

## ELECTROCHEMICALLY INDUCED $S_{RN}1$ SUBSTITUTION IN ACETONITRILE. SYNTHESIS OF ARENES SUBSTITUTED BY PHENYLSELENO- AND PHENYLTELLURO GROUPS

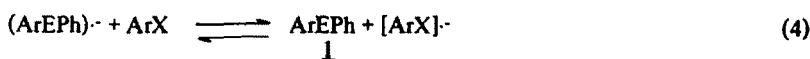
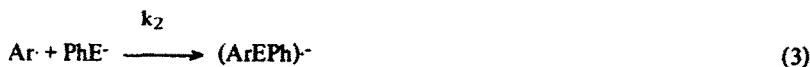
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**Abstract.** In MeCN, the direct or mediated cathodic reduction of unactivated ArBr (Ar = 4-biphenyl, 2-fluorenyl, 9-anthryl) in the presence of an equivalent of PhE- (E = Se, Te) leads to ArEPh in interesting isolated yields (53-74 %) by  $S_{RN}1$  substitution. The electrochemical synthesis of 9-phenylchalcogenoanthracene proceeds in better yields in MeCN than in DMSO. The 4,4'-disubstituted biphenyl PhSeC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>SePh was prepared in 46 % yield in MeCN whereas its synthesis by photostimulation in liquid ammonia failed.

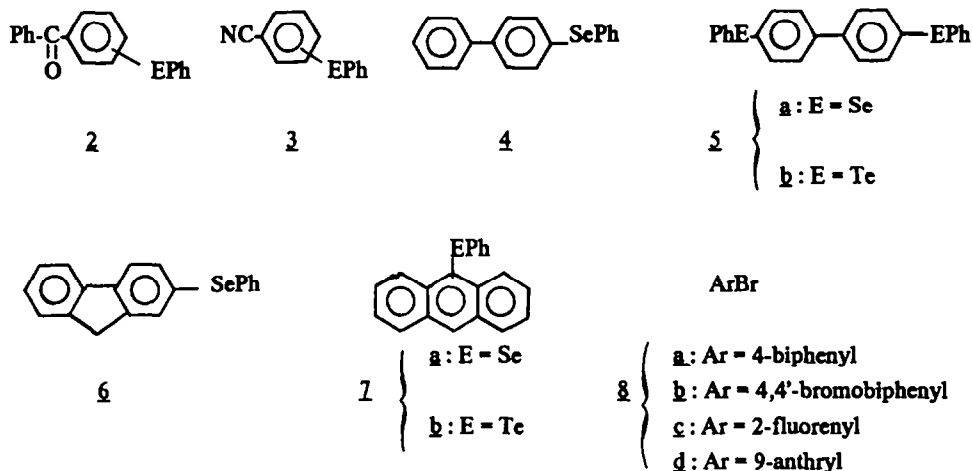
In a recent series of publications <sup>1-3</sup> our group has shown that the synthesis of phenylchalcogenoderivatives of type **1** (E = Se, Te) by electrochemically induced  $S_{RN}1$  substitution (eqs (1)-(4))<sup>4,5</sup> can be carried out in interesting yields in acetonitrile when the aromatic ring Ar is substituted by electron attracting groups. Hence substituted benzophenone **2**<sup>2</sup> and benzonitrile **3**<sup>1</sup> (E = Se, Te) were isolated in yields ranging from 39 to 86 % from commercially available PhEEPh and ArX, in one-pot preparative electrolyses. Although MeCN is known to be a good H-atom donor<sup>4-6</sup>, the side reaction (5) did not compete with the key-step (3), due to the high electrophilicity of the intermediate radicals PhCOC<sub>6</sub>H<sub>4</sub><sup>•</sup> and NCC<sub>6</sub>H<sub>4</sub><sup>•</sup>. Furthermore, the side cathodic reaction (6) was prevented by the use of a redox-mediator.<sup>4c,5,7-10</sup>



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It is shown below that even when ArX is not activated by electron withdrawing groups, the electrochemical technique in MeCN allows the synthesis of various aromatic seleno and telluro derivatives such as **4** and the new compounds **5a,b**, **6** and **7a,b**, in interesting yields (46-74 %), except in the case of **5b** (16 %). Furthermore, it is shown that the electrochemical synthesis of **7a,b** proceeds better in MeCN than in Me<sub>2</sub>SO. Finally, the cathodic behaviour of **4-7** is described.



## RESULTS AND DISCUSSION

### *Electrochemical synthesis of 4-7*

The electrochemical synthesis of the seleno and telluro derivatives **4-7** were carried out from the aryl bromides **8a-d** and PhEPh. A redox mediator (med) was present in most of the electrolyses. Under such conditions, the aryl radicals Ar $\cdot$  were generated in the bulk of the cathodic solution according to reactions (7) and (8) and thus the further cathodic reduction of Ar $\cdot$  to Ar $^-$  (6) was avoided. In the absence of mediator, this side-reaction is competing with the key-step (3) when Ar $\cdot$  is generated close to the electrode, that is to say when the cleavage rate  $k_1$  is high.



The choice of the redox mediators which were used, resulted from a preliminary voltammetric study at a glassy carbon stationary disc electrode (SDE). An example is shown in Fig. 1. The indirect reduction of 2-bromofluorene (**8c**) by anthracene, the  $E_{1/2}$  values of which differ by 0.30 V (Table I), is observed in this figure since the cathodic peak current of anthracene increases upon addition of **8c**, whereas its anodic peak current decreases. In the case of **8a** and **8b**, 2,3-dimethylquinoxaline was chosen as redox mediator. For 9-bromoanthracene (**8d**), kinetic data published by SAVEANT et al.<sup>6</sup> indicate that the decomposition rate of the **8d**<sup>-</sup> radical anion is moderate in MeCN ( $k_1 = 1.5 \times 10^5 \text{ s}^{-1}$ ) and therefore that the side-reaction (6) is negligible in the absence of mediator.

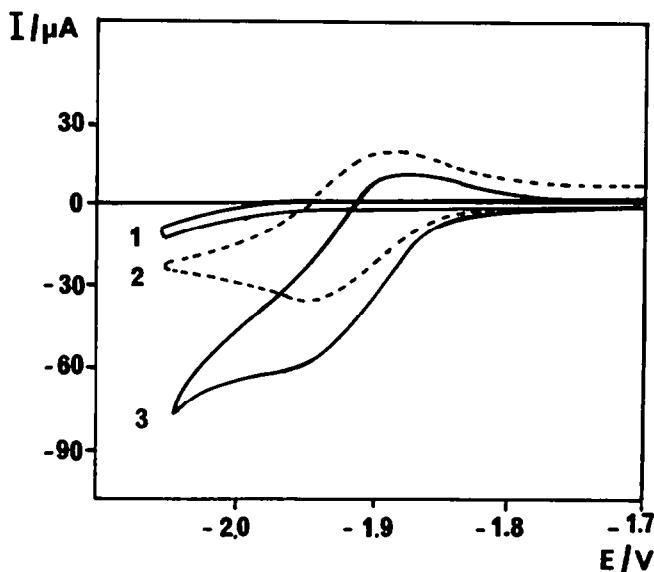


Fig. 1 Cyclic voltammograms in MeCN of anthracene (1 mM) in the absence (curve 2) and presence (curve 3) of 2-bromofluorene (5 mM). Curve 1 corresponds to 2-bromofluorene (5 mM) alone. The scan rate is  $0.1 \text{ V s}^{-1}$ .

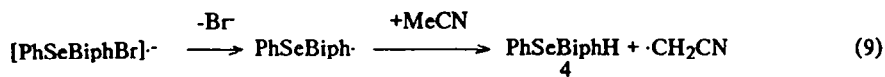
A series of large-scale electrolyses was carried out at a graphite tissue cathode, in MeCN containing  $0.1 \text{ M Bu}_4\text{NPF}_6$ , according to the technique previously described<sup>1c,2</sup>. First PhEPh was introduced in the cathodic compartment of an H-type cell equipped with ionic membranes, and reduced to the corresponding PhE<sup>-</sup> anions. Then an equivalent of **8a-d** was added and reduced indirectly by a redox mediator (0.1 equiv., case of **8a-c**) or directly (case of **8d**). The potentials which were applied during electrolysis are indicated in Table I. The development of the electrolyses was

followed by thin layer chromatography and so, most of the electrolyses were interrupted after consumption of 8a-d. After treatment of the cathodic solution, the crude product was purified by column chromatography. The isolated yields of the substituted derivatives are given in Table II.

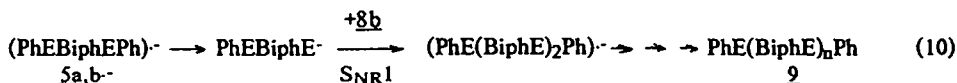
Table I. Working potential values ( $E_w$ ) applied during large-scale electrolysis of 8a-d, and  $E_{1/2}$  values corresponding to the first reduction step of 8a-d and med eventually added

ArBr	$-E_{1/2}/V$	med	$-E_{1/2}/V$	$-E_w/V$
<u>8a</u>	2.15	2,3-dimethylquinoxaline	1.89	1.80
<u>8b</u>	2.09	2,3-dimethylquinoxaline	1.89	1.80 ± 0.1
<u>8c</u>	2.22	anthracene	1.92	1.95 ± 0.5
<u>8d</u>	1.59			1.40 ± 0.05

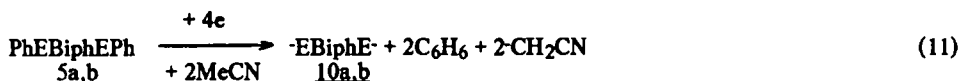
The synthesis of the monoseleno derivative 4 by  $S_{NR}1$  substitution proceeds better by electrochemical stimulation in MeCN (entry 1 of Table II, yield = 65 %) than by photostimulation in liquid ammonia (yield = 35 %) <sup>11</sup>. Furthermore, the electrochemical method competes advantageously with the chemical synthesis of 4 (yield = 60 %) which is a multiple-step process since it involves the synthesis of a lithio derivative and PhSeCN <sup>12</sup>. The electrolyses leading to the dichalcogenobiphenyl 5a and 5b involve a double  $S_{NR}1$  substitution <sup>13</sup> (entries 2 and 3). The formation of the seleno derivative 5a in 46 % yield (entry 2) is accompanied by the formation of 8a resulting from the side-reaction (5) ( $Ar = 4-BrC_6H_4C_6H_4$ ), and of the monoselenobiphenyl 4 in low yield. As this electrolysis was interrupted as soon as 8b was consumed, 8a was not further reduced or only partially reduced. The formation of 4 in low yield could occur according to (9) (Biph = 4,4'-biphenyl) and/or by partial reduction of 8a. However, if this latter assumption was valid, some biphenyl should have been isolated (cf. entry 1). Since this compound was not found, we may reasonably conclude that reaction (9) was prevailing. It is worth noting that an attempt to the synthesis of 5a by photostimulated  $S_{NR}1$  substitution in liquid ammonia failed, due to the insolubility of 8b in this solvent <sup>13</sup>.



Unidentified polymeric materials were isolated in small amounts in electrolysis n° 2 of Table II and in larger amount in electrolysis n° 3 where PhTe<sup>-</sup> is the nucleophile. It indicates that the intermediate telluro radical anion 5b<sup>-</sup> was very unstable, and so new nucleophiles were generated, which interfered in the  $S_{NR}1$  substitution process and led to polymeric materials such as 9.



In electrolysis n° 3 of Table II, the high yields of polymeric species and side-product **8a** explain the low yield of the expected ditelluroderivative **5b**. The dichalcogenoderivatives **5a** and **5b** are interesting molecules because their cathodic reduction gives the dichalcogenate species **10a,b** (vide infra) which are potential precursors of new polymeric materials.



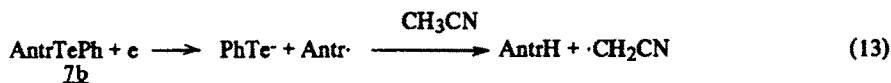
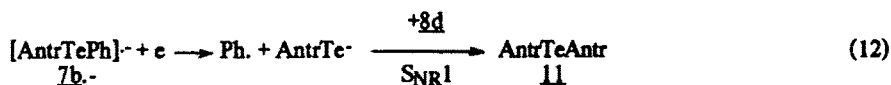
The electrochemical synthesis of 2-phenylselenofluorene (**6**) (entry 4 of Table II) was carried out in the presence of a weak acid (diethyl malonate) to avoid a deprotonation of the fluorenyl unit of **8c** by the  $\cdot\text{CH}_2\text{CN}$  anions generated through the side-reaction (5). In water, the pK<sub>A</sub> values of MeCN, 2-bromofluorene (**8c**) and diethylmalonate are 25<sup>14</sup>, 20.6<sup>15</sup> and 13<sup>14</sup>, respectively.

Table II. Electrolyses of **8a-d** in the presence of PhE<sup>-</sup> in MeCN and DMSO. Electrolysis products and isolated yields

Entry n°	ArBr(mmol)	Solvent	PhE <sup>-</sup> (equiv)	ArH (yield %)	substituted derivatives (yield %)
1	<b>8a</b> (4)	MeCN	PhSe <sup>-</sup> (1)	Biphenyl(18)	<b>4</b> (65)
2	<b>8b</b> (3)		PhSe <sup>-</sup> (2)	<b>8a</b> (36)	<b>5a</b> (46) + <b>4</b> (9)
3	<b>8b</b> (3)		PhTe <sup>-</sup> (2)	<b>8a</b> (52)	<b>5b</b> (16)
4	<b>8c</b> (4)		PhSe <sup>-</sup> (1)	Fluorene(23)	<b>6</b> (53)
5	<b>8d</b> (4)		PhSe <sup>-</sup> (1)	Anthracene(18)	<b>7a</b> (74)
6	<b>8d</b> (4)		PhTe <sup>-</sup> (1)	Anthracene(11)	<b>7b</b> (68) + <b>11</b> (9)
7	<b>8d</b> (4)	DMSO	PhSe <sup>-</sup> (1)	Anthracene(36)	<b>7a</b> (43)
8	<b>8d</b> (2)		PhTe <sup>-</sup> (1)	Anthracene(42)	<b>7b</b> (49) + <b>11</b> (6)

In MeCN, the cathodic reduction of 9-bromoanthracene (**8d**) in the presence of PhSe<sup>-</sup> and PhTe<sup>-</sup> led to good isolated yields of substitution products **7a** and **7b** (entries 5 and 6 of Table II). The synthesis of the symmetrical telluride **11** (Antr = 9-anthryl) as minor compound in electrolysis n° 6 cannot be correlated to a cleavage of the intermediate **7b**<sup>-</sup> radical anion according to (12) because the

reductive cleavage of 7b leads exclusively to anthracene according to (13) (*vide infra*). The origin of 11 is not yet elucidated.

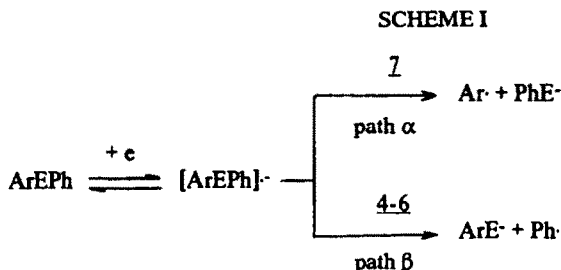


The electrochemical synthesis of 7a and 7b was also carried out in a mixture  $\text{Me}_2\text{SO}/\text{H}_2\text{O}$  (9/1) containing 0.1 M  $\text{LiClO}_4$ . Surprisingly, lower yields of substituted compounds were obtained under these conditions, although it is known that the hydrogenation reaction (5) occurs more readily in MeCN than in  $\text{Me}_2\text{SO}$  ( $k_{\text{H}}^{\text{MeCN}} = 2.3 k_{\text{H}}^{\text{Me}_2\text{SO}}$ )<sup>6</sup>. Since the yield R of 7a and 7b depends on the ratio  $k_{\text{H}}/k_2$  and is given by (14) when the nucleophile is in excess<sup>16</sup>, it can be concluded that the  $k_2$  values corresponding to the attack of  $\text{PhE}^-$  upon 9-anthryl radicals, are definitely higher in MeCN than in DMSO. A quantitative determination of this effect has been performed by cyclic voltammetry and is described elsewhere<sup>17</sup>.

$$R(\%) = \frac{100}{1 + \frac{k_{\text{H}}}{k_2(\text{PhE}^-)}} \quad (14)$$

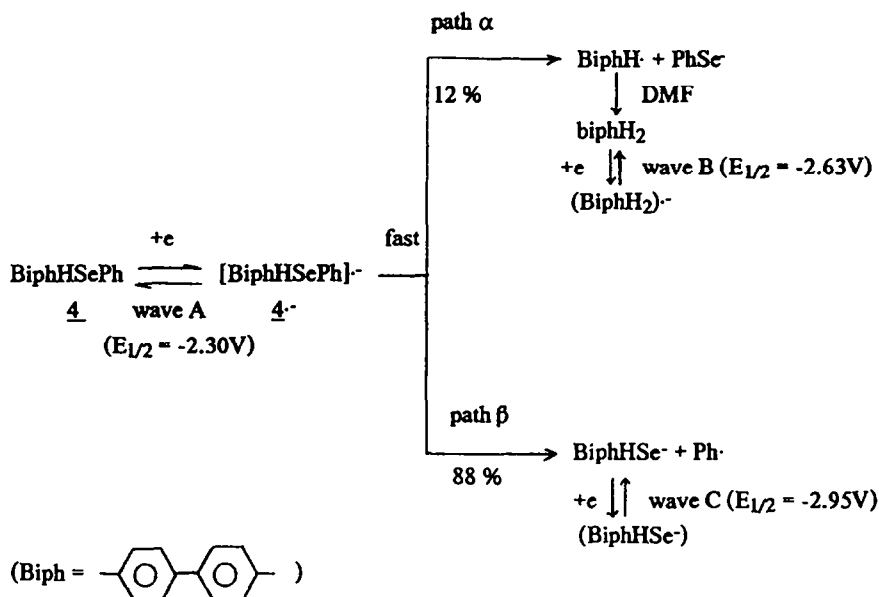
#### Cathodic behaviour of 4-7

The cathodic properties of 4-7 were examined in *N,N*-dimethylformamide (DMF) by voltammetry at SDE and rotating disc electrode (RDE). The salient results of this study are that the first reduction step of 4-7 corresponds to a reductive cleavage, with formation of  $\text{PhE}^-$  (path  $\alpha$  of scheme I) or  $\text{ArE}^-$  (path  $\beta$ ). As detailed below, path  $\alpha$  is exclusive for 7 whereas path  $\beta$  is major or exclusive in the other cases.



In the case of the substituted biphenyl 4, 5a and 5b, the reductive cleavage is rapid since the first step is totally irreversible (Fig. 2). For 4, paths  $\alpha$  and  $\beta$  of scheme I compete because the first reduction wave A (Fig. 2a) is followed by a wave B of small amplitude, corresponding to the reversible reduction of biphenyl, and by a wave C at very negative potentials. The percentages of paths  $\alpha$  (12 %) and  $\beta$  (88 %) were evaluated from the limiting currents of waves B and C, assuming that one electron was involved for the corresponding reduction steps. Scheme II summarizes the results of Fig. 2a.

## SCHEME II



The cathodic behaviour of the diselenobiphenyl 5a which is shown in Fig. 2b is summarized by Scheme III. The reductive cleavage of the diselenobiphenyl 5a proceeds exclusively according to path  $\beta$  of Scheme I. Indeed path  $\alpha$  would lead to 4, to which would be three waves A, B and C of Fig. 2a and scheme II. Scheme III accounts also for the Te homologue 5b for which the reversible uptake of a third electron is observed at very negative potentials (wave C of Fig. 2b). For 5a, this wave is beyond the discharge of the supporting electrolyte, in agreement with the electron donating properties of the Se<sup>-</sup> and Te<sup>-</sup> substituents, the Hammett  $\sigma$  constants being - 0.84 and - 0.72<sup>18</sup>. As already stressed, the dianions 10a,b are potential precursors of polymers by oxidation or addition of dielectrophiles.

## SCHEME III

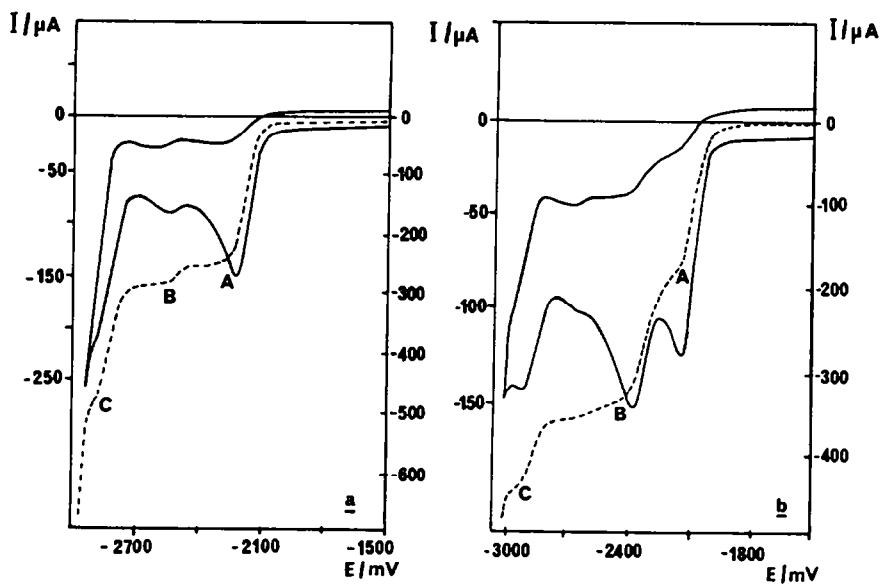
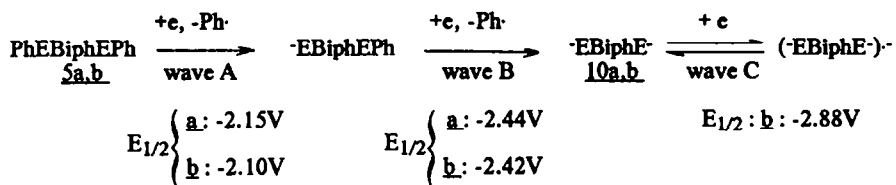


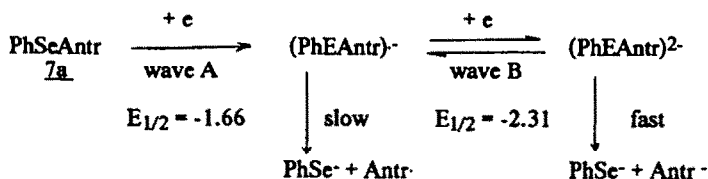
Fig. 2 Voltammograms of 4 (4.7 mM) (Fig. a) and 5b (4.0 mM) (Fig. b) at RDE (dotted curves) and SDE in DMF. The scan rate was  $0.1 \text{ V s}^{-1}$ .



The cathodic response of the substituted fluorene **6** is a one-step process ( $E_{1/2} = -2.19\text{V}$ ). The reductive cleavage is rapid again since the single wave is irreversible. Furthermore, it occurs exclusively according to path  $\beta$  of scheme I since no wave corresponding to the reduction of fluorene is observed at  $-2.70\text{V}$ .

The voltammograms of **7a** at a RDE presents two waves (Fig. 3a). Wave A corresponds to the reversible uptake of an electron (Fig. 3b). However, a coulometry carried out at potentials corresponding to the plateau of this wave indicates a two-electron consumption and the formation of anthracene and  $\text{PhSe}^-$ . It is shown in Fig. 4 which corresponds to the voltammogram of the cathodic solution after coulometry. The reduction waves E and F at  $E_{1/2} = -1.90\text{V}$  and  $-2.48\text{V}$  depict the cathodic response of anthracene, and the oxidation wave G the anodic activity of  $\text{PhSe}^-$ . Since we have observed elsewhere<sup>19</sup> that the reduction of 9-anthrylselenate anions ( $9\text{-AntrSe}^-$ ) takes place at  $E_{1/2} = -2.36\text{V}$  in DMF, the formation of these anions can be ruled out from the results of Fig. 4. Thus the slow reductive cleavage of **7a** occurs in the bulk of the solution during electrolysis and gives exclusively anthracene. Scheme IV summarizes the results of Figs 3 and 4. Anthracene is generated at the potentials of wave A by hydrogenation of  $\text{Antr}^-$  by the solvent and, at the potentials of wave B, by protonation of  $\text{Antr}^-$ . At the potentials of the latter wave, anthracene is further reduced to its radical anion and so wave B is bielectronic.

Scheme IV



The telluro derivative **7b** behaves similarly but the cleavage is more rapid and so the formation of anthracene can be observed by voltammetry at RDE (waves E and F of Fig. 5). Again, anthracene is quantitatively generated when **7b** is cathodically reduced at  $-1.7 \pm 0.05\text{V}$  by coulometry.

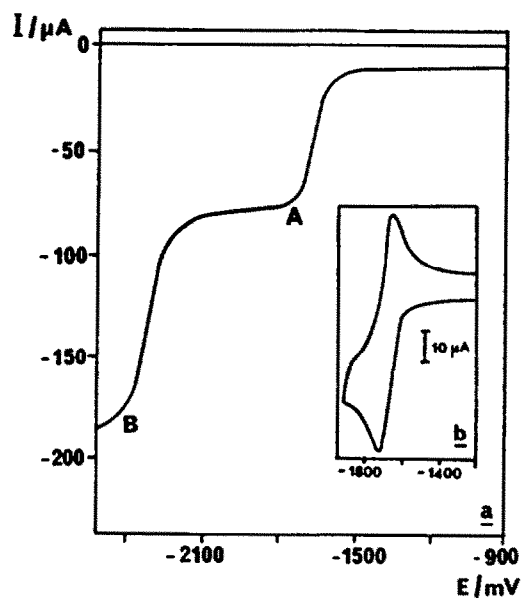


Fig. 3 Voltammograms of  $7a$  (2.5 mM) at RDE (curve a) and SDE in DMF. The scan rate was  $0.1 \text{ V s}^{-1}$ .

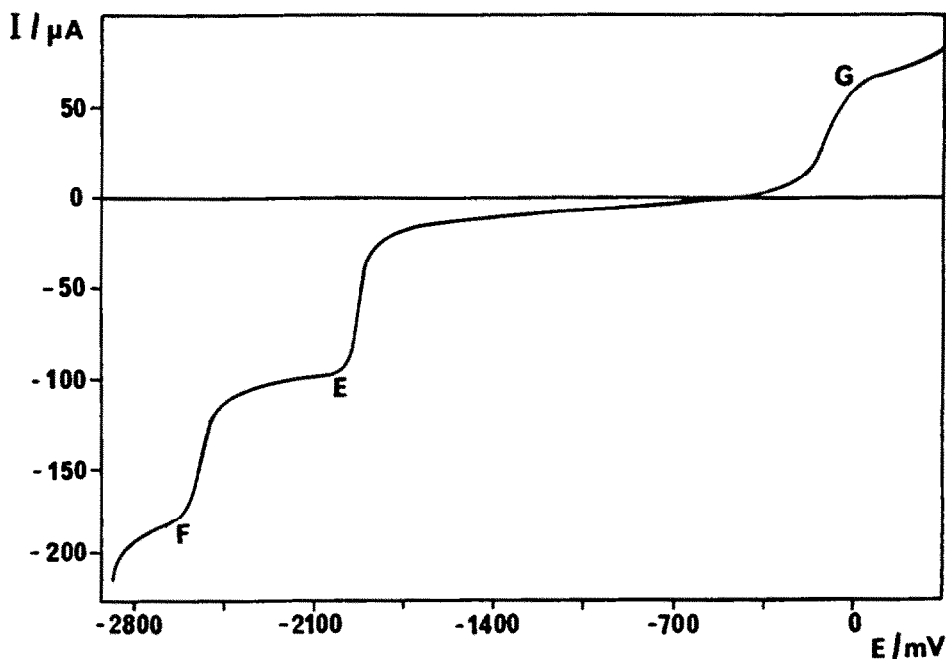


Fig. 4 Voltammogram recorded after reduction at  $-1.7 \text{ V}$  of the solution corresponding to Fig. 3. Two electron equivalents were consumed. The scan rate was  $0.1 \text{ V s}^{-1}$ .

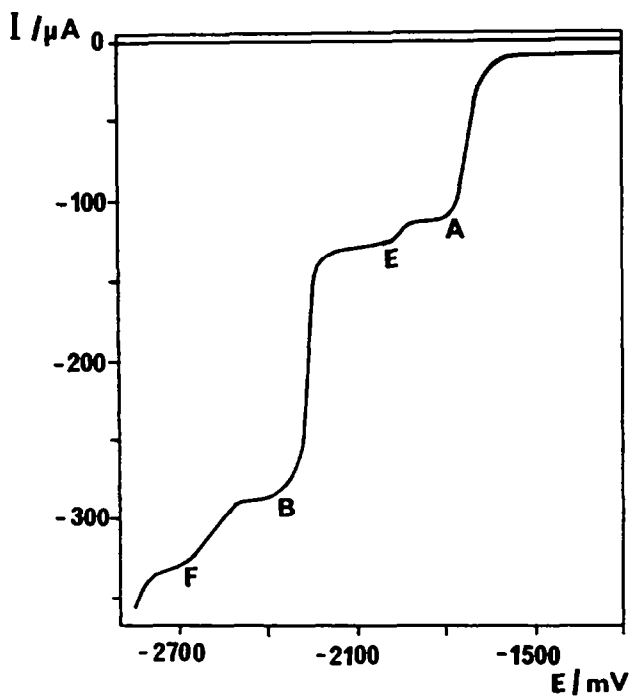


Fig. 5 Voltammogram at RDE of 7b (3.4 mM) in DMF

### CONCLUSION

The one-pot electrochemical synthesis of arenes substituted by phenylseleno and phenyltelluro groups can be achieved in interesting yields in MeCN by electrochemically induced S<sub>RN</sub>1 substitution. MeCN is a versatile solvent in which solubility problems are usually avoided. Since very few chemical methods allow the synthesis of activated and unactivated telluro derivatives of type 1<sup>20</sup>, the electrochemical technique competes advantageously with them. Finally, we have shown that aryl anions ArE<sup>-</sup> (Ar = 4-biphenyl, 2-fluorenyl) and dianions <sup>-</sup>EArE<sup>-</sup> (Ar = 4,4'-biphenyl) are available by cathodic reduction of the corresponding ArEPh and PhEArEPh molecules.

## EXPERIMENTAL

The solvents, supporting electrolyte and compounds **8a-d** were from commercial origin. Analytical grade MeCN (spectrosol SDS) was carefully dried on neutral alumina.

Elemental analyses were performed by Service Central d'Analyses, CNRS, Lyon.

Voltammograms at a glassy carbon, stationary or rotating disc electrode (V25 Carbone Lorraine ; diameter = 3 mm) were obtained by using an IR-Compensated potentiostat driven by a Dacfamov 05 programmer and an Apple IIC computer. 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 referred to the aqueous saturated calomel electrode (SCE).

The electrochemical synthesis of **4-7** was carried out in an H-type cell, the three compartments of which were separated by ion-exchange membranes Ionax MA 3475 (anodic side) and MC 3470 (cathodic side). The cathode was a graphite cloth of cylindric shape and the anode a Pt grid. The cathodic solution (100 ml) was stirred mechanically and deaerated with argon prior and during electrolysis.

In a typical experiment (Entry 1 of table II), PhSeSePh (2 mmol) was introduced and reduced to PhSe<sup>-</sup> in MeCN containing Bu<sub>4</sub>NPF<sub>6</sub> 0.1 M. The potential had to be changed from - 0.8 V to - 2.1 V whereas the faradaic current dropped from 120 mA (initial value) to a negligible value, after consumption of 386C (4 mmol of electrons). The electrolysis was interrupted and **8a** (4 mmol) together with 2,3-dimethylquinoxaline (0.4 mmol) were added and reduced at - 1.8 V. The faradaic current dropped from 20 mA (initial value) to 4 mA after consumption of 160C (1.65 mmol of electrons). The cathodic solution was diluted with water and the electrolysis products were extracted with diethyl ether. After the solution was dried, the ether was removed. The crude product (1.20 g) was separated by column chromatography (Kieselgel) with 5/95 CH<sub>2</sub>Cl<sub>2</sub>/hexane, and the compounds were isolated in the order : **8a** (238 mg, 1.01 mmol, 25 %), biphenyl (84 mg, 0.55 mmol), PhSeSePh (48 mg, 0.15 mmol), **4** (600 mg, 1.94 mmol), mp 67° (litt. 21 : 66-7°), a mixture (48 mg) of two minor unidentified compounds. Taking into account some **8a** left, the isolated yields of biphenyl, PhSeSePh and **4** are 18 %, 10 % and 65 %, respectively.

*Electrochemical reduction of **8b** in the presence of PhSe<sup>-</sup> (Entry 2 of table II).* PhSe<sup>-</sup> (6 mmol) was generated as above then **8b** (3 mmol) was added as well as 2,3-methylquinoxaline (0.3 mmol) which was reduced at - 1.75 ± 0.05 V. The current dropped from 40 mA (initial value) to 5 mA after consumption of 135C (1.40 mmol of electrons) and disappearance of **8b**. The crude product (1.33 g) was separated as above and the compounds were isolated in the order : **8a** (149 mg, 1.07 mmol, 36 %), PhSeSePh (73 mg, 0.24 mmol, 8 %), **4** (84 mg, 0.27 mmol, 9 %), **5a** (643 mg,

1.39 mmol, 46 %). Then the column was eluted with acetone and thus a mixture (82 mg) of 2,3-dimethylquinoxaline and polymeric materials was isolated.

*4,4'-bis(phenylseleno)-biphenyl (5a)*. Nacreous powder mp = 119°C (CH<sub>2</sub>Cl<sub>2</sub> + hexane).

Anal. Calcd for C<sub>24</sub>H<sub>18</sub>Se<sub>2</sub>: C, 62.08; H, 3.91; Se, 34.01. Found: C, 61.92; H, 3.76; Se, 33.78.

*Electrochemical reduction of 8b in the presence of PhTe<sup>+</sup> (Entry 3 of table II)*. PhTe<sup>+</sup> (6 mmol) was generated from PhTeTePh (3 mmol) by shifting the applied potential from -0.8 V to -2.2V, then 8b (3 mmol) and 2,3-dimethylquinoxaline (0.3 mmol) were added, and the electrolysis was carried out at 1.8 ± 0.10 V and stopped after consumption of 125C (1.30 mmol of electrons). The crude product (1.58 g) was separated as above and the compounds were isolated in the order: a mixture (408 mg) of 8a (1.42 mmol) and 8b (0.25 mmol), a mixture (259 mg) of PhTeTePh (0.40 mmol) and PhTePh (0.34 mmol), a minor unidentified compound (24 mg), 5b (239 mg, 0.43 mmol), a minor unidentified compound (28 mg). Then the column was eluted with acetone and thus a mixture (197 mg) of 2,3-dimethylquinoxaline and polymeric species was isolated. Taking into account some 8b left, the isolated yields of 8a, PhTeTePh, PhTePh and 5b are 52 %, 15 %, 12 % and 16 %, respectively.

*4,4'-bis(phenyltelluro)biphenyl (5b)*. Yellow powder, mp = 140°C (CH<sub>2</sub>Cl<sub>2</sub> + hexane).

Anal. Calc. for C<sub>24</sub>H<sub>18</sub>Te<sub>2</sub>: C, 51.32; H, 3.21; Te, 45.47. Found: C, 51.36; H, 3.15; Te, 45.42.

*Electrochemical reduction of 8c in the presence of PhSe<sup>+</sup> (Entry 4 of table II)*. PhSe<sup>+</sup> (4 mmol) was generated electrochemically, then 8c (4 mmol), anthracene (0.4 mmol) and diethyl malonate (4 mmol) were added, and the electrolysis was carried out at -1.95 ± 0.05 V. The current dropped from 30 mA (initial value) to 2 mA after consumption of 290C (3 mmol of electrons). The crude product (1.62 g) was separated by column chromatography with 3/7 acetone/hexane, and the compounds were isolated in the order: a mixture (270 mg) of fluorene (0.85 mmol), 8c (0.24 mmol), PhSeSePh (0.08 mmol), anthracene (traces) and 9,10-dihydroanthracene (0.3 mmol), 6 (640 mg, 2.0 mmol), at least six unidentified minor compounds and diethyl malonate (213 mg, 1.33 mmol). Taking into account some 8c left, the yield of fluorene and 6 were 23 % and 53 %.

*2-phenylselenofluorene (6)*. White powder mp = 82°C (diethyl ether-hexane). Anal.

Calcd. for C<sub>19</sub>H<sub>14</sub>Se: C, 71.03; H, 4.39; Se, 24.57. Found: C, 71.29; H, 4.33; Se, 24.23.

*Electrochemical reduction of 8d in the presence of PhSe<sup>+</sup> in MeCN (Entry 5 of table II)*.

PhSe<sup>+</sup> (4 mmol) was generated electrochemically, then 8d (4 mmol) was added and reduced at 1.40 ± 0.05 V. The faradaic current dropped from 20 mA (initial value) to 4 mA, after consumption of 116C

(1.2 mmol of electrons) and disappearance of **8d** as observed by thin layer chromatography. The crude product (1.23 g) was separated by column chromatography with 1/9 CH<sub>2</sub>Cl<sub>2</sub>/hexane, and the compounds were isolated in the order : a mixture (216 mg) of anthracene (0.72 mmol, 18 %) and PhSeSePh (0.28 mmol, 14 %), then **7a** (987 mg, 2.96 mmol, 74 %).

*9-Phenylselenoanthracene (7a)*. Yellow powder, mp = 117°C (CH<sub>2</sub>Cl<sub>2</sub>-hexane). Anal. Calcd. for C<sub>20</sub>H<sub>14</sub>Se : C, 72.07 ; H, 4.23 ; Se, 23.69. Found : C, 72.01 ; H, 4.21 ; Se, 24.05.

*Electrochemical reduction of 8d in the presence of PhTe<sup>-</sup> in MeCN (Entry 6 of table II)*. PhTe<sup>-</sup> (4 mmol) was generated electrochemically, then **8d** (4 mmol) was added and reduced at - 1.40 ± 0.05 V. The faradaic current dropped from 20 mA (initial value) to 1 mA, after consumption of 81C (0.84 mmol of electron). The crude product (1.30 g) was separated by column chromatography with 1/9 CH<sub>2</sub>Cl<sub>2</sub>/hexane, and the compounds were isolated in the order : **8d** (16 mg, 0.06 mmol, 1 %), anthracene (79 mg, 0.44 mmol), **7b** (1029 mg, 2.69 mmol), **8** (85 mg, 0.177 mmol). Taking into account some **8d** left, the isolated yields of anthracene, **7b** and **8** are 11 %, 68 % and 9 %, respectively.

*9-Phenyltelluroanthracene (7b)*. Yellow powder, mp 127°C (CH<sub>2</sub>Cl<sub>2</sub> + hexane). Anal. Calcd. for C<sub>20</sub>H<sub>14</sub>Te : C, 62.90 ; H, 3.69 ; Te, 33.41. Found : C, 62.70 ; H, 3.58 ; Te, 33.44.

*Bis(9-anthryl)telluride (8)*. Yellow powder, mp 264-266°C (CH<sub>2</sub>Cl<sub>2</sub> + hexane). Anal. Calcd. for C<sub>28</sub>H<sub>18</sub>Te : C, 69.76 ; H, 3.76 ; Te, 26.47. Found : C, 69.73 ; H, 3.63 ; Te, 26.62.

*Electrochemical reduction of 8d in the presence of PhSe<sup>-</sup> in a mixture Me<sub>2</sub>SO/H<sub>2</sub>O 9/1 containing LiClO<sub>4</sub>, 0.1 M (Entry 7 of table II)*. PhSe<sup>-</sup> (4 mmol) was generated electrochemically, then **8d** (4 mmol) was added and reduced at - 1.40 ± 0.05 V. The faradaic current dropped from 22 mA (initial value) to 8 mA after consumption of 316C (3.3 mmol of electrons). The crude product (1.00 g) was separated as above and the compounds were isolated in the order : **8d** (162 mg, 0.63 mmol, 16 %), a mixture (334 mg) of anthracene (215 mg, 1.20 mmol) and PhSeSePh (116 mg, 0.38 mmol), then **7a** (486 mg, 1.46 mmol). Taking into account some **8d** left, the isolated yields of anthracene, PhSeSePh and **7a** are 36 %, 22 % and 43 %, respectively.

*Electrochemical reduction of 8d in the presence of PhTe<sup>-</sup> in a mixture Me<sub>2</sub>SO/H<sub>2</sub>O 9/1 containing LiClO<sub>4</sub>, 0.1 M (Entry 8 of table II)*. PhTe<sup>-</sup> (2 mmol) was generated electrochemically, then **8d** (2 mmol) was added and reduced at - 1.40 ± 0.1 V. The faradaic current dropped from 20 mA (initial value) to 8 mA after consumption of 94.5C (0.98 mmol of electrons). The crude product (684 mg) was separated as above and the compounds were isolated in the order : **8d** (118 mg, 0.46 mmol, 23 %), a mixture (170 mg) of PhTeTePh (53 mg, 0.13 mmol) and anthracene (117 mg, 0.65

mmol), then **7b** (286 mg, 0.75 mmol) and **8** (21 mg). Taking into account some **8d** left, the yields of anthracene, **7b** and **8** are 42.5 %, 49 % and 6 %, respectively.

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