathodic reduction of 2c because the aqueous phase was neglected. The results of Table II are consistent with scheme I. Indeed, the concomitant formation of the expected diselenide 1a-c and PhSeSePh in low yield was compatible with a competition between pathways 1 and 2. In the absence of added acid, some amide 3 was generated (electrolyses no 1 and 3), showing that some adventitious water was present during electrolysis and that HO^- anions were liberated, which reacted with the starting material to give electrochemically inactive anions and finally amides after treatment of the cathodic solution (eq 9).



$$PhSeC_6H_4CN \xrightarrow{+\ HO^-} PhSeC_6H_4\underset{OH}{\underset{|}{C}}{=}N^- \rightleftarrows PhSeC_6H_4\underset{O}{\underset{\|}{C}}NH^- \xrightarrow{H^+{}_3O} PhSeC_6H_4\underset{O}{\underset{\|}{C}}NH_2 \qquad (9)$$

2a,b 3a,b

Since the amides 3a and 3b were isolated in 16 and 25 % yields in electrolyses no 1 and 3, only 84 and 75 % of 2a and 2b were available for reduction and so the numbers of electrons consumed per mole of 2a and 2b were 1.87 and 1.44, that is to say less than 2, in agreement with a competition between reduction and hydrogenation (cf scheme I). Addition of an acid such as phenol, fluorene or Bu_4NSO_4H which was used as supporting electrolyte, suppressed the formation of amides and so 2a, 2b and 2c could be isolated in 59 %, 70 % and 75 % yields, respectively. Addition of phenol or Bu_4NSO_4H surprisingly increased the values of n_1 and n_2 for reasons which have not yet been clearly established. A bielectronic reduction of benzonitrile might take place. In the case of phenol in DMF, a contribution from the dimer $(PhOH)_2$ as proton donor could not be excluded.[10]

Cathodic reduction of 1a-c to $NCC_6H_4Se^-$ occurred readily as shown by voltammetry (Fig. 3) ($E_{1/2}$ = - 0.48 V (1a) ; - 0.58 V (1b) ; - 0.52 V (1c). In cyclic voltammetry, the anodic oxidation of the $NCC_6H_4Se^-$ anions took place at peak potential values (E_p = - 0.28 V, - 0.38 V and - 0.42 V for the o-, m- and p- isomers, respectively) definitely more positive than the reduction potential of dioxygen (about - 1 V). As already mentioned, this indicates that in situ oxidation by air of $NCC_6H_4Se^-$ anions to diselenide proceeded very slowly.

Conclusion

The results of ref. 4 concerning the electrochemical synthesis of 2a-c, combined with the above results, show that the new diselenides 1a-c which are not available by the Grignard method can be generated electrochemically in interesting global yields (36 %,48 % and 52.5 %, respectively) from commercially available PhSeSePh and chlorobenzonitrile. The electrochemical synthesis of 1a-c from diselenides which are cheaper than PhSeSePh is currently under way. These precursors are prepared by electrochemical reduction with sonication, of non-expensive Se powder followed by addition of alkyl halides.[11] A similar study is concomitantly performed for the Te homologues.

Experimental

The electrochemical synthesis of 2a-c is described in ref. 4.

Elemental analyses were performed by Service Central d'Analyse, CNRS, Lyon. Spectra were recorded by means of the following instruments : infrared, Perkin-Elmer 580B, ^1H NMR, JEOL FX100.

Polarograms were obtained with a Tacussel Tipol instrument. The characteristics of the capillary were : m = 2.6 mg s^{-1} ; t = 1 s. Cyclic voltammograms at a HMDE or glassy carbon SDE (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 IG5-N integrator were used in coulometry and preparative electrolysis. All the potentials of the experiments and figures referred to the aqueous saturated calomel electrode (SCE). Unless otherwise stated Bu_4NPF_6 (0.1 M) was used as supporting electrolyte.

Large-scale electrolyses at 18°C with sonication (vat Bransonic B 32) or magnetic stirring 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 DMF or acetonitrile. The working electrode was a cylindrical Pt grid, graphite cloth or a mercury pool (surface = 9 cm^2) and the counter electrode was a Pt grid. The cathodic solution (100 ml) was deaerated with argon before and during electrolysis. If not otherwise specified 2 mmol were reduced. Specific details of the electrolyses of Table II are given below.

- *Electrolysis n° 1* - Compound 2a was reduced at controlled potentials corresponding to wave A of Fig. 1, at 2.1 ± 0.2 V. The faradaic current dropped from 100 mA (initial value) to a negligible value and 303 Cb (3.14 mmol of electrons) were consumed. The potential was shifted anodically (up to + 0.2 V) and anodic oxidation started at - 1 V (initial current = 80 mA). At this potential oxidation of PhSe$^-$ to PhSeSePh took place whereas the oxidation of $NCC_6H_4Se^-$ occurred later at less negative values. The electrolysis was stopped after consumption of 201 cb (2.08 mmol of electrons) when the anodic current became negligible. The solution was diluted with water and the electrolysis products were extracted with diethyl ether. The ethereal solution was dried, ether was removed and the crude product (311 mg) was subjected to column chromatography with acetone/hexane as eluent. The compounds were isolated in the order : PhSeSePh (0.09 mmol), 1a (0.42 mmol) and 3a[4] (0.32 mmol).

2,2'-Dicyanodiphenyl diselenide (1a) : yellow powder, mp 119°C (CH_2Cl_2-hexane) ; IR (KBr) 2226 (C≡N stretching), 767 (ortho substitution band) cm^{-1} ; ^1H NMR ($CDCl_3$) 7.25-7.69 (m, 6H) ;[7.84 (dd, J_{ortho} = 9Hz, J_{meta} = 2Hz, 2H)]. Anal. Calcd. for $C_{14}H_8N_2Se_2$: C, 46.43 ; H, 2.23 ; N, 7.73 ; Se, 43.61. Found : C, 46.37 ; H, 2.27 ; N, 7.59 ; Se, 43.52.

- *Electrolysis n° 2* - Compound 2a (1 mmol) was reduced in the presence of Bu_4NSO_4H (0.1 M) as supporting electrolyte, at - 1.60 0.05 V. After consumption of 218 cb (2.26 mmol of electrons), the anodic oxidation was carried out as previously. After treatment of the solution and column chromatography of the crude product (219 mg), the compounds were isolated in the order : PhSeSePh (0.09 mmol), 2a (0.26 mmol) and 1a (0.22 mmol).

- *Electrolysis n° 3* - Compound 2b was reduced at - 2.1 V. When the electrolysis was stopped, air was bubbling for 10 min before the cathodic solution was diluted with water containing NaOH 10^{-2}M (pH 12). The electrolysis products were partially extracted with diethyl ether. The crude product (265 mg) was subjected to column chromatography and the compounds were isolated in the order : PhSeSePh (0.05 mmol), 1b (0.09 mmol), 3b[4] (0.50 mmol). From the aqueous phase which was allowed to stand overnight, pure 1b (0.42 mmol) was extracted by diethyl ether.

3,3'-Dicyanodiphenyl diselenide (1b) : yellow powder ; mp 111°C (ether-hexane) ; IR (KBr) 2238 (C≡N stretching), 792 (meta substitution band) cm^{-} ; ^1H NMR ($CDCl_3$) 7.25-7.75 (m, 6H), 7.85 (s, 2H). Anal. Calcd. for $C_{14}H_8N_2Se_2$: C, 46.43 ; H, 2.23 ; N, 7.73 ; Se, 43.61. Found : C, 46.60 ; H, 2.21 ; N, 7.75 ; Se, 43.88.

- *Electrolysis n° 4* - Compound 2b was reduced at 2.0 0.2 V in the presence of phenol, then the anodic oxidation proceeded as previously (see electrolyses n° 1 and 2). The solution was diluted with water containing NaOH 10^{-2} M (pH 12) and treatment was carried out under the conditions of electrolyses n° 1 and 2.

- *Electrolyses n° 5 and 6* - Compound 2c was reduced in the presence of fluorene or phenol. After electrolysis, air was introduced and the cathodic solution was treated under the conditions of electrolysis n° 3.

4,4'-Dicyanodiphenyl diselenide[9] (1c) : yellow powder, mp 158°C (diethyl ether-hexane) ; IR (KBr) 2240 (C≡N stretching) 830, 822 (two para substitution bands) ; ^{1}H NMR (CDCl$_3$) 7.48-7.73 (pseudo q, 8 H).

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