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Electrochemical synthesis in an undivided cell of aromatic mono and dichalcogeno derivatives by $S_{RN}1$ substitution reactions in MeCN

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The two-step electrochemical synthesis of chalcogeno derivatives ArEPh (**1**) and ArEEAr (**3**) resulting from the oxidation of ArE^- (**2**) (AR = 4 – NCC_6H_4, 1-naphthyl, 2-quinolyl; E = S, Se, Te) can be conveniently carried out in MeCN, by reduction of an aryl halide (ArX) in the presence of electrogenerated PhE^- or E_2^{2-} anions ($S_{RN}1$ substitution reaction). To circumvent the disadvantages connected with the use of a divided cell equipped with degradable membranes, a method based on a beaker-type cell has been developed. Thus, the synthesis of substituted compounds **1** and **3** can be carried out in an undivided cell equipped with a magnesium anode, if a fluoride salt, such as $Et_4NF.2H_2O$ is purposely added before electrolysis (for **3**) or after the first step (for **1**). Under such conditions, the yields are competitive with those obtained in a divided cell.

1. Introduction

Aromatic seleno and telluro derivatives are widely used as reagents in organic synthesis [1–4] and they find applications as organic metals [5, 6], liquid crystals [7, 8], radioimaging agents and biologically active compounds [9].

Our group has developed the electrochemical synthesis in acetonitrile of aromatic chalcogeno derivatives of types **1** and **2** (E = Se, Te) [10–14], from aryl halides ArX and electrogenerated PhE^- and E_2^{2-} anions, by $S_{RN}1$ induced substitution reaction [15–18]. The chalcogenate anions **2** which are precursors of numerous chalcogeno derivatives, are stored in their oxidized form **3** (electrochemical or chemical oxidation). See Table 1.

The one-pot cathodic synthesis of **1** and **2** takes place in two steps. The nucleophile PhE^- or E_2^{2-} is generated first by reduction of PhEEPh (graphite cloth cathode) [10, 11] or E (tea bag-type cathode made from a piece of graphite cloth and Se granules or Te pellets) [12–14] (Equation 1). Then *one equivalent* of aryl halide (ArX) is introduced and reduced to $Ar^\cdot$ (Equations 2 and 3), directly or indirectly by a redox mediator (med). The aryl radical can then react with the nucleophile (keystep 4) or undergo a side reaction (**5**) with further reduction of $^\cdot CH_2CN$ to $^-CH_2CN$. Hence, in the second step, the formation of ArE^- and ArH consumes one and two electrons, respectively.

$$PhEEPh\ (\text{or } 2E) + 2e^- \rightleftharpoons 2\ PhE^-\ (\text{or } E_2^{2-}) \quad (1)$$

$$ArX + e^- \rightleftharpoons [ArX]^{\cdot -} \quad (2)$$

$$[ArX]^{\cdot -} \xrightarrow{k_1} Ar^\cdot + X^- \quad (3)$$

$$Ar^\cdot + PhE^-(\text{or } E_2^{2-}) \xrightarrow{k_2} [ArEPh]^{\cdot -}(\text{or } [ArE_2^-]^{\cdot -}) \quad (4)$$

$$Ar^\cdot + CH_3CN \xrightarrow{k_H} ArH + {}^\cdot CH_2CN \quad (5)$$

Previous results have shown that this electrochemical technique can compete favourably with classical chemical methods [19, 20]. It is especially useful for aryl halides which are either unactivated, and therefore sluggish in S_NAr reactions [21], or substituted by unsaturated groups (C=O, C≡N) [10, 22, 23] since, in the latter case, they cannot be converted into Grignard or lithium reagents that react with selenium or tellurium by insertion. Furthermore, although it is generally observed that the hydrogenation reaction (5) is slightly faster in MeCN than in DMSO [24–28], it has been shown that the keystep (4) is more rapid in MeCN than in DMSO [14, 29], and that the yields of substituted compounds are therefore higher in the former solvents. Hence, MeCN is a more suitable solvent for the electrochemical synthesis of **1**–**3**.

Up to now, all of the electrolyses have been carried out at controlled potential in a three-compartment cell equipped with membranes, in order to minimize migration of the nucleophiles PhE^- and E_2^{2-} to the anodic compartment. However, a main disadvantage of such a cell is that degradation of the membranes takes place as the electrolysis proceeds. Indeed the ion-exchange membranes (area: $6\,cm^2$) Ionax MA 3475 (anodic side) and MC 3470 (cathodic side) become too resistive after passage of $1.4\,mF\,cm^{-2}$, and so only small amounts of chalcogeno derivatives can

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Table 1.

ArEPh	*ArE*$^-$	*ArEEAr*
1	**2**	**3**
a: Ar = 4-NCC$_6$H$_4$, E = Se		**a**: Ar = 2-quinolyl, E = Se
b: Ar = 1-Naphthyl, E = S		**b**: Ar = 2-quinolyl, E = Te

be prepared. To circumvent this problem, a method was investigated, involving an undivided cell, which avoids the problems due to separators, and a sacrificial anode which is more readily oxidized than the PhE$^-$ and E$_2^{2-}$ anions. Sacrificial magnesium, zinc and aluminium anodes [30–33] are commonly used in synthetic electrochemistry carried out in an undivided cell, because their oxidized cationic forms Mg^{2+}, Zn^{2+} and Al^{3+} can either play a beneficial role in the electrochemical process, or give insoluble or nonelectroactive salts. The undivided cell can also simplify the scaling-up process.

It is shown below, by means of voltammetry and preparative electrolysis, that the synthesis of the chalcogeno prototypes **1a, b** and **3a, b** can be carried out at constant current, in an undivided cell equipped with a sacrificial magnesium anode, in yields comparable to those previously obtained, if a fluoride salt is added either before the electrolysis (case of E$_2^{2-}$) or after the first step (case of PhE$^-$). The F$^-$ anions prevent the formation of the complexes MgE$_2$ and Mg(EPh)$_2$, and as a consequence, the electrogenerated nucleophiles PhE$^-$ and E$_2^{2-}$ remain available for reaction with Ar$^{\cdot}$.

2. Experimental details

Magnesium rod (diam.: 6 mm; 99%), aluminium rod (diam.: 6.35 mm; 99.999%), zinc wire (diam.: 2.0 mm; 99.9999%), selenium and tellurium granules (99.99%) were purchased from Aldrich, and graphite cloth was obtained from Carbone Lorraine. Analytical grade MeCN (spectrosol SDS) was carefully dried on neutral alumina.

Voltammograms at a glassy carbon rotating disc electrode (V25 Carbone Lorraine; dia.: 3 mm) were obtained by using a Tacussel PRT 20-2X potentiostat connected to a differential amplificator and a Sefram T6M 107 *X*–*Y* recorder. An Amel 552 potentiostat/galvanostat (200 V output at full load) and a Tacussel IG5-N integrator were used in preparative electrolysis and coulometry. All the potentials referred to the aqueous saturated calomel electrode (SCE). Prior to and during electrolysis, the solution contained in the undivided cell was stirred mechanically and deaerated with argon.

The GC determination of **1b** is described in [29].

2.1. *Electrochemical synthesis of PhE*$^-$ *anions (E = S, Se)*

Electrochemical synthesis of the PhE$^-$ anions generated for the voltammetric study was carried out in an undivided cell which was filled with 50 ml MeCN, 0.1 M supporting electrolyte and 2 mmol PhEEPh. The sacrificial anode was a magnesium rod, aluminium rod or zinc wire. The cathode was a cylindrical graphite cloth, and built from a piece of tissue 10 cm × 3 cm. A constant current (100 mA) was applied giving a current density of about 4 mA cm^{-2}, taking into account the nature of the cathode which is not rigid, and estimating its external area to be 25 cm^2. The electrolysis was stopped after consumption of 4 m*F* or 6 m*F* (case of PhSe$^-$).

2.2. *Preparative electrolysis*

Preparative electrolyses of **1a, b** were carried out in the cell described above, which contained 50 ml MeCN and 0.1 M supporting electrolyte. In the case of **3a, b**, a tea bag-type cathode replaced the cylindrical graphite cloth. The former was built from a piece of graphite cloth (6 cm × 6 cm) and filled with selenium or tellurium granules (4 mmol). Two typical electrolyses are described below.

2.2.1. Preparation of ***1a*** *(entry 1 of Table 3).* PhSeSePh (2.2 mmol) was introduced into the cell containing 0.1 M NaClO$_4$, and reduced to PhSe$^-$ at constant current (100 mA). After consumption of 4.4 m*F* and interruption of electrolysis, Et$_4$NF.2H$_2$O (6 mmol; 0.12 M), 4-chlorobenzonitrile (4 mmol; 0.8 M) and *t*-BuOH (16 mmol; 0.32 M) were introduced and a current of 20–50 mA was applied. After consumption of 2.72 m*F*, the electrolysis was stopped. Air was bubbled for 30 min, then the electrolysis solution was diluted with water (200 ml) and extracted with diethyl ether (150 ml × 3). After the solution was dried and the ether removed, the crude product was separated by column chromatography (Kieselgel) with 1/9 acetone/hexane as eluant, and so **1a** and 4,4′-dicyanodiphenyl selenide were successively isolated in 73% and 16% yields.

2.2.2. Preparation of ***3a*** *(entry 5 of Table 3).* In the cell containing selenium granules and Bu$_4$NPF$_6$ (0.1 M), were added 10 mmol Et$_4$NF (0.2 M), then a constant current (100 mA) was applied until consumption of 4.4 m*F*. The electrolysis was interrupted, and 2-chloroquinoline (2 mmol; 0.04 M) was introduced and reduced at a constant current, $I_0 = 25$ mA. The electrolysis was stopped after consumption of 4.5 m*F*. The electrolysis solution was diluted with

Table 2. Voltammetric determination of the amount of uncomplexed PhE^- anions upon addition of $Et_4NF.2H_2O$ after reduction of PhEEPh to PhE^- in an undivided cell filled with $MeCN–Bu_4NPF_6$ (0.1 M) and containing a sacrificial anode

Anode	PhEEPh	$Et_4NF.2H_2O$ /equiv.*	Uncomplexed PhE^- /%
Mg	PhSSPh	0	4
		1.5	100
	PhSeSePh	0	25
		1.5	100
Zn	PhSSPh	0	0
		1	25
		large excess	75
Al	PhSSPh	0	0

* Relative to PhE^-

200 ml deoxygenated water containing 10 mmol $K_3Fe(CN)_6$, and extracted as above. The crude product was purified by chromatography (2/8 acetone/hexane as eluant) and so **3a** was isolated in 79% yield.

3. Voltammetric study of PhE^- anions generated in an undivided cell

In MeCN/toluene, PhE^- anions (E = S, Se) are known to form complexes with metallic cations [34, 35]. Thus, it has been established by Kumar and Tuck [35] that the complex $Zn(SePh)_2$ is generated in high yield according to Equations 6–8 (M = Zn, n = 2, E = Se) when a zinc anode is immersed in an undivided cell filled with a solution of MeCN/toluene-Et_4NClO_4 containing PhSeSePh. In the search for a new method involving an undivided cell to generate about an equivalent of chalcogeno nucleophile PhE^- or E_2^{2-} prior to the introduction of ArX into the cell, complexations 8 or 9 have to be totally avoided. The absence of data in the literature on the fate of these nucleophilic anions in the presence of Mg^{2+}, Zn^{2+}, and Al^{3+} led us to examine first by voltammetry, the electrochemistry in pure CH_3CN of the PhE^- anions when they are electrogenerated in an undivided cell, using magnesium, zinc or

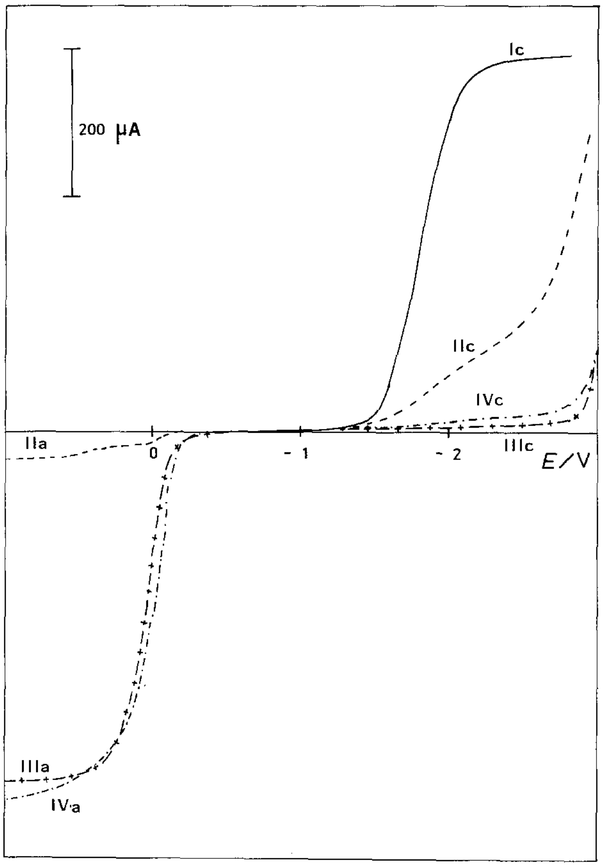

Fig. 1. Voltammetric follow-up of the electrolysis of PhSSPh to PhS^- in a beaker-type cell containing a magnesium anode (see text). The 'a' and 'c' indexed curves relate to the anodic and cathodic currents, respectively. Curve I: Before electrolysis. (PhSSPh) = 4 mM in the voltammetric cell. Curve II: After consumption of 2 equiv. of electrons per mole of PhSSPh. Curve III: PhS^- (8 mM). Curve IV: Curve II + addition of 3 equiv. of Et_4NF. $2H_2O$ per mole of PhSSPh.

Table 3. Results of preparative electrolyses in an undivided cell equipped with a Mg anode

ArX	4-ClC_6H_4CN	1-BrNaPh		2-chloroquinoline		
	1	2	3	4	5	6
mmol	4^a	4^b	8^b	2	2	2
Nucleophile	$PhSe^-$	PhS^-	PhS^-	Se_2^{2-}	Se_2^{2-}	Te_2^{2-}
equiv.	(1.1)	(1.1)	(1.1)	(1)	(1)	(1)
Electrolyte^c (0.1 M)	$NaClO_4$			Bu_4NBr		
Et_4NF/equiv	1.5	2.5	2.5	–	5	5
I_0/mA	20–50	20	20	20	25	50
n_2/equiv.	0.68	0.50	0.44	2.78	2.25	2.60
Product	*1a*	*1b*	*1b*	*3a*	*3a*	*3b*
Yield/%^{d}	73^e	75^f	84^f	8	79	48
Yield/%^{d,g}	(70)	$(88)^f$			(70)	$(38)^h$
	[22]	[29]			[14]	[14]

[a] Addition of t-BuOH (4 equiv.) as proton donor.
[b] Addition of 2-cyanopyridine (0.25 equiv.) as mediator.
[c] Bu_4NPF_6 if no specification.
[d] Isolated yield if not otherwise specified.
[e] 4,4′-dicyanodiphenyl selenide isolated as minor compound (16%).
[f] GC determination taking into account some ArX left.
[g] Divided cell.
[h] Simultaneous reduction of ArX and Te.

aluminium as the anode, and a variety of supporting electrolytes including Bu_4NX ($X = PF_6$, ClO_4, Cl, F), Et_4NF, $MClO_4$ (M = Li, Na).

$$M \xrightarrow[\text{anode}]{-ne^-} M^{n+} \qquad (6)$$

$$\frac{1}{2}\ \text{PhEEPh} \xrightarrow[\text{cathode}]{+e^-} \text{PhE}^- \qquad (7)$$

$$M^{n+} + n\ \text{PhE}^- \rightleftharpoons M(\text{EPh})_n \qquad (8)$$

$$M^{n+} + \frac{n}{2}\ E_2^{2-} \rightleftharpoons ME_n \qquad (9)$$

3.1. *Results and discussion*

This study was carried out at a glassy carbon rotating disc electrode (RDE) under the experimental conditions of a preparative electrolysis. Hence PhEEPh (2 mmol) was introduced into an undivided cell equipped with a cathode made of a cylindrical graphite cloth and a sacrificial anode, and containing 50 ml MeCN+ 0.1 M supporting electrolyte. Prior to electrolysis 1 ml of this solution was transferred to a cell containing 9 ml MeCN + 0.1 M Bu_4NPF_6, and the first voltammogram was recorded (curve I). After application of a constant current (100 mA) and the consumption of 4 m*F*, a second voltammogram was recorded (curve II).

A set of results involving a magnesium anode, Bu_4NPF_6 as supporting electrolyte, and the reduction of PhSSPh to PhS^- is given in Fig. 1. The cathodic wave Ic is assigned to the reduction wave of PhSSPh before electrolysis, and the anodic wave IIa to the oxidation wave of the PhS^- anions which are available after electrolysis, that is to say, which are not complexed. This figure shows that something sequesters PhS^-, possibly $Mg(SPh)_2$ according to Reaction 8 (M = Mg, n = 2, E = S). This complexation takes place almost quantitatively in Bu_4NPF_6, since the amplitude of the limiting current of wave IIa is only 4% of the value obtained in a three compartment-cell (curve IIIa) where there is no complexation. Hence, it can be concluded that about 96% of the PhS^- anions are complexed. The ill-defined cathodic wave IIc may be associated to the reduction of this complex (*vide infra*). The addition of $Et_4NF.2H_2O$ nearly quantitatively regenerates the uncomplexed PhS^- anions (curve IVa). This result shows that Reaction 10 now predominates. Furthermore, there is very little cathodic current left (curve IVc), and so it can be reasonably concluded that the ill-defined wave IIc corresponds to the reduction of the former complex $Mg(SPh)_2$.

$$Mg^{2+} + 2F^- \rightleftharpoons MgF_2 \qquad (10)$$

Uncomplexed PhS^- anions can also be generated in other supporting electrolytes such as Bu_4NBr and Bu_4NCl, in 14% and 44% yields, respectively. Our finding that 14% of PhS^- is not complexed in $MeCN–Bu_4NBr$ is consistent with the results obtained recently by a Russian group [36] which has shown that the addition of thiols to olefins was a catalytic process which could be initiated by electrogenerated thiolate anions, under galvanostatic conditions, in MeCN containing Et_4NBr or Bu_4NBr, and a sacrificial magnesium anode. In the present experiments with Bu_4NBr and Bu_4NCl, it is observed that the uncomplexed PhS^- anions are nearly quantitatively regenerated by the addition of a fluoride salt such as $Et_4NF.2H_2O$ or $Bu_4NF.3H_2O$, after electrolysis.

In the presence of PhSeSePh (2 mmol), a magnesium anode and Bu_4NPF_6 as supporting electrolyte, a voltammetric study gives results which are similar to the preceding ones, albeit more complex, as shown in Fig. 2. The upper curves correspond to a consumption of 4 m*F* as in Fig. 1, and the bottom curves to one of 6 m*F*. Under these latter conditions, the curves are very similar to those of Fig. 1 and it is observed that 25% of $PhSe^-$ anions (wave IIa of Fig. 2) are not complexed to $Mg(SePh)_2$ (wave IIc of Fig. 2) and that the addition of F^- anions (6 mmol) can completely release the complexed $PhSe^-$ anions (wave IVa of Fig. 2). After consumption of only 4 m*F* and addition of F^- anions, there is only 75% of $PhSe^-$ anions available (wave IV′a of Fig. 2) together with 25% of unreduced PhSeSePh (wave IV′c of Fig. 2). Hence more than

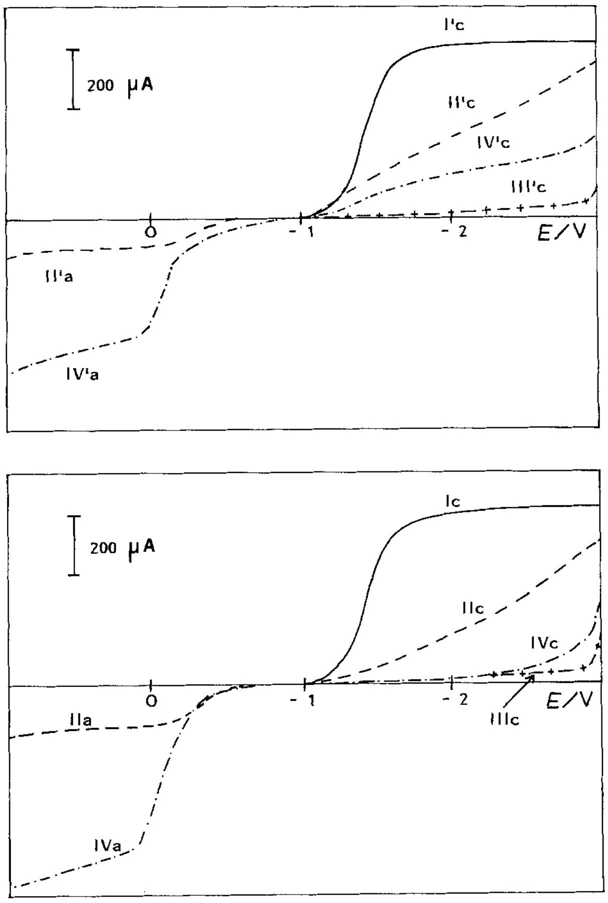

Fig. 2. Voltammetric follow-up of the electrolysis of PhSeSePh to $PhSe^-$ under the same conditions as in Fig. 1. Curves I, I′: Before electrolysis. (PhSeSePh) = 4 mM in the voltammetric cell. Curves II, II′: After consumption of 2 equiv. (curve II′) and 3 equiv. (curve II) of electrons per mole of PhSeSePh. Curves III, III′: Supporting electrolyte. Curve IV, IV′: Curves II, II′ + addition of 3 equiv. of $Et_4NF.2H_2O$ per mole of PhSSPh.

two electrons are consumed to reduce quantitatively PhSeSePh to $PhSe^-$. An overconsumption of electricity is commonly observed in undivided cells [37]. In the present case, it may involve the concomittant cathodic reduction of PhSeSePh and Mg $(SePh)_2$, and the concomittant anodic oxidation of $PhSe^-$ and magnesium. In $NaClO_4$ as supporting electrolyte, the amounts of uncomplexed $PhSe^-$ anions and unreduced PhSeSePh are 86% and 14%, respectively, after consumption of 4 m*F* and addition of F^- anions.

From the above result, it may be concluded that uncomplexed PhE^- anions can be regenerated, whatever the supporting electrolyte, by addition of F^- anions *after electrolysis*. It has been observed that these latter anions react with PhEEPh, which eliminates the possibility of adding F^- *before electrolysis*. This is shown in Fig. 3 in the case of PhSSPh and addition of $Bu_4NF.3H_2O$. Wave Ic of Fig. 3 corresponding to the reduction of PhSSPh is replaced by an ill-defined cathodic wave, IIc, to which is associated an anodic wave IIa. This suggests a nucleophilic attack of the type shown in Reaction 11 ($Ar = Ph$, $Nu^- = F^-$), similar to what occurs when ^-OH [38] or $^-CH_2CN$ [39] anions are present. This investigation has not been pursued further.

$$ArEEAr + Nu^- \longrightarrow ArE^- + ArENu \qquad (11)$$

A voltammetric study carried out with aluminium and zinc anodes shows a nearly quantitative complexation of the PhS^- anions (Table 2), which is consistent with the observations made previously by Kumar and Tuck [35] for a zinc electrode immersed in a MeCN/toluene–Et_4NClO_4 solution containing PhSeSePh. Furthermore, uncomplexed PhS^- anions are only partially regenerated by the addition of excess $Et_4NF.2H_2O$ (Table 2).

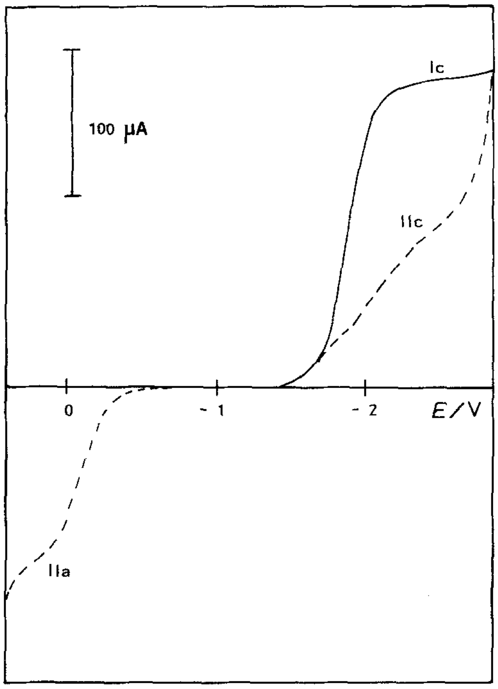

Fig. 3. Voltammograms of PhSSPh (1.46 mM) before (curve I) and after addition (curve II) of $Bu_4NF. 3H_2O$ (0.1 M). The 'a' and 'c' indexed curves relate to the anodic and cathodic currents, respectively.

3.2. *Conclusion*

The results show that PhE^- can be regenerated almost quantitatively in MeCN, only if magnesium is the anode and if the addition of a fluoride salt is made *after electrolysis*, which thus avoids the complexation, Reaction 8. It is worth noting that this reaction did not take place in an undivided cell equipped with a sacrificial magnesium anode and filled with liquid ammonia–KBr or NaCl, and containing PhSSPh [32, 33]. Similarly, it did not occur in MeOH–$NaClO_4$ solutions containing PhSeSePh [40]. In both cases, an insoluble salt MgX_2($X = Br$, Cl, ClO_4) was precipitating during electrolysis, and so PhS^- or $PhSe^-$ were not complexed.

No voltammetric studies were carried out with the air sensitive and unstable E_2^{2-} anions. Nevertheless, it may be reasonably assumed that the conclusions drawn from the preceding voltammetric study will hold, at least qualitatively, for these anions, since we have observed similar nucleophilic properties for PhE^- and E_2^{2-} anions in $S_{RN}1$ reactions.

4. Preparative electrolysis

Preparative electrolyses of **1a, b** were carried out at constant current in an undivided cell equipped with a cylindrical graphite cloth cathode. In the case of **3a, b**, a selenium or tellurium tea bag-type electrode replaces the preceding graphite cloth cathode, and it plays a double role. In the first step of electrolysis, its selenium or tellurium granules (4 mmol) are almost entirely reduced to Se_2^{2-} or Te_2^{2-} (2 mmol) and so its graphite envelope constitutes the cathode in the second step. In the first step, the PhE^- or E_2^{2-} anions are generated at a constant current of 100 mA. In the second step, a lower current (I_0) is applied to minimize competing reactions, such as Reactions 12 and 15, when a redox mediator is necessary (case of **1b**).

The synthesis of **1a** in good yield (entry 1 of Table 3) can be carried out with an inexpensive electrolyte ($NaClO_4$). In the first step of electrolysis, PhSeSePh is reduced to $PhSe^-$, then $Et_4NF.2H_2O$ and *t*-BuOH are added in excess, together with 4-chlorobenzonitrile (1 equiv). During the second step, the synthesis of **1a** is performed in the presence of *t*-BuOH to avoid the formation of ^-OH from residual water and the formation of benzamide derivatives [22]. The synthesis of **1a** is accompanied by that of the symmetrical 4,4′-dicyanodiphenyl selenide in both divided (8%) [22] and undivided (16%) cells.

The synthesis of **1b** from 1-bromonaphthalene (entries 2 and 3) requires a redox mediator in order to avoid the cathodic side reaction $Ar^\cdot + e^- \longrightarrow Ar^-$ [29]. Thus, by addition of 2-cyanopyridine, the naphthyl radicals are generated in the bulk of the undivided cell, according to Reactions 13, 14 and 3. In this indirect synthesis, the inexpensive supporting electrolyte used for the synthesis of **1a** ($NaClO_4$) cannot be used since $med^{\cdot -}$ forms an ion-pair with Na^+ ($med^{\cdot -} + Na^+ \rightarrow medNa^{\cdot}$), and so Bu_4NPF_6 is preferable. By increasing the amount of 1-BrNaPh and PhS^-, the yield of **1b** is increased (compare entries 2 and 3 of Table 3) which is in agreement with the fact that the yields of **1** and **3** increase with $k_2(Nu^-)/k_H$ [11, 14].

In the second step of the synthesis of **1a** and **1b**, the low consumption of electricity ($n_2 < 1$) is consistent with a competition between a pure catalytic process ($n_2 = 0$) and minor bielectronic processes leading to ArH, such as Reactions 5, 12 and 15.

$$Ar^{\cdot} + (ArX)^{\cdot -} \rightleftharpoons Ar^- + ArX \qquad (12)$$

$$med + e^- \rightleftharpoons med^{\cdot -} \qquad (13)$$

$$ArX + med^{\cdot -} \rightleftharpoons [ArX]^{\cdot -} + med \qquad (14)$$

$$Ar^{\cdot} + med^{\cdot -} \rightleftharpoons Ar^- + med \qquad (15)$$

Concerning the synthesis of **3a, b**, a preliminary electrolysis carried out in the absence of F^- anions and with Bu_4NBr as supporting electrolyte, has shown that the indirect synthesis of **3a** proceeds in very low yields (8%) (entry 4 of Table 3), whereas its synthesis in a divided cell can reach 70% [14]. These results suggest that, as in the case of the PhE^- anions, the Se_2^{2-} are sequestered, likely $MgSe_2$, and that the F^- anions can play again a beneficial role in the synthesis of **3a, b**. The fluoride salt can be indifferently added before or after the first step of electrolysis, since there is no attack of the selenium or tellurium granules by the F^- anions. For convenience sake, the two steps are carried out in the presence of $Et_4NF, 3H_2O$ (0.2 M) + Bu_4NPF_6 (0.1 M). The second electrolyte (Bu_4NPF_6) is needed because the electrolysis solution was too resistive in the only presence of the fluoride salt. The final oxidation step is performed chemically, according to the technique described by Engman and Persson [20], by addition of an aqueous solution of $K_3Fe(CN)_6$. Under such oxidative conditions, the nucleophilic attack (Reaction 11) ($Nu^- = F^-$) of the final compounds **3a, b** by excess F^- is not observed.

The results of Table 3 (entries 5 and 6) show that the n_2 values involved in the synthesis of **3a, b**, are higher than the values expected from a competition between the $S_{RN}1$ process ($n_2 = 1$) and the reduction processes leading to ArH ($n_2 = 2$), which suggest an over-consumption of electricity, as already mentioned for the electrogeneration of $PhSe^-$ anions.

In Table 3 are also given in parentheses the yields of **1a, b** and **3a, b** previously obtained in a divided cell with a cathodic compartment of 100 ml. For a given amount of electrogenerated nucleophile, the yields are usually better in a beaker-type cell than in a divided cell, which is consistent with the volumes for the electrolysis compartment, since the initial concentration of nucleophile is 50% lower in the divided cell, making keystep 4, therefore slower (*vide supra*). The only exception is the case of **1b**, whose synthesis involves a redox mediator. Although this discrepancy is not well understood, it may involve some direct cathodic reduction of 1-bromonaphthalene to naphthalene.

5. Conclusion

Although the electrochemical synthesis in a beaker-type cell, of chalcogeno derivatives of types **1–3** appears *a priori* as a challenge in MeCN, it can be carried out successfully in comparable yields to those obtained in a divided cell. The technique consists in equipping the cell with a sacrificial magnesium anode and adding a fluoride salt at an appropriate time in the MeCN/supporting electrolyte solution. Compared to a divided cell, larger amounts of substituted compounds can thus be prepared in comparable yields, by means of inexpensive electrochemical instrumentation. Hence this new methodology is a powerful tool in the synthesis of chalcogeno derivatives.

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