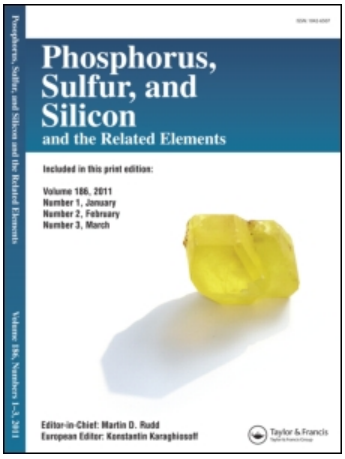

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ELECTROCHEMICAL SYNTHESIS OF SELENO AND TELLURO DERIVATIVES IN MeCN

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Abstract Large-scale electrolysis with concurrent sonication in MeCN allows for the synthesis of a large variety of seleno and telluro derivatives. Aliphatic chalcogenides REER or RER (E = Se, Te) can be prepared by reduction of E powder to E_2^{2-} or E^{2-}, followed by addition of an alkyl halide RX. Depending upon R, substitution can compete with homogeneous electron or H^+ transfers. RE^+ can be prepared by anodic oxidation of REER, and trapped by nucleophiles and olefins. The synthesis of aromatic chalcogenides ArEAr' can be carried out by electrochemically induced $S_{RN}1$ substitution. The yields are improved by redox catalysis. Under such conditions, the synthesis of PhEAr (Ar = NCC_6H_4, $PhCOC_6H_4$) proceeds in good yields. ArEEAr and ArEAr can be prepared by cathodic reduction of PhEAr.

The synthesis of organic seleno and telluro derivatives by electrochemical means has been little explored. The main results have concerned the anodic oxidation of commercially available PhSeSePh to $PhSe^+$ which can be trapped by alkenes and alkynes.[1,2] In MeCN, acetamidoselenation of double and triple bonds has been successfully carried out in high yields. Recently, Berge, et al., have described a method for the electrochemical synthesis of aliphatic and aromatic dichalcogenides in N,N-dimethylformamide (DMF), which involved sacrificial Se and Te electrodes.[3,4]

We now show that a large variety of alkyl and aryl chalcogenides 1-5 can be prepared in high to moderate yields by electrochemical synthesis in MeCN, with sonication, at room temperature. All the large-scale electrolyses were carried out at controlled potential in a H-type cell equipped with membranes and

filled with MeCN containing 0.1 M Bu_4NPF_6 or 0.1 M Bu_4NBF_4. The cell was deaerated by passage of a stream of argon and immersed in a sonic cleaning bath (vat Bransonic) filled with cold water. The cathode was composed of a graphite tissue or a Pt grid, the anode of a Pt grid and the reference cell was a saturated calomel electrode.

REER	ArEEAr	RER	ArEAr	ArEAr'	(E = Se,Te)
1	2	3	4	5	

ELECTROCHEMICAL SYNTHESIS OF ALKYLCHALCOGENIDES 1 AND 3 BY S_N2 SUBSTITUTION

The total insolubility of Se or Te powders in aprotic solvents hinders their cathodic reduction under magnetic stirring. Ultrasonic stirring overcomes this difficulty.[5] In MeCN at a carbon cloth, the ultrasound-induced electrochemical reduction of Se and Te powders occurs beyond -0.8 V and - 1.1 V, respectively.

Ultrasound-induced one-electron reduction of Te powder followed by addition of benzyl chloride (1 equiv.; 15 min. of contact) gave unstable dibenzyl ditelluride in 70% isolated yield. Under the same experimental conditions, reduction of Se powder gave an almost quantitative yield of the diselenide (entry 1 of Table 1). Similar results were observed with p-cyanobenzyl chloride (entry 2), whereas moderate yields of the diselenide were obtained when 9-chlorofluorene (FlCHCl) and phenacyl chloride were used as electrophiles. These latter results indicate the occurrence of competitive reactions. In electrolysis no 4, the homogeneous reduction of readily reduced diphenacyl diselenide ($E_{1/2}$ = - 0.9 V in voltammetry at a carbon rotating disc electrode) by Se_2^{2-} anion occurred (eq. (1)), which gave the corresponding monoselenide 3d. Similarly, formation of fluorene (which could be oxidized to

fluorenone by residual oxygen during electroysis) and acetophenone arose from the homogeneous reduction of FlCHCl and phenacyl chloride (eq. (2)) since both of them are easily reduced ($E_{1/2}$ = - 1.6 V and - 1.3 V, respectively). Formation of bisfluorenylidene FlC=CFl was associated with strong basic conditions in the bulk of the cathodic solution which promoted the deprotonation of FlCHCl (eq. (3)).[6a]

$$Se_2^{2-} + \underset{1}{RSeSeR} \longrightarrow 2Se + 2RSe^- \xrightarrow{+\ 2RX} \underset{\underline{3}}{RSeR} + 2X^- \qquad (1)$$

$$Se_2^{2-} \xrightarrow{+\ RX} 2Se + X^- + R^- \xrightarrow{+\ SH} RH + S^- \qquad (2)$$

(SH = CH_3CN, H_2O)

$$FlCHCl \xrightarrow[-BH]{+\ B^-} Fl\bar{C}Cl \xrightarrow[-\ Cl^-]{+FlCHCl} FlCClCHFl \xrightarrow{-\ HCl} FlC{=}CFl \qquad (3)$$

Taking into account reaction (1), lower yields of diselenide and competitive formation of monoselenide were expected and effectively observed[6c] when RX was present <u>during</u> electroysis (compare entries 1 and 2 with entries 5 and 6 in Table 1).

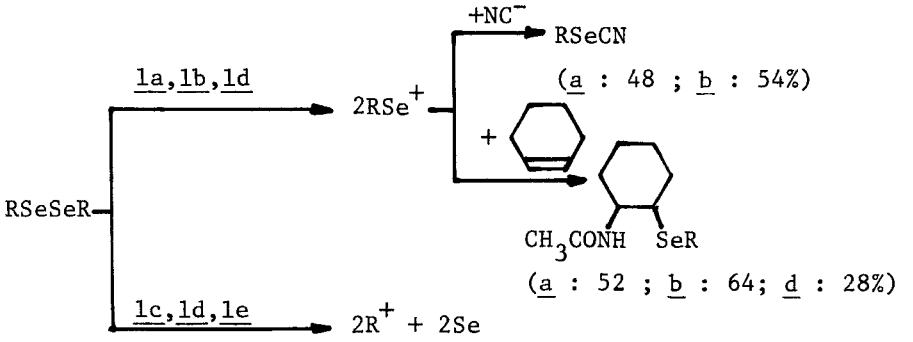
When E^{2-} was generated and RX added afterwards, homogeneous electron-exchanges E^{2-}/RX were even more favorable than with E_2^{2-}. This may explain, at least partially, the moderate yields of dibenzyl selenide (50%) and telluride (37%) reported in ref. 5a (N.B The cell was equipped with fritted glasses which did not prevent E^{2-} migration towards the anodic compartment).

The diselenides <u>1a-d</u> included in Table I and dibenzyhydryldiselenides (<u>1e</u>) were oxidized at a Pt anode grid with sonication or mechanical stirring. The results, which did not depend on the stirring technique, are summarized below.[6b,c]

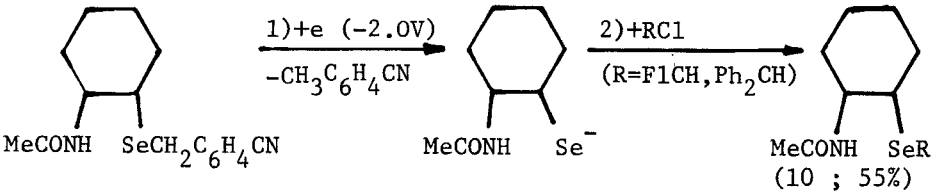
TABLE I Electrochemical synthesis of RSeSeR and RSeR

Entry	RX	RSeSeR (yield %)	RSeR (yield %)	other isolated compounds
1	$PhCH_2Cl$	1a(98)		
2	$p\text{-}NCC_6H_4CH_2Cl$	1b(93)		
3	$FlCHCl$	1c(50)		$FlCH_2$, $FlC{=}CFl$, $FlC{=}O$
4	$PhCOCH_2Cl$	1d(36)	3d(39)	$PhCOCH_3$
5	$PhCH_2Cl$[a]	1a(63)	3a(36)	
6	$p\text{-}NCC_6H_4CH_2Cl$[a]	1b(22)	3b(29)	$NCC_6H_4CH_3$

[a] RX present during electrolysis



In the case of 1c and 1e which gave exclusively the cation R^+, stabilized by resonance, the corresponding seleno acetamides could not be anodically obtained. Nevertheless, they could be cathodically prepared as follows[6c]:



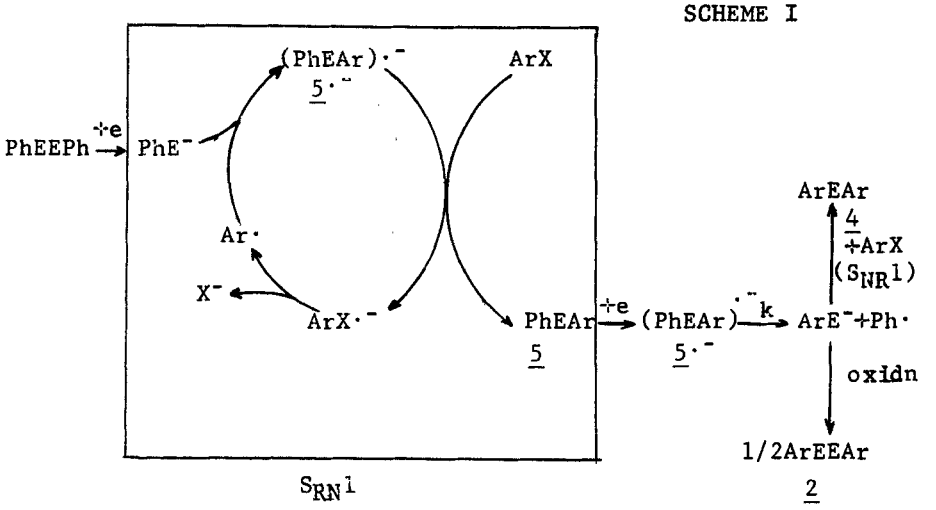
ELECTROCHEMICAL SYNTHESIS OF AROMCATIC CHALCOGENIDES 2, 4 AND 5 BY ELECTROCHEMICALLY INDUCED $S_{RN}1$ SUBSTITUTION

In the aromatic series, substitutions are energetically unfavorable and drastic experimental conditions (high temperatures) are usually required to prepare aromatic chalcogeno derivatives 2 and 4 from chemically generated E_2^{2-} and E^{2-} anions and ArX (see for instance the recent ref. 7). Therefore, under our experimental conditions, the synthesis of the dichalcogenides 2 and 4 by substitution is not expected to be successfuly. Indeed, addition of chloro- or bromobenzonitrile to electrochemically generated Se_2^{2-} or Te_2^{2-} provide no 2. The addition of o-bromonitrobenze to Se_2^{2-} gave the expected diselenide 2 in 62% yield (24% of electrophile was recovered) although, in this case, the synthesis of 2 probably took place through a different mechanism which probably involved the intermediate formation of $NO_2C_6H_4^{\cdot}$ radical (analogy with the $XC_6H_4NO_2/O_2^{\cdot -}$ system, see ref. 9b for a review). It is worth noting that this diselenide was obtained in better yield (92%) by the use of a sacrificial Se electrode.[3a] The synthesis of o-nitrophenylditelluride from o-bromonitrobenzene and one-electron reduction of Te powder, was unsuccessful.[8a] Two minor compounds were isolated, including the corresponding monotelluride.

Since substitution in aromatic series failed under our experimental conditions, we have adopted the strategy summarized in Scheme I in order to prepare 2 and 4. The key-stop is the synthesis of 5 by electrochemically induced $S_{RN}1$ substitution (for reviews on $S_{RN}1$ substitution induced photochemically and electrochemically, see refs. 9-11).

In order to prepare 5, large-scale electrolysis with sonication was performed in two steps, as follows. First, commercially available PhEEPh was cathodically reduced in PhE^-, then ArX (1 equiv.) was added and the applied potential shifted to a value where ArX was reduced. The electrolysis was stopped after total

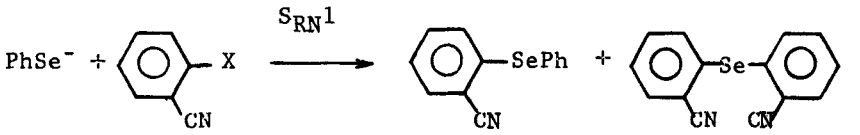
SCHEME I



depletion of the faradaic current (total consumption of ArX).

Electrolysis of PhSeSePh followed by addition and reduction at - 1.7 V of o-bromobenzonitrile gave the expected phenylselenobenzonitrile 5a in 36% yield (Scheme II).[12a] This moderate yield was due to a partial deactivation of the intermediate $NCC_6H_4\cdot$ radical by its further cathodic reduction to $NCC_6H_4^-$. Bromoarene radical anions $ArBr\cdot^-$ are known to be very unstable and to decompose into R· and Br^- close to the electrode. The yield of 5a could be improved by using o-chlorobenzonitrile whose radical anion is more stable. The formation of 4a as a minor compound shows that the intermediate $NCC_6H_4SePh\cdot^-$ was very unstable and gave Ph· and $NCC_6H_4Se^-$ which was involved in the $S_{RN}1$ mechanism.

SCHEME II



5a 36 % (X=Br) 4a traces (X=Br)
58 % (X=Cl) 3 % (X=Cl)

The best yields of substitution products 4a (5%) and 5a (65%) were obtained under the conditions of redox catalysis.[9b,11,13,14] Electrolysis of PhSeSePh to $PhSe^-$ was followed by the addition of a mixture of o-chlorobenzonitrile and 1,2-di(bipyridylethylene) (0.1 equiv.) as mediator, and the electrolysis was carried out at -1.55 V until total depletion of the faradaic current. At this potential, the mediator, P, was the only species reduced at the electrode and so, indirect reduction of ArX by $P\cdot^-$ took place in the bulk of the solution ($P\cdot^- + ArX \longrightarrow P + (ArX)\cdot^-$) and 0.17 electron-equivalent per mole of 2-chlorobenzonitrile was consumed in the $S_{RN}1$ mechanism. Since two electrons were involved in the competition formation of $NCC_6H_4^-$ (protonated to PhCN), the substitution products were thus obtained in 91.5% of theoretical yield (Table II). The two series of isomers 5a-c and 5d-f were isolated in good yields (Table II).[12b] In the Te series, the competitive formation of 4d and 5d in 31 and 47% yields, respectively, indicates a high decomposition rate k for the $5d\cdot^-$ intermediate (scheme I). From the yields of 4d-f in Table II, it can be concluded that k decreases in the order $k_o > k_p >> k_m$. Substituted benzophenone were also prepared under similar conditions (Table II), with azobenzene as mediator.[12c] A weak acid such as fluorene was added to avoid the deprotonation of the solvent and the formation of $^-CH_2CN$ anion which is known to add to the carbonyl group of benzophenone.[15]

Experiments are currently in progress to prepare ArEEAr by the cathodic reduction of ArEPh (Scheme I): Preliminary results show that large-scale electrolysis of 5b or 5c followed by air oxidation of the cathodic solution gave the expected diselenide 2 whereas the ortho-substituted isomer 5a behaved differently.[8b]

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TABLE II Mediated electrochemical synthesis of 4 and 5

E	ArX	isom.	Theoretical (yield/%)	ArEPh (yield/%)	ArEAr (yield/%)
Se	NCC_6H_4Cl	o	91.5	5a(65)[a]	4a(5)
		m	93	5b(72)[a]	4b(9)
		p[b]	89	5c(74)	4c(8)
Te	NCC_6H_4Cl	o	87.5	5d(47)[c]	4d(31)[d]
		m	95	5e(48)[a]	4etraces
		p[b]	92	5f(58)	4f(22)
Se	$PhCOC_6H_4Br$	m	87.5	5g(62)	-
		p	90.5	5f(86)	-
	$PhCOC_6H_4Br$	o	89	5i(75)	-
		m	92.5	5j(48)	4j(31)
		p	94.5 ; 89.5[e]	5k(45 ; 44[e])	4k(36 ; 22[e])

[a]4-5 % amide (hydrolysis of nitrile) ; [b]no mediator ; [c]9 % amide; [d]monoamide ; [e]magnetic stirring

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