Electrochemical Synthesis by the $S_{RN}1$ Mechanism of 4-Phenylselenobenzonitrile and 4-Phenyltellurobenzonitrile

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4-Phenylseleno- and 4-phenyltelluro-benzonitrile are prepared in 57 and 42% yields respectively, by electrochemically induced aromatic nucleophilic substitution in acetonitrile with sonication.

Among the variety of synthetic routes to unsymmetrical diaryl or aryl chalcogenides, one of the most convenient methods involves the arylation of aryl or alkyl chalcogenide anions RE^- (E = S, Se, or Te) by the $S_{NR}1$ mechanism [equations (1)—(4)] (see ref. 1 and references cited therein). Liquid ammonia has mainly been used as solvent, owing to its low acidity and reactivity with aryl radicals.[1—3] Since it is a poor H atom donor, the competitive reaction (5) is prevented. However other solvents such as dimethyl sulphoxide and acetonitrile can give satisfactory results.[4,5]

$$ArX + \text{electron donor} \longrightarrow (ArX)^{\cdot -}\ (+\ \text{residue}) \quad (1)$$

$$(ArX)^{\cdot -} \longrightarrow Ar^{\cdot} + X^- \quad (2)$$

$$Ar^{\cdot} + RE^- \longrightarrow (ArER)^{\cdot -} \quad (3)$$

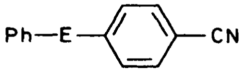
$$(ArER)^{\cdot -} + ArX \longrightarrow ArER + ArX^{\cdot -} \quad (4)$$

$$Ar^{\cdot} + (S)H \longrightarrow ArH + (S)^{\cdot} \quad (5)$$

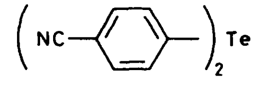
(S) = solvent

Photostimulated reactions of thiolates with halogenoaromatic substrates have led to a large variety of thioderivatives.[1] Electrons supplied from a cathode can also initiate $S_{RN}1$ reactions with thiolates.[3,5—7] Seleno and telluro derivatives have been synthesised by the $S_{NR}1$ mechanism, but only in liquid ammonia and under irradiation.[8,9] We now show that seleno and telluro derivatives can be prepared in acetonitrile with sonication by electrochemically induced aromatic nucleophilic substitution,[5,10] and describe the synthesis of the phenylchalcogenobenzonitriles (**1b**) and (**1c**).

Prior to this work, 4-phenylthiobenzonitrile (**1a**) was synthesised electrochemically in 80% yield (g.l.c.).[5] Benzene-



(**1**) **a**; E = S
b; E = Se
c; E = Te



(**2**)

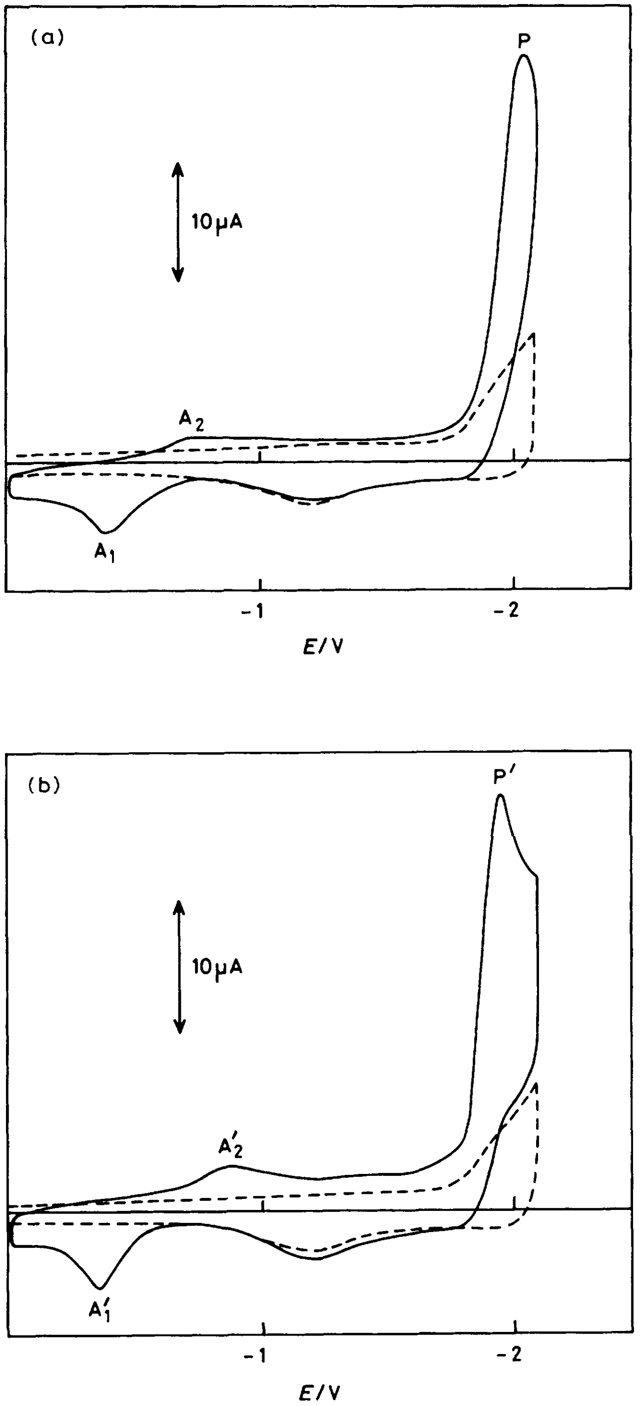


Figure 1. Repetitive cyclic voltammograms at a glassy carbon electrode of (a) (**1c**) and (b) (**2**), at a concentration of 2 mM and a scan rate of 0.5 V s^{-1}. The dotted curves were obtained in the absence of substrate.

thiolate which was prepared chemically from benzenethiol and sodium methoxide in methanol was present in large excess (10 equiv.) during the partial electrolysis of 4-bromobenzonitrile in acetonitrile on a stirred mercury pool (0.2 electron consumed).[5] We have used different conditions for the electrochemical synthesis of (**1b**) and (**1c**) in acetonitrile. The nucleophile PhSe$^-$ or PhTe$^-$ (1 mmol) was generated electrochemically by reducing the corresponding diphenyl dichalcogenide (0.5 mmol) with sonication on a graphite cloth under an inert atmosphere of argon.† 4-Bromobenzonitrile (1 mmol) was then added and partially reduced within 10 min (0.2 mmol electron consumed) at −1.45 ± 0.05 V with sonication.‡ After electrolysis, sonication was maintained for 10 min before treatment of the catholyte and column chromatography of the crude product (acetone–hexane, 1 : 9). The seleno derivative (**1b**) was isolated pure§ in 57% yield as beige crystals, m.p. 52 °C (lit.,[11] 49 °C), together with traces of PhSeSePh and 4-bromobenzonitrile. The moderate yield of (**1b**) indicates that the side reaction (5) is involved. Increasing the amount of nucleophile and using liquid ammonia as solvent[1—3,12] should increase the yield of (**1b**). The electrosynthesis of (**1c**)§ in 42% yield is accompanied by formation of the symmetrical diaryl telluride (**2**)§ in 13% yield, together with some unchanged diphenyl ditelluride (23%). Formation of (**2**) suggests a fragmentation of the intermediate radical anion (**1c**)$^{\cdot-}$ according to equation (6) during electrolysis. Compound (**2**) would be generated through reactions (7) and (8). Such bond fragmentations have been observed previously (see *e.g.* refs. 9 and 13).

$$\underset{(\mathbf{1c})^{\cdot-}}{(\mathrm{PhTeC_6H_4CN})^{\cdot-}} \longrightarrow \mathrm{Ph}\cdot + \underset{(\mathbf{3})}{{}^{-}\mathrm{TeC_6H_4CN}} \tag{6}$$

$$\underset{(\mathbf{3})}{{}^{-}\mathrm{TeC_6H_4CN}} + \mathrm{NCC_6H_4}\cdot \rightleftharpoons \underset{(\mathbf{2})^{\cdot-}}{(\mathrm{NCC_6H_4TeC_6H_4CN})^{\cdot-}} \tag{7}$$

$$\underset{(\mathbf{2})^{\cdot-}}{(\mathrm{NCC_6H_4TeC_6H_4CN})^{\cdot-}} + \mathrm{NCC_6H_4Br} \rightarrow \underset{(\mathbf{2})}{\mathrm{NCC_6H_4TeC_6H_4CN}} + (\mathrm{NCC_6H_4Br})^{\cdot-} \tag{8}$$

The electrochemical behaviour of (**1c**) and (**2**) corroborates the hypothesis that the cleavage reaction (6) occurs. In cyclic voltammetry, the electrochemical reduction of (**1c**) is irreversible, with a reduction peak potential of −2.04 V (peak P in Figure 1). An anodic peak A_1 is related to the reduction peak P. A new cathodic peak A_2, preceding P, is observed on the second and subsequent cathodic scans. The same redox peak system is observed in the case of (**2**) (peaks A'_1 and A'_2) which differs from the system observed in the case of diphenyl ditelluride. It can thus be reasonably concluded that peaks A_1 and A'_1 correspond to the oxidation of the anion (**3**) to the corresponding ditelluride and peaks A_2 and A'_2 to the reduction of the latter compound.

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† The applied potential had to be changed from −0.7 to −1.2 V during the electrolysis which consumed 1 mmol electron. The electrolyses were performed in a H-type cell, the three compartments of which were separated by a glass frit and filled with acetonitrile containing 0.1 M $\mathrm{Bu_4NPF_6}$. The volume of the cathodic compartment was 18 ml, the anode was a Pt cylinder and the reference electrode an aqueous saturated calomel electrode (S.C.E.). Ultrasonication (Bransonic B 32) and cooling of the cell by an ice bath were maintained during electrolysis.

‡ Sonication facilitates the electrochemical reduction of 4-bromobenzonitrile since its reduction is observed with an E_p value of −1.98 V *vs.* S.C.E. in cyclic voltammetry. Ultrasound has been shown to increase the rate of electrolysis in a few other cases.[14—16]

§ Compounds (**1b**) and (**1c**) were recrystallized from hexane: (**1c**) m.p. 39 °C; $\nu_{\max}$ (KBr) 2220 (C≡N) cm^{-1}; ^{1}H n.m.r. δ ($\mathrm{CDCl_3}$) 7.20—7.60 (7H, m) and 7.78—7.89 (2H, m). (**2**), m.p. 141 °C; $\nu_{\max}$ (KBr) 2224 (C≡N) cm^{-1}; ^{1}H n.m.r. δ ($\mathrm{CDCl_3}$) 7.49 (4H, d, *J* 8 Hz) and 7.76 (4H, d, *J* 8 Hz).

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