Application of the Hammett Equation to the Electrochemical Oxidation of Diaryl Chalcogenides and Aryl Methyl Chalcogenides

Lars Engman,[*,a] **Joachim Persson,**[a] **Carl M. Andersson**[*,b] **and Mats Berglund**[b]
[a] *Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden*
[b] *Department of Medicinal Chemistry, Preclinical R & D, Astra Draco AB, PO Box 34, S-221 00 Lund, Sweden*

The electrochemical oxidation of symmetrical 4,4′-disubstituted diaryl selenides and tellurides and 4-substituted aryl methyl sulfides, selenides and tellurides has been studied. Peak oxidation potentials show good correlation with Hammett σ_p^+-values for all series of compounds (diaryl selenides, R = 0.98, n = 10; diaryl tellurides, R = 0.98, n = 14; aryl methyl sulfides, R = 0.97, n = 5; aryl methyl selenides, R = 0.98, n = 5; aryl methyl tellurides, R = 0.98, n = 5). From the slope of the Hammett plots (methyl aryl chalcogenides) it was concluded that the degree of conjugation of a heteroatom with a *para*-substituent through an aromatic ring decreases in the following order: S > Se > Te. Results from the electrochemical oxidation of unsymmetrical diaryl selenides and tellurides indicate that the heteroatom is interacting with only one of the aromatic rings in diaryl chalcogenides.

^{125}Te chemical shifts of symmetrical 4,4′-disubstituted diaryl tellurides correlate well with Hammett σ_p-values (R = 0.98, n = 13).

Owing to their many interesting effects in biological systems, organoselenium compounds have recently attracted considerable attention in the pharmaceutical industry.[1] This interest stems from the early finding by Foltz and Schwarz that selenium is an essential microelement to man, present in the enzyme glutathione peroxidase. The most studied synthetic organoselenium compound to date, 2-phenyl-1,2-benzisoselenazol-3(2*H*)-one (Ebselen), is known to mimic the properties of glutathione peroxidase[2] and to act as an antioxidant.[3] In addition, it shows antiinflammatory activity[4] and interferes with the formation of biologically active arachidonate metabolites.[5]

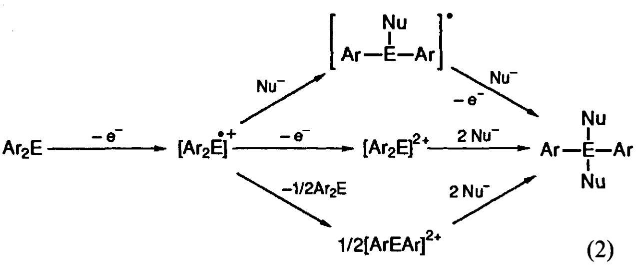
We have recently reported the *in vitro* antioxidant effects of diaryl chalcogenides containing selenium and tellurium (ADP-Fe^{2+}-ascorbate-induced peroxidation of lipids in liver microsomes and *tert*-butylhydroperoxide-induced lipid peroxidation in suspensions of rat hepatocytes).[6,7] The antioxidant capacity of these compounds is conceivably related to the ability of the electron-rich heteroatoms to donate an electron to a reactive hydroxyl or peroxyl radical, eqn. (1). The chalcogenides are thus acting as chain-breaking agents.

(1)

These interesting biological results prompted us to study the oxidation of diaryl chalcogenides and related compounds under well-defined conditions. Reported below are the results of a cyclovoltammetric study of the electrochemical oxidation of diaryl chalcogenides **1–24** and aryl methyl chalcogenides **25–39**.

Results

Electrochemical Oxidation Reactions.—The electrochemical oxidation of diaryl chalcogenides Ar_2E (E = O,[8] S,[9–13] Se,[14] and Te[15]) has been studied under various conditions. These investigations showed that the chalcogen atom (E = S, Se, Te) is oxidized from the divalent to the tetravalent state in the reaction, *via* transfer of two electrons. The oxidation reaction is usually irreversible and accompanied by attack of any nucleophile present in the system. The overall process has been suggested[9] to involve either nucleophilic attack on the radical cation or dication (formed *via* oxidation or disproportionation[15] of the radical cation) as shown in eqn. (2). In the case of diaryl sulfides and selenides, products were also isolated which result from secondary reactions of the radical cation.



(2)

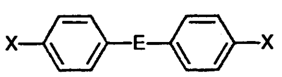
The electrochemical oxidation of compounds **1–39** was carried out in acetonitrile containing tetraethylammonium perchlorate as the electrolyte using a scan rate of 100 mV s^{-1}. With some exceptions, only one, irreversible oxidation peak was observed in the cyclic voltammogram. The peak potentials *vs.* Ag/AgCl are reported in Table 1. Considering the differences in solvents and electrolytes used, the values are in good agreement with the few oxidation potentials reported in the literature.[14,15] However, a considerably lower oxidation potential has been reported for compound **11**.†

Correlation Analysis.—Substituted aromatic compounds X-Ar-Z, containing a substituent X and a redox centre Z, have been frequently studied by electrochemical methods. The half-wave oxidation/reduction potential shifts, $\Delta E_{1/2}$, are often well correlated with the Hammett σ constants according to eqn. (3).[16]

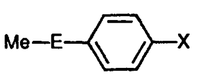
To the best of our knowledge, in the series of diaryl

---

† Liftman and Albeck[15] reported a lower oxidation potential (0.80 V) for compound **11** than for compounds **16** (1.06 V) and **20** (0.86 V).



1 E = Se; X = NO$_2$
2 E = Se; X = CO$_2$H
3 E = Se; X = Cl
4 E = Se; X = H
5 E = Se; X = F
6 E = Se; X = Me
7 E = Se; X = NHAc
8 E = Se; X = OMe
9 E = Se; X = NH$_2$
10 E = Se; X = NMe$_2$
11 E = Te; X = NO$_2$
12 E = Te; X = CF$_3$
13 E = Te; X = CO$_2$Me
14 E = Te; X = Br
15 E = Te; X = Cl
16 E = Te; X = H
17 E = Te; X = F
18 E = Te; X = Ph
19 E = Te; X = Me
20 E = Te; X = OMe
21 E = Te; X = OH
22 E = Te; X = NHPh
23 E = Te; X = NH$_2$
24 E = Te; X = NMe$_2$



25 E = S ; X = CF$_3$
26 E = S ; X = H
27 E = S ; X = Me
28 E = S ; X = OMe
29 E = S ; X = NMe$_2$
30 E = Se; X = CF$_3$
31 E = Se; X = H
32 E = Se; X = Me
33 E = Se; X = OMe
34 E = Se; X = NMe$_2$
35 E = Te; X = CF$_3$
36 E = Te; X = H
37 E = Te; X = Me
38 E = Te; X = OMe
39 E = Te; X = NMe$_2$

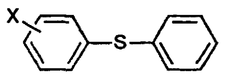
Table 1 Peak oxidation potentials for compounds **1–39**, **43–48**

Compound	$E_p{}^a$/V	Compound	$E_p{}^a$/V
1	1.76	**23**	0.56^b
2	1.54	**24**	0.50^b
3	1.44	**25**	1.80^b
4	1.38	**26**	1.56^b
5	1.38	**27**	1.48^b
6	1.32	**28**	1.43^b
7	1.25	**29**	0.88^b
8	1.22	**30**	1.34
9	0.80^b	**31**	1.22
10	0.68^b	**32**	1.20
11	1.14	**33**	1.12
12	1.12	**34**	0.80^b
13	1.02	**35**	0.78
14	0.96	**36**	0.77
15	0.98	**37**	0.71
16	0.95	**38**	0.66
17	0.98	**39**	0.52^b
18	0.89	**43**	1.44^b
19	0.89	**44**	0.98^b
20	0.80	**45**	0.84^b
21	0.80^b	**46**	0.88^b
22	0.66^b	**47**	0.65^b
		48	0.93^b

[a] Values given are peak potentials of the first oxidation peak in V *vs.* Ag/AgCl. [b] More than one oxidation peak was observed in the cyclic voltammogram.

$$\Delta E_{\frac{1}{2}} = (E_{\frac{1}{2}})_x - (E_{\frac{1}{2}})_H = \rho\sigma \qquad (3)$$

chalcogenides and aryl alkyl chalcogenides, only one such correlation has been attempted. It was found that the oxidation potential of five unsymmetrical diaryl sulfides **40** correlated well with Hammett σ_o-values.[12]



40 X = 4-H, 3-Me, 4-Me, 3-OH, 4-OH

Our attempts to correlate oxidation peak potentials of symmetrical diaryl selenides and tellurides **1–24** with Hammett σ-values are shown in Fig. 1. A slightly better correlation with $\sigma_p{}^+$ (selenides **1–10**, $R = 0.98$; tellurides **11–24**, $R = 0.98$) than with σ_p (selenide series, $R = 0.95$; telluride series, $R = 0.95$) was observed. The ρ-values for the two series were 0.41 and 0.24, respectively.

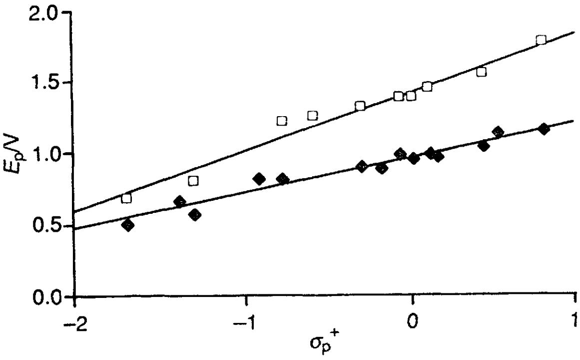


Fig. 1 Correlation of peak oxidation potentials of diaryl selenides **1–10** and diaryl tellurides **11–24** with Hammett $\sigma_p{}^+$-values: □, $E_p = 1.417 + 0.411\ \sigma_p{}^+$ (ArSeAr); ◆, $E_p = 0.955 + 0.244\ \sigma_p{}^+$ (ArTeAr)

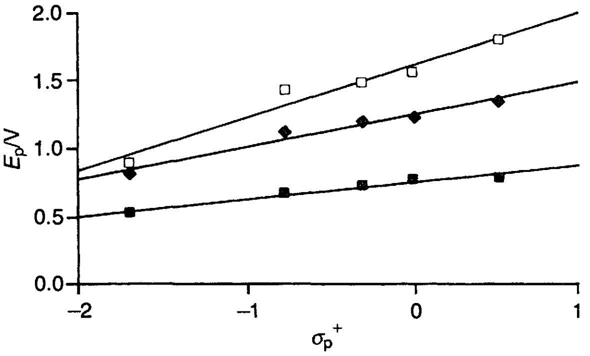


Fig. 2 Correlation of peak oxidation potentials of aryl methyl sulfides **25–29**, aryl methyl selenides **30–34** and aryl methyl tellurides **35–39** with Hammett $\sigma_p{}^+$-values: □, $E_p = 1.607 + 0.391\ \sigma_p{}^+$ (ArSMe); ◆, $E_p = 1.242 + 0.236\ \sigma_p{}^+$(ArSeMe); ■, $E_p = 0.743 + 0.122\ \sigma_p{}^+$ (ArTeMe)

Equally good correlations of peak oxidation potentials with $\sigma_p{}^+$ were obtained for the three series of aryl methyl chalcogenides (sulfides **25–29**, $R = 0.98$; selenides **30–34**, $R = 0.98$; tellurides **35–39**, $R = 0.98$). The graphical representations are shown in Fig. 2. The ρ-values were 0.39, 0.24 and 0.12, respectively.

^{125}Te *NMR Studies*.—^{77}Se NMR spectra of symmetrical 4,4′-disubstituted diaryl selenides have been previously recorded.[17] In that report it was also shown that the ^{77}Se chemical shift correlated very well with Hammett σ_p ($R = 0.97$) or $\sigma_p{}^+$-values ($R = 0.98$). We were curious to see if similar correlations could be obtained in the series of diaryl tellurides. ^{125}Te data for compounds **11–12** and **14–24** are reported in Table 2. In contrast to the selenium series, it was found that the chemical shift of the heteroatom correlated slightly better with Hammett σ_p (R = 0.98; Fig. 3) than with $\sigma_p{}^+$-values ($R = 0.95$; not shown).

Discussion

It is reasonable to assume that the oxidation of diaryl chalcogenides and aryl methyl chalcogenides occurs by removal of electrons from the electron-rich chalcogen atom.[18] Therefore, we have assigned the first (and often only) irreversible oxidation peak in the cyclic voltammograms of compounds **1–39** to heteroatom oxidation. Some compounds containing strongly donating substituents (*e.g.* amines), which could be easily

Table 2 ^{125}Te-chemical shifts of compounds **11–12**, **14–24** in $CDCl_3$ at 126.242 MHz relative to Me_2Te

Compound	δ ^{125}Te
11	753
12	727
14	699
15	697
16	689
17	687
18	670
19	661
20	649
21	657
22	649
23	637
24	612

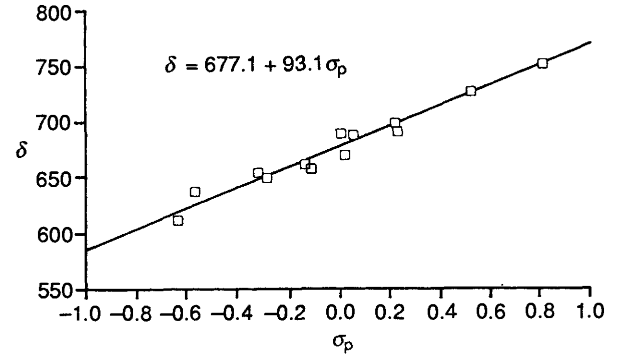
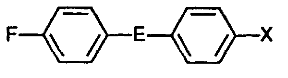


Fig. 3 Correlation of ^{125}Te-chemical shifts of diaryl tellurides **11–12** and **14–24** with Hammett σ_p-values

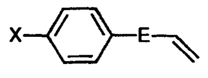
oxidized themselves, showed quite complex cyclic voltammograms with several oxidation peaks. However, the fit in the Hammett plots of these compounds seems to indicate that our assumption concerning the site of first oxidation is valid.

The oxidation potential of diorganyl chalcogenides can thus be considered a localized physical property,[19] which is determined primarily by the electron density of the heteroatom. This, in turn, is related to the ability of the chalcogen atom to interact electronically with organic groups bonded to it, and reflected by its NMR chemical shift (^{125}Te in this work, ^{77}Se in others[17]).

There has been considerable interest in the relative abilities of heteroatoms to transmit electronic effects. Thus, changes in ^{19}F and ^{13}C NMR shifts were used to monitor the degree of conjugation, through the heteroatom, between aryl groups (compounds **41**[20]) and an aryl and a vinyl group (compounds **42**[21]). The following order of transmittance was found: O > S > Se. In the tellurium series the dipole moments, basicity constants and ^{1}H NMR data of 4-substituted phenyl(4-dimethylaminophenyl) tellurides were determined to study the transmission of electronic effects through a bridging tellurium atom.[22]



41

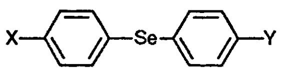


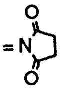
42

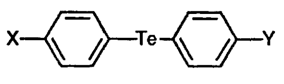
The slope of the lines correlating peak oxidation potentials with $\sigma_p{}^+$-values for the three series of aryl methyl chalcogenides would reflect the degree of conjugation, through an aromatic nucleus, between a heteroatom and a *para*-substituent. As seen from Fig. 2 the order S > Se > Te indicates decreasing conjugation with increasing chalcogen substitution. For substances in which two aryl groups are attached to an electroactive group, the change in half-wave potential due to substituents in the 4,4′-positions has been expressed by eqn. (4).[23] For symmetrically substituted compounds ($\sigma_1 = \sigma_2$)

$$\Delta E_{1/2} = \rho_1\sigma_1 + \rho_2\sigma_2 \qquad (4)$$

this equation is reduced to eqn. (3) ($\rho = \rho_1 + \rho_2$). The good correlations observed between peak oxidation potentials and $\sigma_p{}^+$values for 4,4′-disubstituted diaryl selenides **1–10** and tellurides **11–24** are therefore not surprising (Fig. 1). A similarly good correlation was recently found between ^{13}C chemical shifts and $\sigma_I/\sigma_R{}^\circ$-values for a series of symmetrical 4,4′-disubstituted diaryl sulfides.[24] However, the good correlation results can also be explained assuming interaction between the heteroatom and only one of the aryl groups, the other one serving, owing to lack of conjugation, as a 'dummy'.[24] To discriminate between the two explanations, the peak oxidation potentials for four unsymmetrical diarylselenides **43–46** and two unsymmetrical diaryltellurides **47–48** were determined (Table 1). It was not possible to fit these values into eqn. (4). However, the peak oxidation potentials of compounds **43–46** were found to fit reasonably well into the Hammett plot of Fig. 1 (selenide series) if only the more negative σ-value of the two was used (the deviations from the straight line for compounds **43–46** were 0.27, 0.09, −0.05 and −0.01 V, respectively). Similarly, compounds **47–48** were fitted into the Hammett plot of Fig. 1, telluride series (the deviations from the straight line were 0.11 and 0.20 V, respectively, for compounds **47** and **48**). These results seem to support the idea that the heteroatom is interacting with only one of the aryl groups.



43 X = NO_2; Y = NHAc
44 X = NO_2; Y = NH_2
45 X = NH_2; Y = NHAc
46 X = NH_2; Y = 



47 X = NMe_2; Y = OMe
48 X = OH ; Y = H

Experimental

Melting points (uncorrected) were determined by using a Büchi 510 melting point apparatus. ^{1}H NMR spectra were obtained with Bruker AC-F250 and Varian VXR-300 instruments operating at 250 and 300 MHz, respectively, and recorded for solutions containing tetramethylsilane as the internal standard. ^{125}Te spectra were recorded using a Bruker AM 400 spectrometer operating at 126.242 MHz with a spectral window of 50 000 Hz. The solutions were 0.05 mol dm^{-3} or saturated. $CDCl_3$ was used as solvent and the temperature was maintained at 25 °C. Chemical shifts are reported in ppm relative to an external reference of dimethyl telluride containing *ca.* 3% $CDCl_3$ for locking purposes. Elemental analyses were performed by Analytical Laboratories, Engelskirchen, Germany and Mikrokemi, Uppsala, Sweden.

Compounds **1**,[25] **2**,[17] **3**,[26] **4**,[27] **5**,[28] **6**,[29] **7**,[30] **8**,[31] **9**,[30] **10**,[32] **11**,[33] **14**,[34] **15**,[34] **16**,[34] **17**,[35] **18**,[36] **19**,[34] **20**,[33] **28**,[37] **29**,[37] **33**,[37] **34**,[37] **37**,[38] **38**,[37] **39**,[37] **44**,[39] and **47**[40] were prepared according to literature methods. Compound **12**, m.p. 52–53 °C (Found: C, 40.1; H, 1.8. $C_{14}H_8F_6Te$ requires C, 40.25; H, 1.93%), was prepared from the corresponding ditelluride[41] by using a known procedure.[34] δ_H(250 MHz; $CDCl_3$) 7.47 (d, 4 H) and 7.79 (d, 4 H). Compounds **25**, m.p. 34–36 °C (lit.,[42] 37 °C) and **30**, m.p. 39–40 °C (lit.,[43] 32–33 °C) were prepared in analogy with a published procedure[37] as well as compounds **26**, **27**, **31**, **32** and **36**. The NMR spectra of these materials were in good agreement with literature data.[44] Compound **35** was obtained in analogy with a published procedure,[38] m.p. 32–33 °C; δ_H(250 MHz; $CDCl_3$) 2.25 (s, 3 H), 7.42 (d, 2 H) and 7.70 (d, 2 H). *The material* was analysed as a Te,Te-dichloride, m.p. 115–116 °C (Found: C, 26.9; H, 2.0. $C_8H_7Cl_2F_3Te$ requires C, 26.79; H, 1.97%); δ_H(250 MHz; $CDCl_3$), 3.35 (d, 2 H), 7.82 (d, 2 H) and 8.33 (d, 2 H), obtained in 66% isolated yield as a precipitate by addition of sulfuryl chloride (0.029 g, 0.22 mmol) in hexanes (2 cm^3) to a solution of the telluride (0.062 g, 0.22 mmol) in hexanes (6 cm^3).

Bis(4-*methoxycarbonylphenyl*) *Telluride* (**13**).—To a suspension of finely crushed elemental tellurium (1.0 g, 7.84 mmol) in water (12 cm^3) was added $NaBH_4$ (0.82 g, 21.7 mmol) and the mixture heated under nitrogen until an exothermic reaction started. To the cooled, stirred reaction mixture was added 4-methoxycarbonylbenzenediazonium tetrafluoroborate (5.0 g, 20.0 mmol). After 2 h, methanol (10 cm^3) was added and stirring continued overnight. Work-up included filtration from precipitated elemental tellurium, extraction with CH_2Cl_2 and drying. Flash chromatography (SiO_2/CH_2Cl_2) afforded compound **13**, contaminated by the corresponding ditelluride. After treatment of the mixture in refluxing dioxane (15 cm^3) with freshly prepared copper powder[45] (0.8 g) for 1.5 h, 0.615 g (20%) of pure compound **13**, m.p. 93 °C (Found: C, 48.2; H, 3.4. $C_{16}O_4Te$ requires C, 48.30; H, 3.55%); δ_H(250 MHz, $CDCl_3$): 3.91 (s, 6 H), 7.70 (d, 4 H) and 7.90 (d, 4 H), was isolated.

Bis(4-*hydroxyphenyl*) *Telluride* (**21**).—4-Hydroxyphenyltellurium(III) chloride[46] (5.0 g, 15.3 mmol) was added to a separating funnel containing $Na_2S_2O_5$ (6.0 g, 31.6 mmol) in water (100 cm^3) and CH_2Cl_2 (100 cm^3). Vigorous shaking produced a reddish-black heterogeneous mixture which was filtered to remove insoluble material. This was extracted with boiling CH_2Cl_2 (100 cm^3) and combined with the organic phase from the separating funnel. Following drying and evaporation the residue was dissolved in dioxane (30 cm^3) and heated at reflux with activated copper powder[45] for 1 h. This treatment caused a decoloration of the solution. Filtration from copper residues, evaporation under reduced pressure and recrystallization from CH_2Cl_2/hexanes afforded 0.55 g (23%) of compound **21**, m.p. 102–103 °C (Found: C, 45.7; H, 3.2. $C_{12}H_{10}O_2Te$ requires C, 45.93; H, 3.21%); δ_H(250 MHz; $CDCl_3$) 4.68 (s, 2 H), 6.69 (d, 4 H) and 7.58 (d, 4 H).

The preparation of bis[4-(phenylamino)phenyl] telluride (**22**), m.p. 91 °C (Found: C, 62.0; H, 4.3. $C_{24}H_{20}N_2Te$ requires C, 62.12; H, 4.34%); δ_H(250 MHz; $CDCl_3$) 5.67 (s, 2 H), 6.88 (d, 4 H), 6.94 (m, 2 H), 7.05 (d, 4 H), 7.25 (m, 4 H) and 7.58 (d, 4 H), bis(4-aminophenyl)telluride (**23**), m.p. 127–128 °C (Found: C, 46.1; H, 3.8. $C_{12}H_{12}N_2Te$ requires C, 46.22; H, 3.88%); δ_H(250 MHz; $CDCl_3$) 3.66 (s, 4 H), 6.52 (d, 4 H) and 7.49 (d, 4 H) and bis[4-(dimethylamino)phenyl] telluride (**24**), m.p. 130 °C (lit., 128–130 °C);[47] δ_H(250 MHz; $CDCl_3$) 2.91 (s, 12 H), 6.56 (d, 4 H) and 7.58 (d, 4 H) will be described elsewhere.[48]

(4-*Acetamidophenyl*) 4-*Nitrophenyl Selenide* (**43**).—Acetic anhydride (0.5 cm^3) was added dropwise to a solution of compound **44** (0.50 g, 1.7 mmol) in THF (25 cm^3). After being stirred at ambient temperature overnight, TLC (EtOAc) indicated complete acetylation of the starting material. Evaporation of the solvent afforded an orange, crystalline product which was washed with methanol and dried to give 0.35 g (61%) of pure compound **43** (Found: C, 50.5; H, 3.4; N, 7.9. $C_{14}H_{12}N_2O_3Se$ requires C, 50.2; H, 3.6; N, 8.4%); δ_H(300 MHz; $CDCl_3$) 2.23 (s, 3 H), 7.31 (d, 2 H), 7.39 (s, 1 H), 7.59 (s, 4 H) and 8.02 (d, 2 H).

(4-*Acetamidophenyl*) 4-*Aminophenyl Selenide* (**45**).—A solution of compound **9** (2.6 g, 10.0 mmol) in THF (50 cm^3) containing triethylamine (3 cm^3) and acetic anhydride (0.95 cm^3, 10.0 mmol) was left overnight at ambient temperature. Evaporation afforded an oil which was dissolved in CH_2Cl_2 and washed with water. Following drying, evaporation and trituration with diethyl ether, 1.15 g of white crystals were obtained (mixture of mono- and di-acetylated compound). Flash chromatography (SiO_2/EtOAc) afforded 0.60 g (20%) of compound **45**, m.p. 108–109 °C (Found: C, 55.1; H, 4.6; N, 9.3. $C_{14}H_{14}N_2OSe$ requires C, 55.1; H, 4.6; N, 9.2%); δ_H(300 MHz; [$^2H_6$]DMSO), 2.02 (s, 3 H), 5.41 (s, 2 H), 6.56 (d, 2 H), 7.20 (d, 2 H), 7.23 (d, 2 H), 7.47 (d, 2 H) and 9.95 (s, 1 H).

(4-*Aminophenyl*) 4-*Succinimidophenyl Selenide* (**46**).—Compound **44** (1.17 g, 4.0 mmol) was acylated using the procedure described above for the preparation of compound **43**, except that succinic anhydride (0.50 g, 5.0 mmol) replaced acetic anhydride. After evaporation of the solvent, 1.5 g (100%) of crude (4-nitrophenyl) 4-succinimidophenyl selenide was obtained. To a solution of this material (0.40 g, 1.07 mmol) in acetic acid (5 cm^3), was added $SnCl_2{\cdot}2\ H_2O$ (0.72 g, 3.2 mmol) in conc. HCl (0.5 cm^3). The reaction mixture was stirred for 6 h at ambient temperature when another portion of tin(II) chloride (0.72 g in 0.5 cm^3 HCl) was added. TLC (EtOAc) after another 6 h indicated complete reduction of the starting material. After being made alkaline with NaOH, extraction into chloroform, drying and evaporation, 0.20 g (54%) of compound **46**, m.p. 210 °C (decomp.) was obtained after recrystallization from water (Found: C, 55.2; H, 4.1; N, 8.1. $C_{16}H_{14}N_2O_2Se$ requires C, 55.7; H, 4.2; N, 8.1%); δ_H(300 MHz; [$^2H_6$]DMSO): 2.77 (s, 4 H), 5.52 (s, 2 H), 6.61 (d, 2 H), 7.12 (d, 2 H), 7.27 (d, 2 H) and 7.31 (d, 2 H).

Phenyl (4-*Hydroxyphenyl*) *Telluride* (**48**).—A solution of phenyltellurenyl bromide was prepared under nitrogen at −78 °C by addition of bromine (63 mm^3, 1.23 mmol) to a solution of diphenyl ditelluride (0.50 g, 1.22 mmol) in dry THF (15 cm^3). To this solution was added by syringe a solution of 1-lithio-4-(*tert*-butyldimethylsilyloxy)benzene, prepared from the reaction of *tert*-butyllithium (2.9 cm^3; 1.7 mol dm^{-3}, 4.9 mmol) and 1-bromo-4(*tert*-butyldimethylsilyloxy)benzene (0.70 g, 2.4 mmol) in dry THF (10 cm^3) at −78 °C. After 1 h at −78 °C the cooling-bath was removed and stirring continued for 2 h. The work-up included evaporation of the solvent, extraction of the product into CH_2Cl_2, washing with water and drying of the organic phase. After evaporation the residue was dissolved in dry THF (10 cm^3) and treated with tetrabutylammonium fluoride (2 cm^3; 1.0 mol dm^{-3}, 2.0 mmol) in an ice-bath for 30 min to remove the silyl protecting group. Work-up as described above and chromatography (SiO_2/CH_2Cl_2) afforded a crude product. To remove some remaining phenol the product was dissolved in CH_2Cl_2–hexane, 1:1 and SO_2Cl_2 was added until no more phenyl(4-hydroxyphenyl)tellurium dichloride was precipitated. The dichloride was then reduced with $Na_2S_2O_5$ in water–ether in a separating funnel and the product passed through a short silica column (CH_2Cl_2). The yield of compound **48**, m.p. 65 °C (Found: C, 48.6; H, 3.3. $C_{12}H_{10}OTe$ requires C, 48.40; H, 3.38%); δ_H(250 MHz; $CDCl_3$) 4.81 (s, 1 H), 6.73 (d, 2 H), 7.14–7.26 (several peaks, 3 H), 7.57 (m, 2 H) and 7.68 (d, 2 H), was 0.10 g (14%).

1-Bromo-4-(*tert*-butyldimethylsilyloxy)benzene was prepared in 89% yield by stirring 4-bromophenol (1.70 g, 9.8 mmol) and *tert*-butyldimethylsilyl chloride (1.50 g, 10.0 mmol) in triethylamine (4 cm^3) for 24 h, followed by chromatography (SiO_2/CH_2Cl_2) of a diethyl ether extract (50 cm^3) of the reaction mixture.

Electrochemistry.—The oxidation potentials, given as the peak potentials (E_p), were determined from cyclic voltammograms using a BAS voltammograph, CV-27, and an Ag/AgCl electrode as reference. A glassy carbon electrode was used as working electrode and a platinum electrode as auxiliary for IR compensation.

The working electrode was polished between every sample to avoid deactivation of the surface. The voltammogram was scanned positively with a linear scan-rate of 100 mV s^{-1} in CH_3CN, containing $<0.02\%$ water, and using 35 mmol dm^{-3} NEt_4ClO_4 (Kodak, recrystallized from ethanol before use), as the electrolyte. Sample concentration was 1–3 mmol dm^{-3}.

The reference electrode was compared with a new saturated calomel electrode (SCE) before every analysis. The potential *vs.* the SCE was -40 mV measured in 50 mmol dm^{-3} phosphate buffer, pH = 3. The oxidation potentials for 2,3,7,8-tetramethoxythianthrene were determined as a reference (0.92; 1.38 V) giving less than 1% difference in oxidation potentials from time to time.

Hammett σ-values were from reference 19 (except for *N*-phenylamino[49] and succinimido[50] substituents).

Acknowledgements

Financial support by the National Swedish Board for Technical Development and the Swedish Natural Science Research Council is gratefully acknowledged. The authors are grateful to Professor L. Eberson, University of Lund, for valuable comments on the manuscript.

References

1 M. J. Parnham and E. Graf, *Prog. Drug Res.*, 1991, **36**, 9; D. L. Klayman in *Organic Selenium Compounds: Their Chemistry and Biology*, eds. D. L. Klayman and W. H. Günther, Wiley, New York, 1973, p. 727; R. J. Shamberger in *Biochemistry of Selenium*, New York, Plenum Press, 1983, 273.

2 A. Wendel, M. Fausel, H. Safayhi, G. Tiegs and R. Otter, *Biochem. Pharmacol.*, 1984, **33**, 3241.

3 A. Müller, E. Cadenas, P. Graf and H. Sies, *Biochem. Pharmacol.*, 1984, **33**, 3235.

4 M. J. Parnham, E. Graf, P. Kuhl and S. Leyck in *Advances in Inflammation Research*, vol. 12, eds. A. Lewis, N. Ackerman and I. Ofterness, Raven Press Ltd, New York, 1988, p. 257.

5 P. Kuhl, H. O. Borbe, H. Fischer, A. Römer and H. Safayhi, *Prostaglandins*, 1986, **31**, 1029.

6 I. A. Cotgreave, P. Moldéus, L. Engman and A. Hallberg, *Biochem. Pharmacol.*, 1991, **42**, 1481.

7 I. A. Cotgreave, P. Moldéus, A. Hallberg, M. Lindén, R. Brattsand and C. M. Andersson, manuscript in preparation.

8 H. Behret and G. Sandstede, *Electroanal. Chem. Interfac. Electrochem.*, 1974, **56**, 455.

9 D. S. Houghton and A. A. Humffray, *Electrochim. Acta*, 1972, **17**, 1421.

10 F. Magno and G. Bontempelli, *Electroanal. Chem. Interfac. Electrochem.*, 1972, **36**, 389.

11 S. Torii, Y. Matsuyama, K. Kawasaki and K. Uneyama, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 2912.

12 M. G. Voronkov, E. N. Deryagina, N. M. Deriglazov, L. G. Shagun and M. I. Anisimova, *Zh. Obshch. Khim.*, 1980, **50**, 2603.

13 H. Wendt and H. Hoffelner, *Electrochim. Acta*, 1983, **28**, 1453.

14 R. Seeber, A. Cinquantini, P. Zanello and G. A. Mazzocchin, *J. Electroanal. Chem.*, 1978, **88**, 137.

15 Y. Liftman and M. Albeck, *Electrochim. Acta*, 1983, **28**, 1841.

16 P. Zuman, *Substituent Effects in Organic Polarography*, Plenum Press, New York, 1967, p. 43.

17 S. Gronowitz, A. Konar and A.-B. Hörnfeldt, *Org. Magn. Reson.*, 1977, **9**, 213. For alkyl aryl selenides see also W. McFarlane and R. J. Wood, *J. Chem. Soc., Dalton Trans.*, 1972, 1397.

18 G. Distefano, V. Galasso, K. J. Irgolic and G. C. Pappalardo, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1109; G. Tschmutowa and H. Bock, *Z. Naturforsch., Teil B*, 1976, **31**, 1611; F. P. Colonna, G. Distefano, V. Galasso, K. J. Irgolic, C. E. King and G. Pappalardo, *J. Organomet. Chem.*, 1978, **146**, 235; J. F. Muller, *Helv. Chim. Acta*, 1975, **58**, 2646.

19 O. Exner, *Correlation Analysis of Chemical Data*, Plenum Press, New York, 1988, p. 176.

20 I. R. Ager, L. Phillips and S. J. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1972, 1988.

21 W. F. Reynolds and R. A. McClelland, *Can. J. Chem.*, 1977, **55**, 536.

22 I. D. Sadekov, M. L. Cherkinskaya, V. L. Pavlova, V. A. Bren and V. I. Minkin, *Zh. Obshch. Khim.*, 1977, **47**, 2774.

23 See ref. 16, p. 44.

24 R. Chandrasekaran, S. Perumal and D. A. Wilson, *Magn. Reson. Chem.*, 1987, **25**, 1001.

25 H. Rheinboldt in *Methoden der Organischen Chemie*, Houben-Weyl, band IX, ed. E. Müller, Georg Thieme Verlag, Stuttgart, 1955, p. 993.

26 M. T. Rogers and T. W. Campbell, *J. Am. Chem. Soc.*, 1947, **69**, 2039.

27 H. M. Leicester, *Org. Synth.*, Coll. Vol. II, 1943. 238.

28 J. D. McCullough and B. A. Eckerson, *J. Am. Chem. Soc.*, 1945, **67**, 707.

29 H. M. Leicester and F. W. Bergstrom, *J. Am. Chem. Soc.*, 1931, **53**, 4428.

30 J. Matti, *Bull. Soc. Chim. Fr.*, 1940, 617.

31 Ref. 25, p. 992.

32 O. Behaghel and K. Hofmann, *Ber. Dtsch. Chem. Ges.*, 1939, 72, 582.

33 L. Engman, *J. Org. Chem.*, 1983, **48**, 2920.

34 I. D. Sadekov, A. Ya. Bushkov and V. I. Minkin, *Zh. Obshch. Khim.*, 1973, **43**, 815.

35 I. D. Sadekov, A. Ya. Bushkov and V. I. Minkin, *Zh. Obshch. Khim.*, 1977, **47**, 631.

36 W. S. Haller and K. J. Irgolic, *J. Organomet. Chem.*, 1972, **38**, 97.

37 L. Engman and J. S. E. Hellberg, *J. Organomet. Chem.*, 1985, **296**, 357.

38 J. L. Piette and M. Renson, *Bull. Soc. Chim. Belg.*, 1970, **79**, 353.

39 L. M. Litvinenko and R. S. Chesko, *Zh. Obshch. Khim.*, 1960, **30**, 3682.

40 N. Petragnani, *Tetrahedron*, 1961, **12**, 219.

41 L. Engman and J. Persson, *J. Organomet. Chem.*, 1990, **388**, 71.

42 E. T. McBee and P. J. Graham, *J. Am. Chem. Soc.*, 1950, **72**, 4235.

43 E. S. Lewis, T. I. Yousaf and T. A. Douglas, *J. Am. Chem. Soc.*, 1987, **109**, 2152.

44 G. Llabres, M. Baiwir, J. Christiaens, J. Denoel, L. Laitem and J.-L. Piette, *Can. J. Chem.*, 1978, **56**, 2008.

45 A.I. Vogel, *Practical Organic Chemistry*, 3rd edn., Longman, London, 1957, p. 192.

46 L. Reichel and E. Kirschbaum, *Ann. Chem.*, 1936, **523**, 211.

47 G. T. Morgan and H. Burgess, *J. Chem. Soc.*, 1929, 1103.

48 L. Engman and J. Persson, manuscript in preparation.

49 O. Exner in *Correlation Analysis in Chemistry*, eds. N. B. Chapman and J. Shorter, Plenum Press, New York, 1978.

50 C. Hansch and A. Leo, *Substituent Constants for Correlation Analysis in Chemistry and Biology*, John Wiley and Sons, New York, 1979.

Paper 2/00984F
Received 25*th February* 1992
Accepted 6*th April* 1992