Electrochemical Determination of New Hammett σ Constants Corresponding to PhSe, PhTe, Se^-, and Te^- Substituents

Rita Prest and Chantal Degrand *

Laboratoire de Synthèse et d'Électrosynthèse Organométalliques associé au CNRS (UA 33), Faculté des Sciences, 6 bd Gabriel, 21000 Dijon, France

Hammett σ_m and σ_p constants for PhTe and Te^- substituents have been derived and compared with those of the Se homologues derived from the half-wave potential shift of the first reduction step of phenylchalcogenobenzophenone and the third reduction step of symmetrical bis(cyanophenyl) chalcogenide.† For the PhTe, PhSe, Te^-, and Se^- substituents, the σ_m values are 0.20, 0.20, −0.57, and −0.59 and the σ_p values are 0.29, 0.22, −0.72, and −0.84, respectively. The σ_p value of the Te^- group and all of the σ_m values have been determined for the first time.

Quantitative data on the directing and activating effects of selenium- and tellurium-containing groups were collected for the first time in 1986.[1] These data show that Hammett σ constants and Taft σ_I and σ_R constants are very scarce for groups containing bivalent tellurium atoms whereas a large amount of data on the electronic effects of *p*-seleno substituents has been provided.

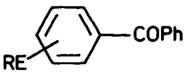
In the case of telluro derivatives, the stability of which can be low, synthetic as well as chemical difficulties may preclude the quantitative determination of reactivity data resulting from ionization and substitution reactions. Physical measurements may be carried out more conveniently and thus ^{19}F n.m.r. studies[2,3] have been performed to determine the Hammett and Taft constants of the *p*-TeMe and PhTe substituents, which are so far the only groups to be examined which contain bivalent Te atoms.

For substituted aromatic molecules YArZ containing a substituent Y and a redox centre Z, electrochemical measurements can be easily performed. The half-wave potential shifts $\Delta E_{1/2}$ are correlated with the Hammett σ constants according to equation (1) where ρ is the reaction constant,[4] and

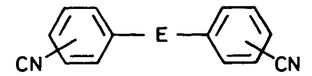
$$\Delta E_{1/2} = (E_{1/2})_Y - (E_{1/2})_H = \rho\sigma \qquad (1)$$

so unknown σ values can be easily derived. This method has been applied to determine the σ value of the *p*-Se^- substituent from the half-wave reduction potential of bis(nitrophenyl) diselenide.[5]

We carried out a cathodic study in aprotic media of phenylseleno- and phenyltelluro-benzophenone (**1a–g**) and the symmetrical chalcogenides (**2a–f**), which allowed us to determine the Hammett σ constants for the PhTe and Te^- substituents, and to compare these values with those of the Se homologues. The benzophenone derivatives (**1a–f**) were prepared from electrogenerated PhE^- anion and bromobenzophenone, by electrochemically induced $S_{RN}1$ substitution.[6] The symmetrical chalcogenides (**2a–c,f**) were isolated as minor compounds in the synthesis of phenylseleno- and phenyltellurobenzonitrile from PhE^- and chlorobenzonitrile by the same electrochemical process.[7,8] Compounds (**1g**) and (**2d,e**) are new chalcogeno derivatives which were also prepared according to the above method.



(1)	E
a	2-SePh
b	3-SePh
c	4-SePh
d	2-TePh
e	3-TePh
f	4-TePh
g	4-SeCH$_2$Ph



(2)	E
a	2,2'-Se
b	3,3'-Se
c	4,4'-Se
d	2,2'-Te
e	3,3'-Te
f	4,4'-Te

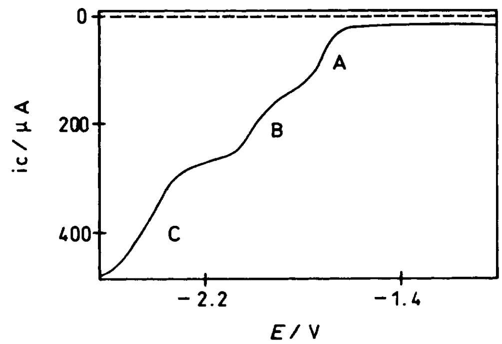


Figure 1. Voltammogram of (**1f**) (2 mmol dm^{-3}) in MeCN at an RDE.

Results and Discussion

Cathodic Behaviour of (**1a–g**) *and* (**2a–f**).—A voltammetric study was carried out in aprotic media [*N,N*-dimethylformamide (DMF), acetonitrile] at a glassy-carbon rotating-disc electrode (RDE) or stationary-disc electrode (SDE). In the case of the ketones (**1a–g**), the number of electrons involved in each reduction step was determined by comparison of the limiting currents of the successive waves with the one-electron limiting current of both waves of benzophenone. For the dinitrile derivative (**2a–f**), the comparison was made with the single two-electron reduction wave of diphenyl selenide[9a] or telluride.[9b]

Ketones substituted with a PhE group presented three waves A, B, and C corresponding to the successive uptake of one, one, and two electrons (Figure 1). Wave C, which was observed at rather negative potentials, was better defined in DMF than in

---

† In this paper, *chalcogeno* refers to the heteroatoms Se and Te.

Table. Half-wave potentials for the first reversible reduction step of benzophenone substituted by PhE and 4-Se$^-$ groups (MeCN) and of benzonitrile substituted by E$^-$ groups (DMF), and corresponding σ values of the substituents (E = Se, Te).

		$-E_{1/2}$/V			σ		
Product	Substituent	Wave A^a	Wave B	Wave C^b	*ortho*	*meta*	*para*
PhCOPh	H	1.785			0	0	0
(1a)	2-SePh	1.735			0.12		
(1b)	3-SePh	1.710				0.20	
(1c)	4-SePh	1.705					0.22(0.13^{13}, 0.42^{14}, 0.23^{15})
(1d)	2-TePh	1.622			0.47		
(1e)	3-TePh	1.710				0.20	
(1f)	4-TePh	1.680					0.29(0.34^3)
(1g)	4-Se$^-$		2.040^c				−0.84(−0.98^5)
PhCN	H		2.315^b		0	0	0
(2a)	2-Se$^-$			2.665	−0.64		
(2b)	3-Se$^-$			2.640		−0.59	
(2c)	4-Se$^-$			2.775			−0.84(−0.98^5)
(2d)	2-Te$^-$			2.735	−0.77		
(2e)	3-Te$^-$			2.630		−0.57	
(2f)	4-Te$^-$			2.710			−0.72

^{a} Scheme 1. ^{b} Scheme 3. ^{c} Scheme 2.

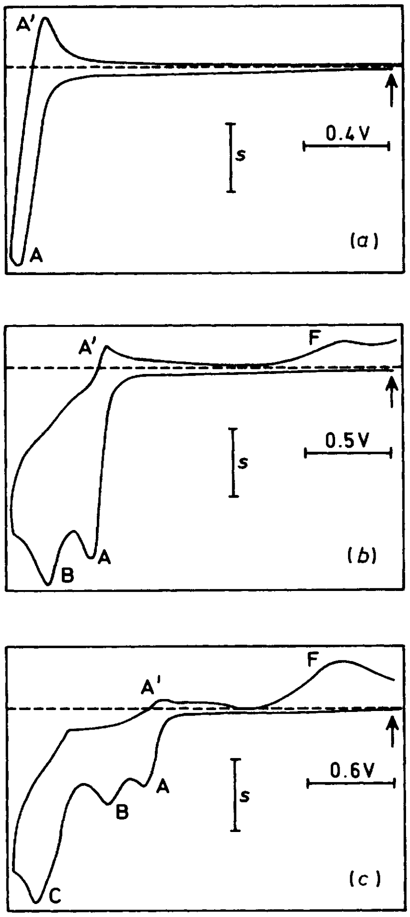
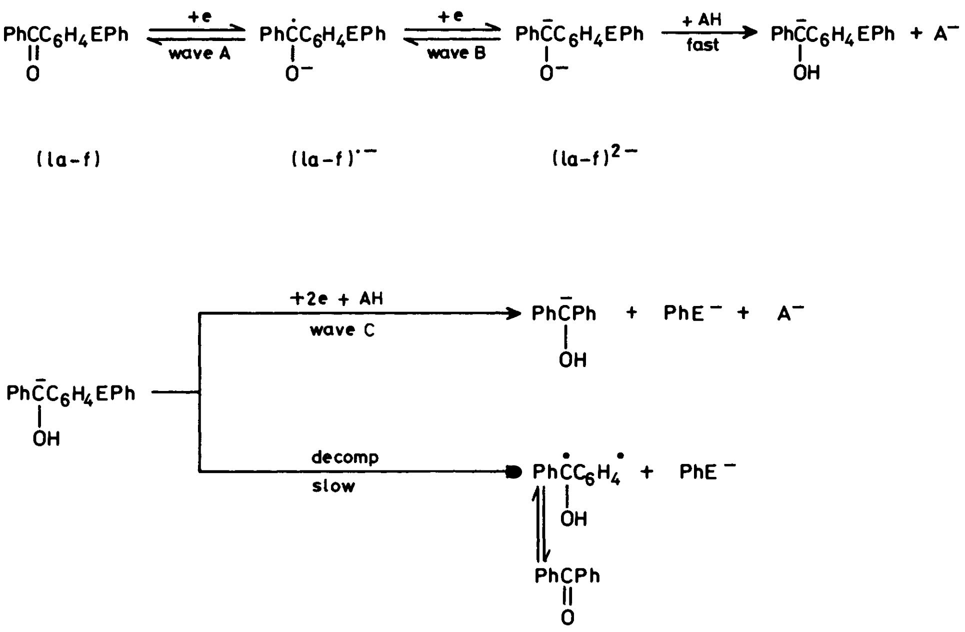


Figure 2. Cyclic voltammograms of **(1f)** (2 mmol dm^{-3}) in MeCN at an SDE. The initial potential is 0 V and indicated by an arrow. The sensitivity s = 20 μA (*a*) and (*b*) and 40 μA (*c*) (scan rate 100 mV s^{-1}).

MeCN, because the cathodic discharge of the supporting electrolyte took place at slightly more negative potentials in DMF than in MeCN. In cyclic voltammetry, a reversible redox system was associated with the first reduction step (Figure 2). The overall reduction process is suggested to correspond with Scheme 1. At the potentials of waves A and B, the reduction mechanism was the same as that of benzophenone itself, *i.e.* a fast protonation of the dianion by some acid AH [solvent (SH), residual water and/or supporting electrolyte] was involved in the apparent irreversibility of the second reduction step. The presence of the electron-withdrawing group PhE facilitated the reduction of the ketones (**1a–f**) which were reduced at potentials less negative than in the case of benzophenone (Table). Furthermore, at the potentials of wave B, a slow decomposition of the final anion took place since an anodic peak F was already visible on the cyclic voltammogram of Figure 2(*b*), which corresponded to the oxidation of the PhE$^-$ anion which was quantitatively generated at the potentials of wave C [Figure 2(*c*)]. The voltammetric behaviour of ketone (**1g**), substituted with a benzylseleno group was different, as shown in Figure 3. The first irreversible bielectronic wave was followed by a monoelectronic reversible wave B. Scheme 2 accounts for these results. At the potentials of wave B, the first reduction step of the carbonyl function was hindered by the electron-donating ability of the Se$^-$ substituent and so it was 0.25 V negative to the reduction of benzophenone (Table). All the symmetrical chalcogenides (**2a–f**) exhibited the same voltammetric behaviour. Three waves were observed, each of them involving a monelectronic process (Figure 4). A redox peak system was associated with the second wave (Figure 5), the $E_{1/2}$ value of which was constant and identical to that of benzonitrile. The third reduction step, which was also reversible, was observed at very negative potentials and so it was well defined only in DMF. These results are consistent with Scheme 3. Since a single electron was involved in the first reduction step, it shows that the cleavage rate k following the first electron transfer was not very high. The unstable intermediate radical anions $(\mathbf{2a\text{–}f})^{-\cdot}$ could diffuse away from the electrode and the $NCC_6H_4^{\cdot}$ radicals were therefore generated in the bulk of the solution where they were hydrogenated by solvent molecules. Benzonitrile was thus generated and reversibly reduced at the potentials of wave B. The nitrile group of $NCC_6H_4E^-$ anion was also reversibly reduced. However, this reduction took place at very negative potential values since E$^-$ was a strong electron-donating group, and so wave C could be observed in DMF.

As already mentioned, compounds (**2a–f**) were isolated in low yields, as minor compounds in the synthesis of phenylseleno- and phenyltellurobenzonitrile,[7,8] and so large-scale electrolyses could not be carried out in order to ascertain the formation of



Scheme 1.

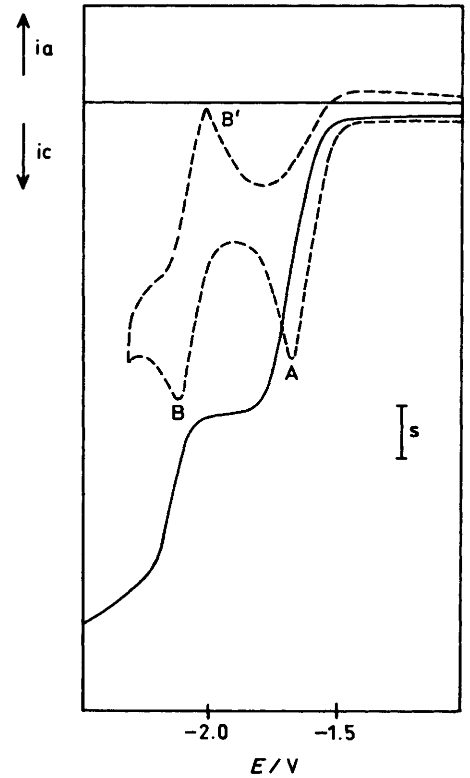
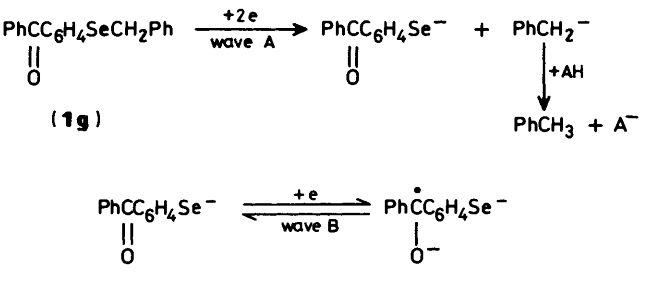


Figure 3. Voltammograms in MeCN of (**1g**) (2.1 mmol dm^{-3}) at an RDE (——) and SDE (- - - -). For the cyclic voltammogram, the scan rate is 100 mV s^{-1} and *s* = 20 μA. For the voltammogram at an RDE, *s* = 40 μA.



Scheme 2.

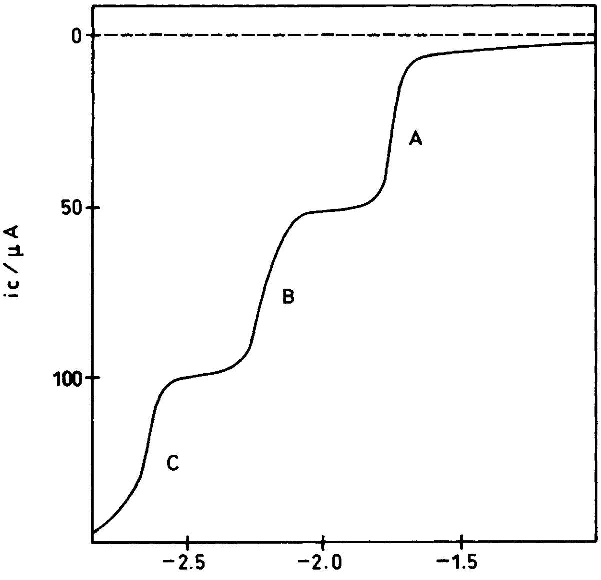


Figure 4. Voltammogram of (**2f**) (1.24 mmol dm^{-3}) in DMF at an RDE.

$NCC_6H_4E^-$ anions at the potentials of wave A, and their further reduction at potentials of wave C. However, we have shown elsewhere[10] that the reductive cleavage of phenylselenobenzonitrile and phenyltellurobenzonitrile give again the $NCC_6H_4E^-$ anions which are reversibly reduced at $E_{1/2}$ values identical to those of wave C for compounds (**2a–f**). These anions can be anodically oxidised to $(NCC_6H_4E)_2$ derivatives which were isolated in 62–70% yields for the diselenides[10a] and 59–75% yields for the ditellurides.[10b]

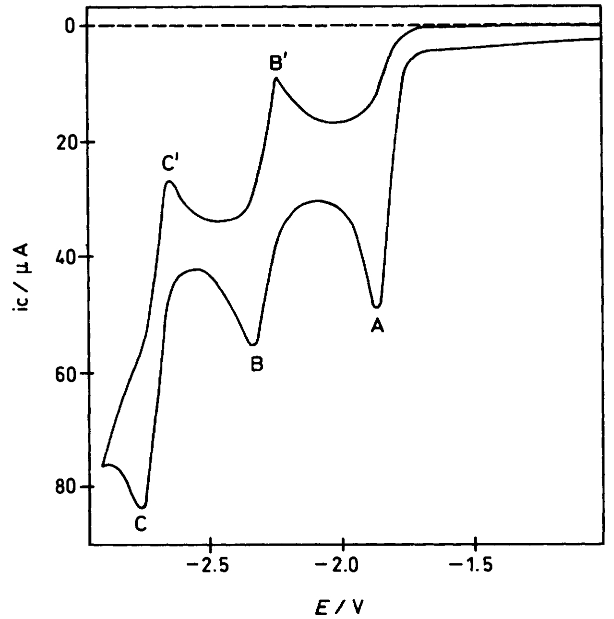
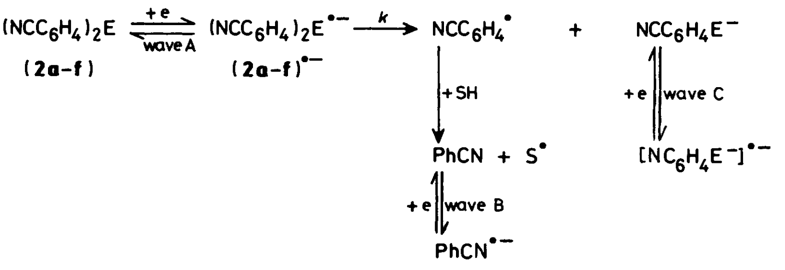


Figure 5. Cyclic voltammogram of (**2f**) (1.69 mmol dm^{-3}) in DMF at an SDE (scan rate 100 mV s^{-1}).

Determination of the Hammett σ Constants of PhE and E$^-$.—Since the first reduction wave of the ketones (**1a–f**) was reversible, the Hammett σ constants of the PhE substituents were calculated in the following manner. Firstly the $E_{1/2}$ values of the first reversible wave of monosubstituted benzophenone were measured in MeCN and correlated with the known σ Hammett constants[11] (○ in Figure 6). For the 4-NMe$_2$, 4-OMe, 4-Me, 3-Me, and 3-Cl substituents, the $E_{1/2}$ values were −1.960 V, −1.860 V, −1.825, −1.799, and −1.656 V, respectively. The Hammett reaction ρ constant was slightly lower in MeCN (0.32 V) than in DMF[12] (0.38 V). The correlation was then used to derive the σ values of the PhE substituents of the ketones (**1a–f**), taking into account the $E_{1/2}$ values of their first reduction step (■ in Figure 6). The $E_{1/2}$ and σ values are given in the Table. The same correlation was used to derive the σ_p value of the *p*-Se$^-$ substituent of the ketone (**1g**), from the $E_{1/2}$ value of wave B (Scheme 2).

The same treatment was applied to wave C (Scheme 3) of compounds (**2a–f**) and carried out in DMF where wave C was well developed. The Hammett reaction ρ constant was derived from equation (1) for a series of standard substituted benzonitriles (○ in Figure 6). For the 4-NMe$_2$, 4-OMe, 4-Me, and 3-OMe substituents, the $E_{1/2}$ values corresponding to the reversible electron uptake were −2.660 V, −2.470 V, −2.385 V, and −2.260 V, respectively. The ρ value was higher (ρ = 0.54) than in the preceding case, which is consistent with the fact that the more negative the $E_{1/2}$ values of reduced aromatic series, the higher the ρ values.[4a] The σ values of the Se$^-$ and Te$^-$ substituents were then derived (Table).



Scheme 3.

The σ_m values in the Table are a measure of polar effects (inductive and/or field). For the E$^-$ groups, the electron-donating inductive $^+$I effect increased very slightly from Te$^-$ to Se$^-$ whereas for the PhE substituents, the electron-withdrawing $^-$I effect was the same in both cases. These results are consistent with previous studies which have shown the occurrence of a negligible increase in the inductive effect σ_I as marking from the PhTe to the PhO substituents (Table of ref. 1).

For the *p*-substituents, the strong electron-donor power of the E$^-$ groups increased from Te$^-$ to Se$^-$ as expected on the basis of the $^+$M effect. The σ_p value of the *p*-Se$^-$ substituent was derived from two independent measurements, compounds (**1g**) and (**2c**), and found to be identical, as expected. This value was slightly lower than the value obtained from the reduction of *p*-nitrophenyl diselenide.[5] For the PhSe substituent, several σ_p values varying from 0.13[13] to 0.42[14] have been reported. It is not surprising that our value is almost identical with the value derived from a kinetic study of the aromatic nucleophilic substitution taking place between C$_6$F$_5$SePh and sodium methoxide, since a negative charge was developed in the transition state in both methods.[15] The σ_p values of PhTe and PhSe have been discussed in terms of the $^-$I inductive effect and push–pull resonance effects ($^+$M and $^-$M).

Values for *o*-σ_o have been also derived from $E_{1/2}$ measurements and reported in the Table although they have no real significance because of the interplay between steric, polar, and mesomeric effects. To our knowledge, the σ_o and σ_m values of the Table and the σ_p value of the Te$^-$ substituent are published for the first time.

Experimental

The synthesis of (**1a–g**) was carried out by electrochemically induced S$_{RN}$1 substitution. The electrochemical synthesis of (**1b–f**) is described in ref. 6. Compounds (**1a**)[16] and (**1g**) were prepared under the same experimental conditions. In the case of (**1a**), which was isolated in 72% yield, the added acid was malononitrile and 0.13 mol of electrons was consumed. In the case of (**1g**), PhCH$_2$Se$^-$ anion was generated as the nucleophile in the following manner. Selenium powder (4 mmol) was reduced to Se$_2^{2-}$ with sonication[17] in acetonitrile. After consumption of 386 C (4 mmol of electrons), benzyl chloride (4 mmol) was added and dibenzyl diselenide (2 mmol) was generated quantitatively. This was then reduced to PhCH$_2$Se$^-$ (4 mmol) at 1.2 ± 0.2 V. A mixture of 4-bromobenzophenone (4 mmol), azobenzene (0.4 mmol), and phenol (2 mmol) was then added and the electrolysis was continued, as in the preceding experiments, when 0.68 mol of electrons was concerned in the substitution process. After treatment of the cathodic solution, two main compounds were isolated including (**1g**) (1.40 mmol; 35%).

4-*Benzylselenobenzophenone* (**1g**).—White powder; recrystallisation from Et$_2$O–pentane: m.p. 90 °C; δ_H 4.21 (2 H, s, CH$_2$)

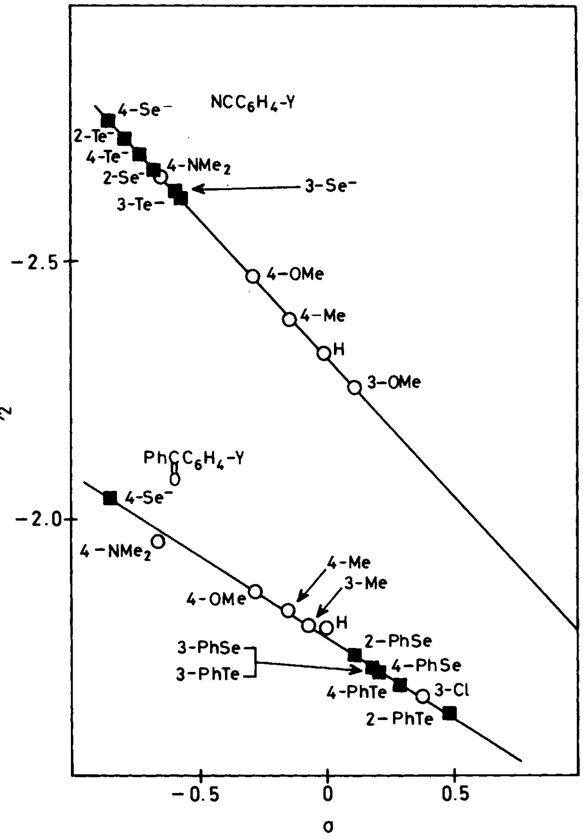


Figure 6. Substituted benzophenones in MeCN and benzonitriles in DMF: Hammett correlation. (○) Half-wave potential corresponding to standard derivatives. (■) Half-wave potential corresponding to chalcogeno derivatives.

and 7.26–7.81 (14 H, m, Ph); $\nu_{max.}$ 1 651 (C=O) and 837 cm^{-1} (*para*-substitution); *m*/*z* 352 (*M*$^+$, 46) and 91 ($PhCH_2^+$, 100) (Found: C, 68.64; H, 4.65; Se, 22.15. $C_{20}H_{16}OSe$ requires C, 68.38; H, 4.55; Se, 22.48%).

The symmetrical chalcogenides (**2a,b**),[8b] (**2c**),[8a] and (**2f**)[7] were isolated as minor compounds when the electrochemical synthesis of phenylchalcogenobenzonitrile was performed. However, the yields of (**2d**) and (**2e**) were so low (4% and 5%) during the synthesis of phenyltellurobenzonitrile,[8b] that these compounds were not described in reference 8(*b*). Compound (**2d**) was isolated as a yellow powder. Recrystallisation from Et_2O–pentane; m.p. 160 °C; δ_H 7.38–7.47 (4 H, m, Ph) and 7.82–7.91 (4 H, m. Ph); $\nu_{max.}$ 2 215 (C≡N) and 765 cm^{-1} (*ortho*-substitution); *m*/*z* 334 (*M*$^+$, 53) and 102 ($NCPh^+$, 100). Compound (**2e**) was isolated as a pale yellow powder; recrystallisation from CH_2Cl_2–pentane; m.p. 112 °C; δ_H 7.26–7.95 (8 H, m, Ph); $\nu_{max.}$ 2 224 (C≡N) and 729 (*meta*-substitution); *m*/*z* 334 (*M*$^+$, 38) and 102 ($NCPh^+$, 100).

Cyclic voltammetry experiments were carried out in a three-electrode single-compartment cell with a calomel reference electrode and Pt wire counter electrode. The working electrode was a glassy carbon disc electrode (V 25 Carbone Lorraine; diameter 3 mm). The electrolyte was a solution of Bu_4NPF_6 (0.1 mol dm^{-3}) in MeCN or DMF and was treated with argon prior to the introduction of the depolarizer. An inert atmosphere was maintained over the solution during the experiments.

Current-potential curves were obtained using an IR-compensated potentiostat driven by a DACFAMOV 05 programmer and an APPLE IIc computer. Repetitive determination of $E_{1/2}$ values has shown that their reproducibility is < 3 mV and so the σ values are given with a precision of 0.01.

Acknowledgements

The work was supported by CNRS (Pirsem grant) and by EDF (Club Electrochimie Organique).

References

1 F. Fringuelli and A. Taticchi, in 'The Chemistry of Organic Selenium Tellurium Compounds,' vol. 1, eds. S. Patai and Z. Rappoport, Wiley, 1986, ch. 15.
2 I. D. Sadekov, A. Ya. Bushkov, V. S. Yur'eva, and V. I. Minkin, *Zh. Obshch. Khim.*, 1977, **47**, 2541; *Zh. Obshch. Khim., Int. Ed. Engl.*, 2321.
3 I. D. Sadekov and A. Ya. Bushkov, *Zh. Obshch. Khim.*, 1977, **47**, 631; *Zh. Obshch. Khim., Int. Ed. Engl.*, 576.
4 (*a*) P. Zuman, 'Substituent Effects in Organic Polarography,' Plenum Press, New York, N.Y. 1967; (*b*) 'Correlation Analysis in Chemistry: Recent Advances,' eds. N. B. Chapman and J. Shorter, Plenum Press, New York, 1978.
5 Yu. M. Kargin, V. Z. Kondranina, L. M. Kataeva, L. A. Sorokina, V. V. Yanilkin, and M. M. Khysalnov, *Zh. Obshch. Khim.*, 1977, **47**, 672; *Zh. Obshch. Khim., Int. Ed. Engl.*, 611.
6 C. Degrand, R. Prest, and P. L. Compagnon, *J. Org. Chem.*, 1987, **52**, 5229.
7 C. Degrand, *J. Chem. Soc., Chem. Commun.*, 1986, 1113.
8 (*a*) C. Degrand, *J. Org. Chem.*, 1987, **52**, 1421; (*b*) C. Degrand, *J. Electroanal. Chem. Interfacial*, 1987, **238**, 239.
9 (*a*) C. Degrand, C. Gautier, and R. Prest, *J. Electroanal. Chem. Interfacial*, 1988, **248**, 381; (*b*) C. Gautier and C. Degrand, unpublished results.
10 (*a*) C. Degrand, C. Gautier, and M. Kharroubi, *Tetrahedron*, 1988, **19**, 6071; (*b*) C. Degrand, *J. Electroanal. Chem. Interfacial*, 1989, **260**, 137.
11 J. March, 'Advanced Organic Chemistry, Reactions, Mechanisms and Structure,' 3rd edition, Wiley, 1985.
12 L. Nadjo and J. M. Saveant, *J. Electronal. Chem. Interfacial*, 1971, **30**, 41.
13 L. M. Litvinenko, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1962, 1737; *Int. Ed. Engl.*, 1653.
14 E. T. Strom and J. R. Norton, *J. Am. Chem. Soc.*, 1970, **92**, 2327.
15 P. P. Rodionov, G. G. Furin, and G. G. Yakobson, *Kinet. Katal.*, 1985, **26**, 548; *Kinet. Katal., Int. Ed. Engl.*, 471.
16 M. Renson and J. L. Piette, *Bull. Soc. Chim. Belg.*, 1964, **73**, 507.
17. B. Gautheron, G. Tainhimer, and C. Degrand, *J. Am. Chem. Soc.*, 1985, **107**, 5579.

Received 21*st March* 1988; *Paper* 8/01141I