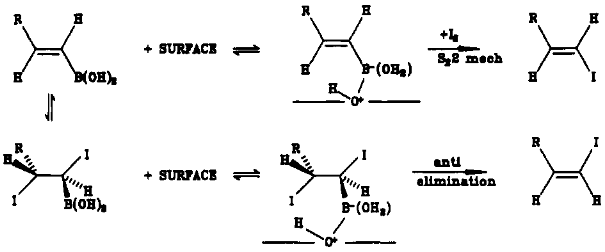
the surface hydroxy groups. Any uncomplexed boronic acid would not be detected in the spectrum.

One can invoke special geometric arrangements of surface hydroxyl groups and the adsorbed vinylboronic acids to explain the unusual stereochemistry of the surface reactions, but this is not necessary. The results can be explained simply, if there is an equilibrium admixture of complexed and uncomplexed vinylboronic acid. In this scheme the complexed boronic acid with its tetracoordinate boron reacts with iodine on the surface with retention of configuration via the S_E2 mechanism. The uncomplexed boronic acid, on the other hand, reacts reversibly first with iodine to produce a saturated boronic acid and then with surface hydroxyl groups to form a surface bound species that yields the (*Z*)-iodoalkene by the anti elimination of boric acid and iodide. The boronic acids derived from phenylacetylene and 3,3-dimethyl-1-butyne react highly stereoselectively on the surface of alumina because their complexed and uncomplexed boronic acids yield the same products by different mechanisms, as they do in solution. Lastly, the ratio of *E*/*Z* products decreases as the ratio of alumina to vinylboronic acid increases because the two reversible reactions involving the surface shift, but to differing degrees.



(12)

Experimental Section

^1H and ^{13}C NMR spectra were recorded on JEOL FX-90Q and Nicolet NT 200 spectrometers in $CDCl_3$ using tetramethylsilane as the internal standard ($\delta = 0$ ppm). The ^{11}B NMR spectra were obtained using the Nicolet spectrometer. GC/MS were recorded on a Hewlett-Packard 5970 series instrument. Gas chromatographs were recorded on a Hewlett-Packard 5890A instrument using a 30 m X $^1/_8$ in. column packed with 30% by weight SE-30 on Chromasorb W. Product yields were obtained from peak areas after calibration with known compounds. (*E*)-Alkenylboronic acids were prepared, via the procedure of Brown,[9] by reacting the corresponding alkyne with catecholborane followed by hydrolysis of the resulting organoborane with water. Unactivated Brockmann neutral alumina was ordinary used in the iodination reactions. When activated alumina was needed, it was prepared according to the procedure of Pagni, Kabalka, et al.[1b]

Preparation of the Alumina-Boronic Acid Complex. To a stirred slurry of alumina (10 g) and ether (15 mL) was added a solution of vinylboronic acid (1.00 mmol) in 15 mL of ether. After stirring for 5 min, the ether was removed in vacuo. If the boronic acid complexes to all surface sites, this concentration corresponds to 1.4% surface coverage if the solid has a surface area of 300 m^2/g.[1b]

Reaction of Alumina-Boronic Acid Complex with Iodine. The following is a representative example of the reaction of a vinylboronic acid with I_2 on alumina. To a stirred slurry of the (*E*)-1-octenylboronic acid complex in ether (15 mL) containing decane (5×10^{-4} mol; GC standard) was added a solution of iodine (1.00 mmol) in 15 mL of ether. The reaction was monitored using GC by removal of 1-mL aliquots at convenient time intervals. After 24 h, the ether was separated from the alumina; evaporation left behind an oily residue. GC analysis showed that a 65% yield of a 56:44 admixture of (*E*)- and (*Z*)-1-iodo-1-octene had been formed in the reaction. The *E* and *Z* isomers were separated by preparatory GC and were identical with independently synthesized compounds.

(*E*)-1-Iodo-1-octene. This compound was synthesized from 1-octyne by the procedure of Brown.[9]

(*Z*)-1-Iodo-1-octene. This compound was synthesized from 1-iodo-1-octyne by the procedure of Brown.[16]

Control Experiments. Several experiments were performed in order to determine if the two 1-iodo-1-alkenes were the initial products of the reaction. In all cases both products were present at very early reaction times. Extrapolation of the *E*/*Z* ratio of products to zero time clearly indicated that both products were initial products of the reaction.

In the case of the reaction of the (*E*)-1-octenylboronic acid with iodine, additional experiments were performed. The less stable (*Z*)-1-iodo-1-octene was subjected to alumina, iodine on alumina, and (*E*)-1-octenylboronic acid on alumina for extended periods of time. In no case did the *Z* isomer isomerize to the *E* isomer.

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Registry No. (*E*)-$C_6H_5CH{=}CHB(OH)_2$, 6783-05-7; (*E*)-$(CH_3)_3CCH{=}CHB(OH)_2$, 86595-37-1; (*E*)-$CH_2(CH_2)_5CH{=}CHB(OH)_2$, 42599-16-6; (*E*)-$CH_2(CH_2)_7CH{=}CHB(OH)_2$, 86883-77-4; (*E*)-$ClCH_2(CH_2)_2CH{=}CHB(OH)_2$, 37490-32-7; (*E*)-$HOCH_2(CH_2)_8CH{=}CHB(OH)_2$, 87096-18-2; $C_6H_5B(OH)_2$, 98-80-6; (*E*)-$CH_3CH_2CH{=}C(CH_2CH_3)B(OH)_2$, 134849-01-7; (*E*)-*n*-PrCH=C-(*n*-Pr)$B(OH)_2$, 81793-07-9; (*E*)-$(CH_3)_3CCH{=}C(CH_3)B(OH)_2$, 134849-02-8; (*E*)-$C_6H_5CH{=}CHI$, 42599-24-6; (*E*)-$(CH_3)_3CCH{=}CHI$, 61382-45-4; (*E*)-$CH_3(CH_2)_5CH{=}CHI$, 42599-17-7; (*Z*)-$CH_3(CH_2)_5CH{=}CHI$, 52356-93-1; (*E*)-$CH_3(CH_2)_7CH{=}CHI$, 66291-52-9; (*Z*)-$CH_3(CH_2)_7CH{=}CHI$, 66291-51-8; (*E*)-$ClCH_2(CH_2)_2CH{=}CHI$, 78461-58-2; (*Z*)-$ClCH_2(CH_2)_2CH{=}CHI$, 95835-51-1; (*E*)-$HOCH_2(CH_2)_8CH{=}CHI$, 87096-20-6; (*Z*)-$HOCH_2(CH_2)_8CH{=}CHI$, 134849-03-9; Alumina, 1344-28-1.

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(16) Brown, H. C.; Blue, C. D.; Nelson, D. J.; Bhat, N. G. *J. Org. Chem.* 1989, *54*, 6064.

Direct Electrochemical Synthesis of Diaryl Dichalcogenides by $S_{RN}1$ Reactions Using Sacrificial Se and Te Cathodes

C. Thobie-Gautier and C. Degrand*

Université Blaise Pascal de Clermont-Ferrand, Laboratoire Thermodynamique et Electrochimie en Solution (URA 434), Equipe Electrochimie Organique, 24, Avenue des Landais, 63177 Aubière Cedex, France

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Diaryl diselenides and ditellurides are useful starting materials for many Se- and Te-containing compounds and reagents.[1,2] In the field of $S_{RN}1$ reactions,[3] it was shown

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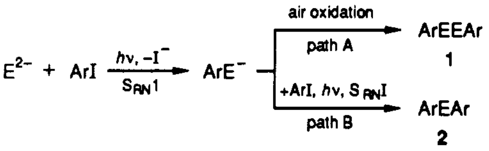
(1) For reviews on organoselenium applications, see: (a) Clive, D. L. J. *Tetrahedron* 1978, *34*, 1049. (b) Reich, H. J. *Acc. Chem. Res.* 1979, *17*, 22. (c) Liotta, D. *Acc. Chem. Res.* 1984, *17*, 28. For reviews on organotellurium applications, see: (d) Irgolic, K. J. *The organic chemistry of tellurium*; Gordon and Breach: New York, 1974. (e) Engman, L. *Acc. Chem. Res.* 1985, *18*, 274. (f) Petragnani, N.; Comasseto, J. V. *Synthesis* 1986, 1. (g) Ohe, K.; Takahashi, H.; Uemura, S.; Sugita, N. *J. Org. Chem.* 1987, *52*, 4859.

(2) For recent publications on the chemical synthesis of diaryl diselenides and ditellurides, as well as reviews on different methods, see refs 2a,b and references cited therein. For references on the electrochemical synthesis of diaryl diselenides and ditellurides, see refs 2c–e. (a) Syper, L.; Mlochowski, J. *Tetrahedron* 1988, *44*, 6119. (b) Engman, L.; Persson, J. *J. Organomet. Chem.* 1990, *388*, 71. (c) Jeroschewski, P.; Ruth, W.; Strubin, B.; Berge, H. *J. Prakt. Chem.* 1982, *324*, 787. (d) Degrand, C.; Gautier, C.; Kharroubi, M. *Tetrahedron* 1988, *44*, 6071. (e) Degrand, C. *J. Electroanal. Chem.* 1989, *260*, 137.

0022-3263/91/1956-5703$02.50/0

Scheme I



by Rossi and Penenory[4a] that a convenient "one-pot" method for the selective synthesis of diaryl diselenides **1** (E = Se) is the photostimulated reaction in liquid ammonia of iodoarenes with Se^{2-} anions by the $S_{RN}1$ mechanism[3] (path A of Scheme I). For instance, PhSeSePh was isolated in 78% yield, together with some PhSePh (18%) generated competitively according to path B of Scheme I, and the further addition of sodium metal gave selectively PhSeSePh in 92% yield. Conversely the synthesis of diaryl ditellurides proceeded in low yields or failed under analogous conditions. Thus PhTeTePh and PhTePh were both isolated in 17% yield. A more pertinent application of $S_{RN}1$ reactions involving chalcogenide anions was given by Sandman et al.[4b] who observed that the synthesis of NaphTeTeNaph from Te_2Na_2 and 2-chloronaphthalene proceeded at room temperature, although in modest yield (22%), when the reaction was initiated with sodium naphthalenide in HMPA.

Very recently, our group has observed somewhat similar results in acetonitrile, with electrogenerated E_2^{2-} anions and by electrochemical stimulation.[5a] The simultaneous generation of E_2^{2-} by cathodic dissolution of a special Se or Te electrode of the tea bag type[6] and the reduction of 4-bromobenzophenone led to the direct synthesis of the new dichalcogeno derivatives **1a** and **1b**, together with **2a** and **2b** as minor compounds.

ArEEAr	ArEAr
1a: E = Se, Ar = 4-C_6H_4COPh	**2a:** E = Se, Ar = 4-C_6H_4COPh
b: E = Te, Ar = 4-C_6H_4COPh	**b:** E = Te, Ar = 4-C_6H_4COPh
c: E = Se, Ar = 2-quinolyl	**c:** E = Se, Ar = 2-quinolyl
d: E = Te, Ar = 2-quinolyl	**d:** E = Te, Ar = 2-quinolyl
e: E = Se, Ar = 9-anthryl	**e:** E = Se, Ar = 9-anthryl

A possible mechanism leading to **1a,b** is suggested by eqs 1–8 of Scheme II,[9] in which an electrochemically induced $S_{RN}1$ reaction is involved and two electrons are consumed to generate ArE^- from ArX and E according to eqs 1–7 (the overall reaction is $2E + 2ArX + 4e \rightarrow 2ArE^- + 2X^-$). The dichalcogeno derivatives **1a,b** were available only after electrolysis, by air oxidation of the cathodic solution (eq 8), whereas the side products **2a,b** were generated during electrolysis, according to the global reaction (9). Thus the side reaction 9 became more favorable as the electrolysis proceeded.

Scheme II

$$2E + 2e \rightleftarrows E_2^{2-} \tag{1}$$

$$ArX + e \rightleftarrows [ArX]^{\bullet -} \xrightarrow{k_1} Ar^{\bullet} + X^- \tag{2}$$

$$Ar^{\bullet} + E_2^{2-} \overset{k_2}{\rightleftarrows} [ArE_2^-]^{\bullet -} \tag{3}$$

$$(ArE_2^-)^{\bullet -} + ArX \rightarrow ArE_2^- + Ar^{\bullet} + X^- \tag{4}$$

$$ArE_2^- + Ar^{\bullet} \rightarrow [ArEEAr]^{\bullet -} \tag{5}$$

$$[ArEEAr]^{\bullet -} \rightarrow ArE^- + \tfrac{1}{2}\underset{\mathbf{1}}{ArEEAr} \tag{6}$$

$$\tfrac{1}{2}\underset{\mathbf{1}}{ArEEAr} + e \rightarrow ArE^- \tag{7}$$

$$ArE^- \xrightarrow{\text{oxidation}} \tfrac{1}{2}\underset{\mathbf{1}}{ArEEAr} \tag{8}$$

$$ArE^- + ArX \xrightarrow[S_{RN}1]{} \underset{\mathbf{2}}{ArEAr} + X^- \tag{9}$$

$$Ar^{\bullet} + e \rightarrow Ar^- \xrightarrow{+SH} ArH + S^- \tag{10}$$

$$Ar^{\bullet} + SH \xrightarrow{k_H} ArH + S^{\bullet} \tag{11}$$

$$Ar^{\bullet} + [ArX]^{\bullet -} \rightarrow Ar^- + ArX \tag{12}$$

$$Ar^{\bullet} + [ArE_2^-]^{\bullet -} \rightarrow Ar^- + ArE_2^- \tag{13}$$

No attempt was made to optimize the yields of **1a,b** which were low (23% and 14%) due to competing reactions such as 9–13 where SH is MeCN, a H-donating solvent. However, these preliminary results convinced us to explore this electrochemical technique more deeply, since it allows the direct synthesis of dichalcogeno derivatives that cannot be prepared by classical means such as lithiation and Se[10] or Te[2b] insertion. Furthermore, this technique can afford a convenient and cheap alternative to troublesome or expensive chemical methods since it is a "one-pot" synthesis involving electricity as reducing species.[5b]

We define below experimental conditions that allow the electrochemical sythesis of the three dichalcogeno prototypes **1c–e** in useful yields (50–70%) from 2-chloroquinoline (ClQ) and 9-bromoanthracene (BrAntr). The above technique (method A) is compared with a modified one in which the E_2^{2-} anions are cathodically generated prior to the introduction and reduction of ClQ or BrAntr, at a graphite cathode (method B). In both techniques, the E_2^{2-} anions are released by reduction of a sacrificial E electrode of the tea bag type. In one more electrolysis, Te

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[3] For reviews on the $S_{RN}1$ substitution, see, for instance: (a) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413. (b) Rossi, R. A. *Acc. Chem. Res.* **1982**, *15*, 164. (c) Rossi, R. A.; Rossi, R. H. *Aromatic Nucleophilic Substitution by the $S_{RN}1$ Mechanism*; American Chemical Society: Washington DC, 1983; ACS Monograph No. 178. (d) Fox, M. A.; Younathan, J.; Fryxell, G. E. *J. Org. Chem.* **1983**, *48*, 3109. For reviews on the electrochemically induced $S_{RN}1$ substitution see: (e) Savéant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323. (f) Andrieux, C. P.; Savéant, J. M. *Investigation of Rates and Mechanisms*; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Vol. 6, 4/E, Part 2, 305. (g) Andrieux, C. P.; Hapiot, P.; Savéant, J. M. *Chem. Rev.* **1990**, *90*, 723.

[4] (a) Rossi, R. A.; Penenory, A. B. *J. Org. Chem.* **1981**, *46*, 4580. (b) Sandman, D. J.; Stark, J. C.; Acampora, L. A.; Gagne, P. *Organometallics* **1983**, *2*, 549.

[5] (a) Degrand, C.; Prest, R. *J. Electroanal. Chem.* **1990**, *282*, 281. (b) Degrand, C.; Prest, R.; Gautier, C. Fr. Demande FR 89, 17493 (Dec 29, 1989).

[6] This electrode was made from a piece of graphite cloth (6 × 6 cm) and Se pearls or Te pellets (see Figure 1C of ref 5a) and the yields of **1a** and **1b** were 23% and 14%, respectively. A Se electrode prepared according to the technique described by Le Guillanton et al.[7] for building carbon/sulfur electrodes did not allow the concomitant generation of Se_2^{2-} and Ar•. In this technique, the electrode was made by plunging a Pt wire into a mixture of graphite powder and chalcogen, introduced into a test tube and then melted. After cooling at room temperature, the glass tube was broken to release the compact electrode. Similarly, the Se electrode built by the technique described by Jeroschewski et al.,[2c] which was similar (a Pt grid support was used instead of a test tube), was unsuccessful, as well as the Te electrode described in ref 8. Conversely, when an electrode of the tea bag type contained a double jacket inserted in a glass-tubing (cf. Figure 1D of ref 5a), instead of a single one, the yield of **1a** reached 40%.

[7] Le Guillanton, G.; Do, Q. T.; Simonet, J. *Tetrahedron Lett.* **1986**, *27*, 2261.

[8] Merkel, G.; Berge, H.; Jeroschewski, P. *J. Prakt. Chem.* **1984**, *326*, 467.

[9] Instead of eqs 6 and 7, the two following reactions can be also considered: $[ArEEAr]^{\bullet -} \rightarrow ArE^- + ArE^{\bullet}$ and $ArE^{\bullet} + e \rightarrow ArE^-$.

[10] Jen, K. Y.; Cava, M. P. *J. Org. Chem.* **1983**, *48*, 1449 and references cited therein.

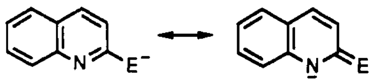
Table I. Electrochemical Synthesis of the Dichalcogenides 1c–e by a $S_{RN}1$-like Coupling of Aryl Halides (2 mmol) with E_2^{2-} Anions Using Sacrificial E Electrodes

entry	E	method[a]	ArX	Med (equiv)	solvent	1 (yield,[b] %)	2 (yield,[b] %)
1	Se	A	ClQ	0.5	MeCN	**1c** (59)	
2	Se	A	ClQ	0.5	DMSO	**1c** (46)	
3	Te	A	ClQ	0.5	MeCN	**1d** (38)	**2d** (4)
4	Te[c]	A	ClQ	0.5	MeCN	**1d** (50)[d]	
5	Se[e]	B	ClQ		MeCN	**1c** (69)	
6	Se[e]	B	ClQ	0.25	MeCN	**1c** (70)	
7	Te[e]	B	ClQ		MeCN		
8	Se[f]	B	BrAntr		MeCN	**1e** (28)[g]	**2e** (30)
9	Se[e]	B	BrAntr		MeCN	**1e** (54)[g,h]	

[a] Method A, simultaneous reduction of E and ArX; method B, reduction of E prior to ArX. [b] Isolated yields. [c] Te powder with sonication. [d] Voltammetric determination in DMF. [e] 2 mmol of E_2^{2-}. [f] 1.5 mmol of Se_2^{2-}. [g] Contaminated by $AntrSe_3Antr$ (10%). [h] Additional electrolysis step at −1.75 V.

powder was reduced to Te_2^{2-} with sonication[11] at a graphite cathode. Moreover, we emphasize the role of a redox mediator and the advantages of acetonitrile over DMSO as solvent.

The dichalcogenides **1c** and **1d** were chosen as prototypes for the following reason. Since the nucleophilic ability of the 2-substituted QE^- anion is expected to be drastically decreased by mesomery, we can anticipate that



the side reaction 9 will not interfere to a large extent, and so our efforts to improve the yields of **1c**,**d** will reflect a better competition of the key step 3 vis-a-vis side reactions such as 10–13, but not 9. Moreover, experimental conditions minimizing this latter side reaction will be exemplified by the electrochemical synthesis of **1e**.

Results and Discussion

All the electrolyses were carried out under an inert atmosphere of argon, in an H-type cell filled with MeCN or DMSO containing 0.1 M Bu_4NPF_6 as supporting electrolyte and equipped with membranes. Unless otherwise stated, mechanical stirring was maintained during a electrolysis.

I. Simultaneous Electrochemical Reduction of ClQ and E (Method A). As previously shown,[5] potentials negative to −1.6 V and −1.7 V vs an aqueous saturated calomel electrode (SCE) had to be applied to Se and Te electrodes of the tea bag type, in order to generate Se_2^{2-} and Te_2^{2-} anions under an inert atmosphere of argon. The electrochemical properties of these anions were examined prior to preparative electrolyses, by voltammetry at glassy carbon rotating disc electrode (RDE) in MeCN. In the case of the Se_2^{2-} anions, their oxidation takes place at potentials positive to −0.7 V, and the corresponding wave is distorted by a maximum, whereas their reduction to Se^{2-} is negligible at potentials positive to −1.8 V. A confident voltammetric study could not be performed in the case of the Te_2^{2-} anions, due to their high instability (vide infra). Now, we consider the redox behavior of ClQ in MeCN: its first reduction step takes place at $E_{1/2} = -1.82$ V ($E_{1/2}$ = half-wave potential value at a glassy carbon RDE), and so the concomitant reduction of ClQ to $Q^•$ cannot be expected to occur during electrolysis, when a working potential of −1.6 or −1.7 V is applied to the Se or Te electrode. In order to compel ClQ to be electroactive even at −1.6 V, a redox mediator (Med) was therefore added and so an endergonic homogeneous electron transfer took place ($Med + e \rightleftarrows Med^{•-}$ and $Med^{•-} + ArX \rightleftarrows Med + [ArX]^{•-}$) because of the continuous removal of the frangible anion-radical $ClQ^{•-}$.[12] Furthermore, we perceived a second advantage by adding a mediator in the fact that the possible cathodic side reaction 10 was eliminated since the $Q^•$ radicals were thus generated in the homogeneous medium.[13] Phtalonitrile, which was previously found suitable for redox catalysis of ClQ in liquid ammonia,[12c] was found efficient in MeCN and DMSO too.

A series of three electrolyses (entries 1–3 of Table I) was carried out under the following experimental conditions. An electrode of the tea bag type containing Se or Te (4 mmol) was polarized at −1.6 V in the presence of ClQ (2 mmol) and phtalonitrile (1 mmol). First a working potential of −1.6 ± 0.1 V was applied, and thus the faradaic current was low (20 ± 5 mA) in order to minimize side reactions such as those in eqs 12 and 13. After consumption of about 6 mmol of electrons,[14] the chalcogenate anions QE^- thus generated and the E_2^{2-} anions in excess were oxidized anodically at 0 V, and so QEEQ was obtained and E regenerated.

The diselenide **1c**[2a] was isolated in 59% yield when an electrolysis was carried out in MeCN (entry 1 of Table I). When the electrolysis was repeated in DMSO, the yield of **1c** dropped to 46% (entry 2). An electrolysis performed

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[11] (a) Gautheron, B.; Tainturier, G.; Degrand, C. *J. Am. Chem. Soc.* **1985**, *107*, 5579. (b) Tainturier, G.; Gautheron, B.; Degrand, C. *Organometallics* **1986**, *5*, 942.

[12] For references in preparative electrochemistry using redox catalysis, see, for instance, refs 4e–g and : (a) Swartz, J. E.; Stenzel, T. T. *J. Am. Chem. Soc.* **1984**, *106*, 2520. (b) Amatore, C.; Oturan, M. A.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1984**, *106*, 6318. (c) Amatore, C.; Oturan, M. A.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1985**, *107*, 3451. (d) Amatore, C.; Combellas, C.; Pinson, J.; Oturan, M. A.; Robveille, S.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1985**, *107*, 4846. (e) Degrand, C. *J. Electroanal. Chem.* **1987**, *238*, 239. (f) Degrand, C.; Prest, R.; Compagnon, P. L. *J. Org. Chem.* **1987**, *52*, 5229. (g) Alam, N.; Amatore, C.; Combellas, C.; Thiébault, A.; Verpeaux, J. N. *J. Org. Chem.* **1990**, *55*, 6347. (h) Degrand, C. *Tetrahedron* **1990**, *46*, 5237. (i) Thobie-Gautier, C.; Genesty, M.; Degrand, C. *J. Org. Chem.* **1991**, *56*, 3452. (j) Degrand, C.; Prest, R. *J. Org. Chem.* **1990**, *55*, 5242.

[13] In the case of ClQ, kinetic data concerning k_1 in MeCN are not available. Conversely it is known that in liquid ammonia, k_1 is moderate ($k_1 = 1.7 \pm 0.2 \times 10^4\ s^{-1}$) (Amatore, C.; Chaussard, J.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1979**, *101*, 6012). Thus we cannot ascertain a priori whether the $Q^•$ radicals are released in the bulk of the cathodic solution when ClQ is directly reduced.

[14] In method A, the synthesis of QE^- and QH consumes 2 electrons in each case, and so the coulometric data allow no evaluation of the $S_{RN}1$ process. Since more than 4 mmol of electrons were consumed, it indicates that E_2^{2-} were generated in excess. A partial one-electron reduction of the mediator has also to be taken into account as well as the in situ air oxidation of the unstable E_2^{2-} anions to E by residual oxygen. In the second step of method B, 1 and 2 electrons are involved in the synthesis of QE^- and QH, respectively, and so an evaluation of the $S_{RN}1$ process should be available from coulometric data. However these data do not provide confident results since the one-electron reduction of a mediator and the reoxidation of E_2^{2-} to E may interfere. Hence it is not an accurate technique.

in MeCN at a Te electrode gave **1d** in 38% yield, together with a very small amount of **2d** (entry 3). The yield of **1d** could be improved (50%) by replacing the Te cathode by an electrode made of a graphite cloth of cylindrical shape and adding Te powder, which was reduced to Te_2^{2-} with sonication[11] (entry 4).

From the data in Table I (entries 1–4), a few salient results emerge. The electrochemical synthesis of **1c** and **1d** is a clean method since no monochalcogenide was isolated, only a trace of **2d** in electrolysis 3. The isolated yield of **1c** was higher in MeCN (entry 1) than in DMSO (entry 2) and so it emphasizes the advantages of the former solvent over the latter, when $S_{RN}1$ reactions with chalcogenide nucleophiles are carried out, as already shown by our group.[12h–j] Indeed, a series of electrolyses in which ArX and PhE^- anions (E = S, Se, Te) were involved led to higher yields of ArEPh derivatives in MeCN than in DMSO. Thus NaphSPh (Naph = 1-naphthyl), AntrSePh, and AntrTePh were isolated in 88, 74, and 68% yield, respectively, in MeCN and in 50, 43, and 49% yield, respectively, in DMSO. From these yields, it could be shown that the nucleophilic attack of $Naph^•$ by PhS^- and those of $Antr^•$ by $PhSe^-$ and $PhTe^-$ were at least 12 times more rapid in MeCN than in DMSO,[12i,j] whereas the H-atom transfer rate constant k_H (eq 11) is known to be only slightly higher in MeCN than in DMSO.[15] Thus, although MeCN is a better H-atom donor than DMSO, $S_{RN}1$ reactions with PhE^- anions are more efficient in the former than in the latter solvent. The same conclusion holds in the present work. However, quantitative data could not be derived from the yields of Table I (entries 1 and 2), due to the unusual experimental conditions of method A.[17] Finally, it is worth noting that the use of sonication and Te powder improved the yield of **1d** (compare entries 3 and 4). Although we have no clear explanation of this result, our feeling is that it is related to a better homogeneity of the medium under sonication and not to cavitation phenomena that are known to create locally high pressures and temperatures.[19] Indeed, when the mechanical stirring was replaced by sonication, the yield of **1d** was not modified under the conditions of electrolysis 3 (Te electrode of the tea bag type).

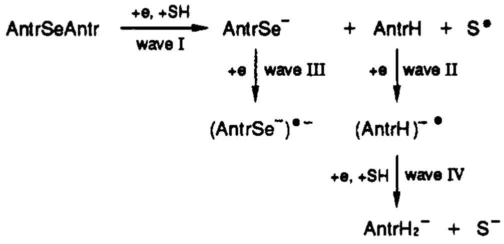
II. Electrosynthesis of E_2^{2-} Prior to the Reduction of ClQ (Method B). By applying this technique, it was expected to generate the $Ar^•$ radicals in the presence of an excess of E_2^{2-} anions and therefore to improve the yields of **1c** and **1d**. From a practical point of view, the cathodic compartment was equipped initially with a Se or Te electrode of the tea bag type, surrounded by a second electrode (graphite cloth of cylindrical shape). First the Se or Te electrode was polarized and thus Se_2^{2-} or Te_2^{2-} anions were generated (2 mmol). After removing this cathode, ClQ (2 mmol) was introduced and reduced, in a second step, at the graphite cathode, either directly or indirectly, by a redox mediator. A low current (30 ± 10 mA) was maintained during this step in order to minimize again side reactions such as eqs 12 and 13, and so 3.1 ± 0.5 mmol of electrons were consumed.[14] Finally the potential was moved to 0 V and so ArEEAr was generated and E recovered from E_2^{2-} in excess. Before starting the second step of electrolysis, it was ascertained that a spontaneous reaction did not occur between E_2^{2-} and ClQ.

Table II. Half-Wave Potentials at a Glassy Carbon RDE in DMF of the Starting Materials and the Isolate Compounds

compounds	wave I, $-E_{1/2}$ (V)	wave II, $-E_{1/2}$ (V)	wave III, $-E_{1/2}$ (V)	wave IV, $-E_{1/2}$ (V)
QCl	1.84	2.16[a]		
QH	2.16[a]			
QSeSeQ	1.04	2.56		
QTeTeQ	1.08	2.46		
BrAntr	1.57	1.93[a]	2.55	
AntrH	1.93[a]	2.55		
AntrSeSeAntr	0.77	2.35[a]		
AntrSeAntr	1.67[b]	1.93[a]	2.35[a]	2.55

[a] Reversible monoelectronic step by cyclic voltammetry at stationary electrode. [b] Partially reversible step by cyclic voltammetry at stationary electrode.

Scheme III



As predicted, the yield of the diselenide **1c** was improved since it reached 69% and 70% in the absence and presence of phtalonitrile (entries 5 and 6 of Table I). Since the yield of **1c** was not modified by addition of phtalonitrile, it was concluded that the cathodic side reaction (10) was negligible, even in the absence of a redox catalyst.[13] Surprisingly, the electrochemical synthesis of the ditelluride **1d** failed with method B, since the crude product was a mixture of six unidentified compounds (entry 7). This result is probably related to the high instability of the intermediate Te_2^{2-} anions, even in the presence of an inert atmosphere of argon. Indeed, it was observed that their red-purple color faded within a few minutes. In conclusion, method A is preferential for preparation of ditelluride derivatives and method B is preferential in the case of the diselenide compounds.

Under the conditions of electrolyses 5 and 6, the key step (3) of Scheme II competed essentially with the H-abstraction reaction (11) and so the ratio k_2/k_H could be calculated from the yield (y, %) of **1c**.[17] Since there was a depletion of E_2^{2-} during electrolysis, k_2/k_H was derived from eq 14 where $C°$ and C_f are the concentrations of E_2^{2-} at the beginning (2 mmol) and at the end of the second electrolysis step.[12j] Thus, it was found that $k_2/k_H = 140$ M^{-1} since $y = 70\%$, $C° = 2 \times 10^{-2}$ M, and $C_f = 1.3 \times 10^{-2}$ M.[17]

$$y\ (\%) = 100\left[1 - \frac{k_H/k_2}{C° - C_f} \ln \frac{k_H/k_2 + C°}{k_H/k_2 + C_f}\right] \quad (14)$$

The cathodic behavior of **1c** and **1d** was studied by voltammetry at glassy carbon stationary and rotating disc

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(15) A few available data indicate that the k_H values are 1.1[16a] or 2.3 times[16b,c] higher in MeCN than in DMSO.

(16) (a) Helgée, B.; Parker, V. D. *Acta Chem. Scand.* 1980, *B34*, 129. (b) Bridger, R. F.; Russel, G. A. *J. Am. Chem. Soc.* 1963, *85*, 3754. (c) M'Halla, F.; Pinson, J.; Savéant, J. M. *J. Am. Chem. Soc.* 1980, *102*, 4120.

(17) When the nucleophile (Nu^-) is in excess during electrolysis, and the substitution product ArNu isolated in y (%) yield, the ratio k_H/k_2 is derived from the equation[18] $y\ (\%) = 100/(1 + k_H k_2^{-1}(Nu^-)^{-1})$. On the other hand, our group has shown that the ratio k_H/k_2 can also be derived from the yield of ArNu when there is a depletion of Nu^- during electrolysis.[12j] Under the experimental conditions of method A, the concentration of Nu^- cannot be controlled, and so none of the above theories can be applied. Conversely, the concentration of Se_2^{2-} is controlled in method B. Since the volume of the cathodic compartment is 100 mL and since 2 mmol of E_2^{2-} are generated, the initial concentration $C°$ of Se_2^{2-} is 2×10^{-2} M and the final concentration $C_f = C° - y\ (\%)/100$, under the conditions of electrolyses 5 and 6.

(18) Amatore, C.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* 1982, *104*, 817.

(19) Mason, T. J.; Lorimer, J. P. *Sonochemistry, Theory, Applications and uses of ultrasound in chemistry*; Ellis Horwood: UK, 1988.

electrode. Their reduction is a two-step process and the corresponding $E_{1/2}$ values in DMF are given in Table II.

III. Electrochemical Reduction of BrAntr According to Method B. The compound was directly reduced at −1.55 ± 0.1 V. No redox catalyst was added because the Antr$^•$ radicals were released for from the electrode where the side reaction (10) did not take place, as shown by kinetic data provided by Savéant et al.[16c] ($k_1 = 1.5 \times 10^5$ s^{-1}). The selectivity for dichalcogenide over monochalcogenide was lost (entry 8) since the crude product contained anthracene (23%), the diselenide **1e**, and monoselenide **2e**[20] in similar amounts,[21] as well as a trace of triselenide derivative. Furthermore, the purification of the mono- and ditelluride by column chromatography was troublesome and the diselenide **1e** remained contaminated by some triselenide.[22] Fortunately the selectivity vis-a-vis **2e** could be restored since the cathodic reduction of **2e** is a four-step process whose first reduction step releases AntrSe$^-$ as shown in Scheme III, which is in agreement with the given $E_{1/2}$ values of Table II. Hence, the further reduction in situ of **2e** at −1.75 V (plateau of wave I) allowed the synthesis of **1e** in 54% yield, together with the corresponding triselenide in 6% yield, the synthesis of which probably resulted from the concomitant anodic oxidation of AntrSe$^-$ and Se_2^{2-}.

Conclusion

Method B will be more widely applicable than method A, which is restricted to aryl halides cathodically reducible at potentials close to those of Se and Te. However the synthesis of ditelluride derivatives requires method A, due to the instability of the Te_2^{2-} anions. Since we were able to prepare **1c–e** in useful yields in MeCN, we can anticipate that many diaryl dichalcogenides will be prepared in high yields by the electrochemical technique, since both 2-quinolyl[12c] and 9-anthryl[12j] radicals belong to the limited category of aryl radicals moderately reactive toward nucleophilic attacks. This technique will be particularly suitable for aryl radicals Ar$^•$ substituted by unsaturated withdrawing groups such as nitrile or carbonyl functions. Indeed, their reactivity toward E_2^{2-} anions is expected to increase, as in the case where PhE$^-$ anions are used as nucleophiles,[12j] whereas their synthesis by classical means (lithiation and Se or Te insertion) cannot be carried out. Finally, it is worth noting that the synthesis of **1c** proceeded selectively in 70% yield at room temperature whereas its recent synthesis by S_NAr reaction under drastic conditions of temperature whereas its recent synthesis by S_NAr reaction under drastic conditions of temperature led to a mixture of **1c** and **2c** in 57% and 23% yields.[2a]

Experimental Section

Instrumentation and electrochemical cell have been described previously.[12h]

Bis(2-quinolyl) ditelluride (1d): orange crystals; mp 143–144 °C (acetone/hexane); ^{1}H NMR δ 7.47–7.53 (m, 2 H), 7.67–7.84 (m, 6 H), 8.02 (d, 2 H, J = 8.5 Hz), 8.20 (d, 2 H, J = 8.5 Hz); MS 512 (2, M$^+$), 128 (100, quinolyl$^+$). Anal. Calcd for $C_{18}H_{12}N_2Te_2$: C, 42.25; H, 2.35; N, 5.48; Te, 49.92. Found: C, 42.88; H, 2.54; N, 5.99; Te 49.36.

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Supplementary Material Available: Experimental details of methods A and B (4 pages). Ordering information is given on any current masthead page.

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[20] This compound was isolated in 31% yield from BrAntr and Na_2Se in DMF (Sandman, D. J. U.S. Patent 4,597,914, 1986).

[21] At the Fourth International Conference on the Organic Chemistry of Selenium and Tellurium, Birmingham, U.K., July 25–29, 1983, D. J. Sandman et al. reported that BrAntr reacted with Na_2Se_2 in DMF to give **1e** and **2e** in yields of 28% and 21%, respectively.

[22] An elemental analysis of the orange powder indicated that it was roughly a mixture of **1e** (90%) and $AntrSe_3Antr$ (10%). This result was confirmed by MS and ^{1}H NMR.

Selective Aerobic Oxidative Dehydrogenation of Alcohols and Amines Catalyzed by a Supported Molybdenum–Vanadium Heteropolyanion Salt $Na_5PMo_2V_2O_{40}$

Ronny Neumann* and Michal Levin

Casali Institute of Applied Chemistry, Graduate School of Applied Science and Technology, The Hebrew University of Jerusalem, Jerusalem, Israel 91904

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Introduction

In recent years there has been a renaissance in the investigation of the chemistry of heteropolyoxometallates[1] with an emphasis on their use as Bronsted acids[2] and oxidation catalysts.[3] An attractive and important aspect of these compounds is their inherent stability toward decomposition under strong oxidizing conditions. In oxidations most catalytic applications utilize the versatility of the Keggin-type heteropolyanions as they may contain a large variety of heteroatoms and are easily transferred into organic phases by lipoophilic cations or complexing agents. The oxidative catalytic activity of heteropolyoxometallates may be divided into four eneral reaction types: first, photoactivation of the catalyst, which in the excited state may catalyze dehydrogenations of alkenes and alkanes;[4] second, use of hydrogen peroxide as oxidant and complete molybdenum or tungsten Keggin compounds as catalyst precursors[5] in oxidations of alcohols, allyl alcohols, alkenes, and alkanes typical of such metal centers;[6] third, catalytic

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