Chemical and Electrochemical Reduction of 2*H*-Indole-3,5-dione and -dione 3-Imine *N*-Oxides

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Five of the title *N*-oxides **1** when reduced either chemically (phenylhydrazine, hydrazobenzene) or electrochemically (DMF–TEAP–protonating agent) were found to afford the corresponding 5-hydroxyindoles **6**. The reduction process takes place in two steps leading initially to 1,5-dihydroxyindoles **4** which undergo loss of water and are eventually converted into the products. EPR spectroscopic studies of the chemical and electrochemical reduction led to the characterization of the intermediate radical anions and neutral radicals, and a mechanism based on these results as well as on polarographic and cyclic voltammetric studies is proposed for the process.

2,2-Disubstituted 1,7a-dihydro-2*H*-indole-3,5-dione *N*-oxides are formed during the oxidation of indoline *N*-oxyls in the presence of water[1] and are the main products when the same aminoxyls are reacted with peroxyl,[2] or alkoxyl radicals in the presence of oxidizing agents,[3] or organic peracids.[4] As these aminoxyls, from which the dione imine *N*-oxides are obtained, are being exploited as antioxidants in polymer extrusion and moulding[5] as well as in lipid peroxidation,[6] a full understanding of the reactivity of the related dione imine *N*-oxides is sought. In a recent investigation it was shown that the latter compounds react with primary aromatic amines yielding mono- and bis-adducts together with the corresponding reduction products.[7] Compounds **1a–e** are actually structurally similar to quinones, which are known to play a crucial role in many biological systems.[8,9] Taking into account the oxidizing character[10] of the quinone imines as well as their ability to add nucleophiles,[10,11] or radicals[12] and in order to gain more information on their reactivity, we have studied the chemical and electrochemical reduction of **1a–e**, and characterized the radical intermediates obtained by both methods.

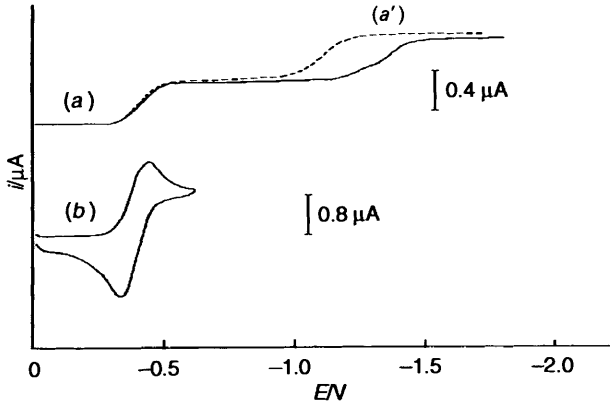


Fig. 1 Sampled polarogram (*a*) and cyclic voltammogram (*b*) of **1a** (0.98×10^{-3} mol dm^{-3}) in DMF–Et_4NClO_4 (0.1 mol dm^{-3}) and sampled polarogram (*a'*) of the same system with 3,4-dimethylphenol as protonating agent (2×10^{-3} mol dm^{-3}). Sweep rate = 5 mV s^{-1}, drop time = 1 s (*a*, *a'*); sweep rate = 200 mV s^{-1} and potential span limited to the first wave (*b*).

Results

Polarographic and Voltammetric Studies.—The electroreduction of compounds **1a–e** at a mercury electrode (LLSDME) in *N*,*N*-dimethylformamide (DMF) with R_4NClO_4 (R = Et, Bu) as supporting electrolyte involves two polarographic steps. The half-wave potentials and the corresponding current values *i* for the different compounds are collected in Table 1, while Fig. 1, curve (*a*) shows as a typical example the polarogram obtained with compound **1a**. In all cases the first reduction step exhibits a very well defined polarographic wave, the half-wave potentials ranging from *ca.* -0.3 to *ca.* -0.5 V. The second polarographic wave is less defined, the half-wave potential lying between -1.3 and -1.5 V [Fig. 1, curve (*a*), and Table 1]. For all the compounds in the range of the concentration (*c*) investigated (5.0×10^{-4}–1.0×10^{-2} mol dm^{-3}) the first reduction process turned out to be mono-electronic, reversible and diffusion-controlled as proved by the following experimental observations: (i) the slope $E'_{\frac{1}{4}} - E'_{\frac{3}{4}}$ value is *ca.* 60–70 mV; (ii) the limiting current i'_l is linearly proportional to the concentration; (iii) the i'_l/c values are very close to the corresponding values determined for the first reversible, diffusion-controlled mono-electronic reduction wave of a structurally similar compound such as 2-phenyl-3-arylimino-3*H*-indole *N*-oxide.[13]

Cyclic voltammetric experiments on **1a–e** in DMF–R_4NClO_4 with potential span limited to the first polarographic wave yield a cathodic–anodic system with $i_{pa}/i_{pc} \cong 1$ and $E'_{pa} - E'_{pc} =$ 70–80 mV at all scan rates used (0.05–2.00 V s^{-1}). Fig. 1, curve (*b*), shows as a typical example the cyclic voltammogram obtained with compound **1a**.

These results suggest that in the first mono-electronic reduction step of **1a–e** a species is produced which is stable during the voltammetric measurement.

Cyclic voltammograms of **1a–e** with potential span also including the second polarographic wave exhibit an ill-resolved second cathodic peak without the anodic counterpart, thus proving the second step to be an irreversible reduction process.

In order to gain further insight into the reduction process of these compounds we also investigated the effect of protonating agents of various strength on their electrochemical behaviour. When increasing amounts of 3,4-dimethylphenol were added to the DMF–R_4NClO_4 solutions of **1a–e** the first reduction step

Table 1 Polarographic data for the reduction of **1a–e**[a]

Compound	$E_{\frac{1}{2}}'^{b}$/V	(i'/c)/μA dm^3 mmol^{-1}	$E_{\frac{1}{2}}''^{b}$/V	(i''/c)/μA dm^3 mmol^{-1}	(i'/i'')
1a	−0.375	0.45	−1.310	0.40	1.12
1b	−0.335	0.28	−1.290	0.26	1.07
1c	−0.487	0.39	−1.285	0.45	0.86
1d	−0.480	0.38	−1.415	0.40	0.95
1e	−0.515	0.32	−1.465	0.30	1.06

[a] Solutions in DMF/Et_4NClO_4 0.1 mol dm^{-3} with about 1 × 10^{-3} mol dm^{-3} depolarizer; T = 25 °C; t_p = 1 s. [b] *vs.* Hg/Hg_2Cl_2

was totally unaffected, while the second one shifted to less negative potentials ($E_{\frac{1}{2}}$ = 240 mV for **1a**, molar ratio protonating agent–depolarizer being 2 : 1), yielding a more resolved wave [see Fig. 1, dotted curve (*a*′)].

In the presence of a stronger protonating agent such as chloroacetic acid both reduction steps shift to less negative potentials, the second tending to merge with the first, so that with a molar ratio of protonating agent–substrate larger than 10 : 1 cyclic voltammograms of **1a–e** exhibit a single ill-resolved, irreversible cathodic system between −0.150 and −1.00 V.

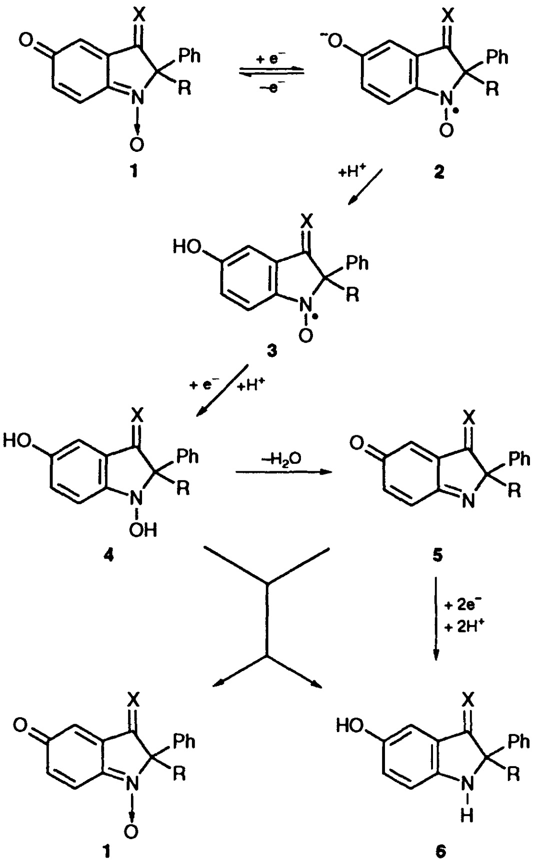
Chemical and Electrochemical Reduction.—Compounds **1a–e** were reacted with phenylhydrazine (molar ratio 1 : 2) at room temperature in benzene solution. While the reaction was very clean in the case of **1a, b, d** and **e**, which afforded **6a, b, d** and **e** in good yield, in the case of **1c** compound **6a** was isolated in substantial amount along with the expected **6c**. The yield of the different products are given in the Experimental section. Upon comparison of the spectroscopic data collected in Table 2 with those of the related **6a**, whose structure had been previously characterized by X-ray analysis,[11] products **6b–e** could be identified. All compounds **6** gave NMR spectra consistent with their structure and mass spectra showing molecular ion peaks and indicating fragmentation consistent with their structure; in all cases OH and NH IR-bands were detected and >C=O and >C=N– absorptions were observed as appropriate.[14]

Controlled potential electrolysis of compounds **1a, b** and **d** with an excess of chloroacetic acid (molar ratio protonating agent–depolarizer being 10 : 1 or 20 : 1) were performed at a single polarographic wave plateau potential (between −1.00 and −1.20 V).

After the current had fallen to its background value, *ca.* 2 F mol^{-1} of depolarizer were involved and the main product of the reaction was the amine **6**. If, however, the electrolysis was resumed after the reaction mixture had remained under a nitrogen atmosphere for several hours (overnight), a further absorption of current was observed followed by an increase of the yield of the compounds **6**.

EPR Study.—*N*-Oxides **1a–e** have been reduced in both protic or aprotic media, either chemically or electrochemically and the resulting paramagnetic species have been investigated by means of EPR spectroscopy.

When DMSO solutions of compounds **1a–e** were treated with potassium butoxide, EPR spectra could be readily observed, which could be attributed to the corresponding radical anions **2a–e**. The spectra exhibited similar patterns, showing coupling of the unpaired electron with the heterocyclic nitrogen and the two ring protons in positions 4 and 7, and in some cases with the proton in position 6 (Table 3). The three 3-arylimino derivatives (**1c–e**) also exhibited coupling with the exocyclic nitrogen atom, while additional hyperfine features due to the coupling with one of the two benzylic hydrogens in position 2 were apparent in the spectra of **2e**. The spectra of the neutral radicals **3a–e** were instead obtained by carrying out the reduction in THF–Bu^{t}OH 4 : 1 v/v (Table 3). The assignment of the hyperfine coupling constants to the different hydrogens in radicals **3** is not straightforward, because one of the small splittings could be due either to the hydrogen in positions 4 or 6 or to the proton of the hydroxy group in position 5. In order to discriminate between these two possibilities compounds **1a** and **b** were reacted with Bu^{t}OK in a 4 : 1 THF–Bu^{t}OD v/v solution: the spectra recorded under these conditions were absolutely identical with those recorded using THF–Bu^{t}OH solutions, indicating that none of the observed splittings could be due to the hydroxylic hydrogen.



a R = Me, X = O
b R = Ph, X = O
c R = Me, X = NPh
d R = Ph, X = NPh
e R = CH$_2$Ph, X = NPh

Scheme 1

Similarly, when current was circulated through an EPR cell containing nitrogen-purged DMF solutions of compounds **1a** and **b** and Et_4NClO_4 (as supporting electrolyte), EPR signals due to the corresponding radical anions could be observed as soon as the appropriate reduction potentials were reached. Increasing the current beyond the reduction potential resulted in stronger signals, but this positive effect was accompanied by loss of resolution and by rapid sample depletion. The spectral features were very similar to those

Table 2 Spectroscopic data of compounds **6b–e** and **1e**

Compound	ν_{max}/cm^{-1}	δ_H(200 MHz; $CDCl_3$; Me_4Si)[a]	m/z (%)	M.p./°C
6b	3410, 3320, 1660, 1585	1.63 (1 H, br s, OH), 5.01 (1 H, br s, NH), 6.88 (1 H, d, 7-H, *J* 8.7), 7.07 (1 H, br d, 4-H, *J* 2.7), 7.13 (1 H, dd, 6-H, *J* 8.7, *J* 2.7), 7.28–7.43 (10 H, m, Ph)	301 (M^+, 69), 272 (100)	185 (from CH_2Cl_2)
6c	3380, 3290, 1625, 1585	1.92 (3 H, s, CH_3), 4.48 (1 H, br s, OH), 4.68 (1 H, br s, NH), 5.83 (1 H, d, 4-H, *J* 2.5), 6.73–6.93 (4 H, m, Ph), 7.09 (1 H, br t, Ph, *J* 7.4), 7.17–7.43 (5 H, m, Ph), 7.55–7.60 (2 H, m, Ph)	314 (M^+, 66), 237 (61)	187 (from light petroleum)
6d	3360, 3170, 1610, 1580	4.2 (1 H, br s, OH), 4.67 (1 H, br s, NH), 5.88 (1 H, d, *J* 2.5, 4-H), 6.73–6.88 (4 H, m, Ph), 7.1 (1 H, br tt, Ph), 7.28–7.4 (8 H, m, Ph), 7.51–7.56 (3 H, m, Ph)	376 (M^+, 56), 299 (100)	185 (from benzene)
6e	3400, 3370, 1625, 1590	3.57 (2 H, dd_{AB}, CH_2, *J* 13.3), 4.35 (1 H, br s, OH), 4.52 (1 H, br s, NH), 5.76 (1 H, d, 4-H, *J* 2.3), 6.64–6.84 (4 H, m, Ph), 7.07–7.41 (10 H, m, Ph), 7.7–7.75 (3 H, m, Ph)	390 (M^+, 6), 299 (100)	110 (from light petroleum)
1e	1680, 1610, 1550, 1510	3.95 (2 H, dd_{AB}, CH_2, *J* 12.6), 5.42 (1 H, d, 4-H, *J* 1.6), 6.51 (1 H, dd, 6-H, *J* 9.9, *J* 1.6), 6.73 (2 H, dt, Ph, *J* 7.4, *J* 1.5), 7.18 (1 H, tt, Ph, *J* 7.4, *J* 1.2), 7.36 (2 H, tt, Ph, *J* 7.2), 7.27–7.64 (9 H, m, Ph), 7.56–7.62 (1 H, dd, Ph, *J* 8.1, *J* 1.8), 7.62 (1 H, d, 7-H)	404 (M^+, 15), 313 (100)	150 (from EtOH)

[a] *J*-values in Hz.

Table 3 EPR spectral parameters[a] for the radical anions **2a–e** and the neutral radicals **3a–e**

Compound	Solvent	$a(N_1)$	$a(H_4)$	$a(H_6)$	$a(H_7)$	a(5-OH)	$a(N_3)$	a(2)	g
2a	DMSO	9.95	0.50	1.20	2.17	—	—	n.r.	2.0056
2a	DMF	10.10	0.50	1.10	2.25	—	—	n.r.	—
2b	DMSO	9.84	0.50	1.41	2.15	—	—	—	2.0053
2b	DMF	10.00	0.50	1.38	2.15	—	—	—	—
2c	DMSO	10.42	0.65	n.r.	2.49	—	1.11	n.r.	2.0052
2c	DMF	10.50	0.40	0.40	2.20	—	1.10	n.r.	—
2d	DMSO	10.42	0.65	n.r.	2.49	—	1.11	—	2.0052
2d	DMF	10.50	0.67	n.r.	2.30	—	1.05	—	—
2e	DMSO	10.42	0.65	n.r.	2.49	—	1.11	0.56 (1 H)	2.0052
2e	DMF	10.40	0.68	n.r.	2.45	—	1.10	0.52 (1 H)	—
3a	THF/Bu^{t}OH (4:1)	10.26	0.70	0.17	2.53	n.r.	—	0.17 (3 H)	2.0055
3a	DMF	10.15	0.67	0.53	2.40	n.r.	—	n.r.	—
3b	THF/Bu^{t}OH (4:1)	10.13	0.68	0.30	2.48	n.r.	—	—	2.0054
3b	DMF	10.14	0.70	0.54	2.40	n.r.	—	—	—
3c	THF/Bu^{t}OH (4:1)	10.47	0.60	n.r.	2.80	n.r.	1.05	0.23 (3 H)	2.0053
3c	DMF[b]	10.18	0.90	0.90	3.01	n.r.	0.95	n.r.	—
3d	THF/Bu^{t}OH (4:1)	10.35	0.51	n.r.	2.59	n.r.	1.02	—	2.0054
3d	DMF[b]	10.18	0.90	0.90	3.01	n.r.	0.95	—	—
3e	THF/Bu^{t}OH(4:1)	10.50	0.51	n.r.	2.59	n.r.	1.02	0.53 (1 H)	2.0052
3e	DMF[b]	10.10	0.80	0.80	3.01	n.r.	0.90	0.65 (1 H)	—

[a] Coupling constants in Gauss = 10^{-4} T. [b] Reducing with hydrazobenzene. [c] n.r. = not resolved.

observed in the chemical reduction, but for a slightly larger value of the heterocyclic nitrogen splitting. The same experiments performed in the presence of the protonating agent 2,4-dimethylphenol gave the spectra of the corresponding neutral radicals **3a–b** (Table 3). While also the electrochemical reduction of the arylimino compounds **1d** and **e** led to the expected radical anions **2d** and **e**, the spectrum of **2c** could only be observed in one out of several experiments: in nearly all cases the electrochemical reduction of **1c** afforded the radical anion **2a**. The addition of protonating agent to solutions of **1c–e** resulted in very poor spectra that could not be interpreted. The correct spectra of **3a–e** could instead be obtained by treating DMF solutions of **1c–e** with one half equivalent of hydrazobenzene (Table 3).

Discussion

The chemical (phenylhydrazine, hydrazobenzene, or hydrogen and catalysts) and electrochemical (DMF–chloroacetic acid as protonating agent) reduction[13,15,16] of 2-phenyl-3-arylimino-3*H*-indole *N*-oxide **7**,[17] which can be regarded as an *ortho*-quinonoid compound, is known to afford the corresponding 3-arylamino-1-hydroxyindole **8**. This can undergo loss of water to give the 3-arylimino-3*H*-indole **9** that under the reaction conditions may lead to the corresponding 3-arylamino-1*H*-indole **10**. When the aryl group is a strong electron-withdrawing group (2-pyridyl-, 1-oxido-4-pyridyl- or 4-cyanophenyl[13,16]) the reduction stops at the intermediate 1-hydroxyindole **8**, while in other cases it proceeds to compound **10** and **8** is not isolated.

On the other hand the analogous reduction of a compound such as 2-phenylindol-3-one *N*-oxide **11** leads to 2,2′-diphenyl-2,2′-biindoline-3,3′-dione **15** through several steps involving the 1,3-dihydroxyindole **12**, the indolone **13**, and probably the intermediacy of the 3-hydroxyindole **14** or its tautomer.[18,19]

The present investigation indicates that, as might be expected, similar reduction of the five *N*-oxides **1a–e** does not affect the carbonyl or imine group in position 3, leading to the 1, 5-dihydroxyindolines **4**. Loss of water from these compounds (see Scheme 1) is crucial for the reaction to proceed further to the final products **6**. The formation of water in the process is further substantiated by the finding that in the reduction of **1c** a significant amount of **6a** is formed along with

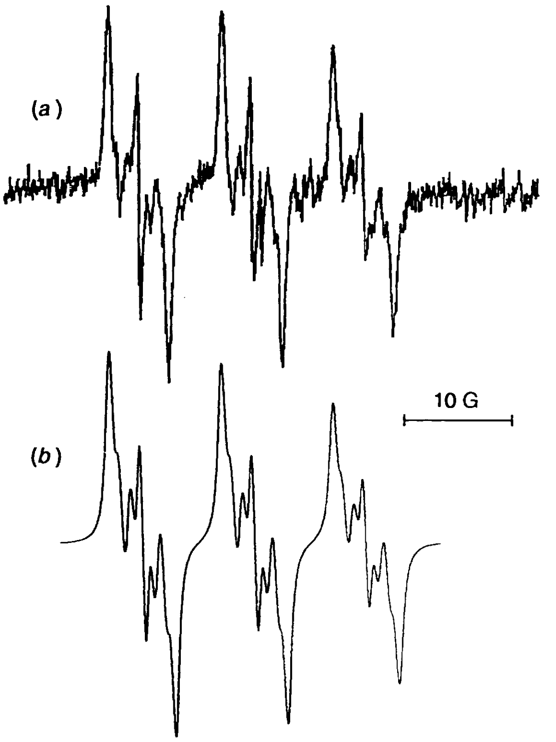
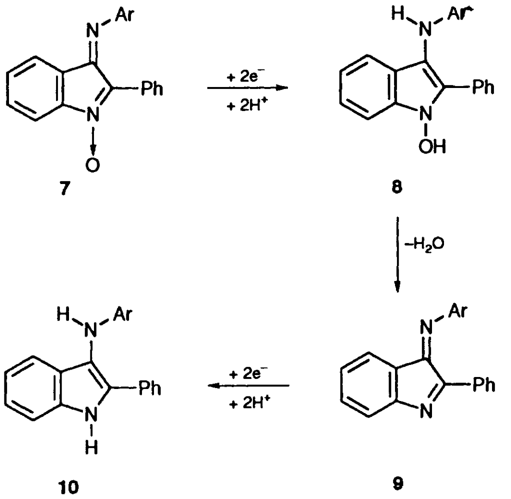
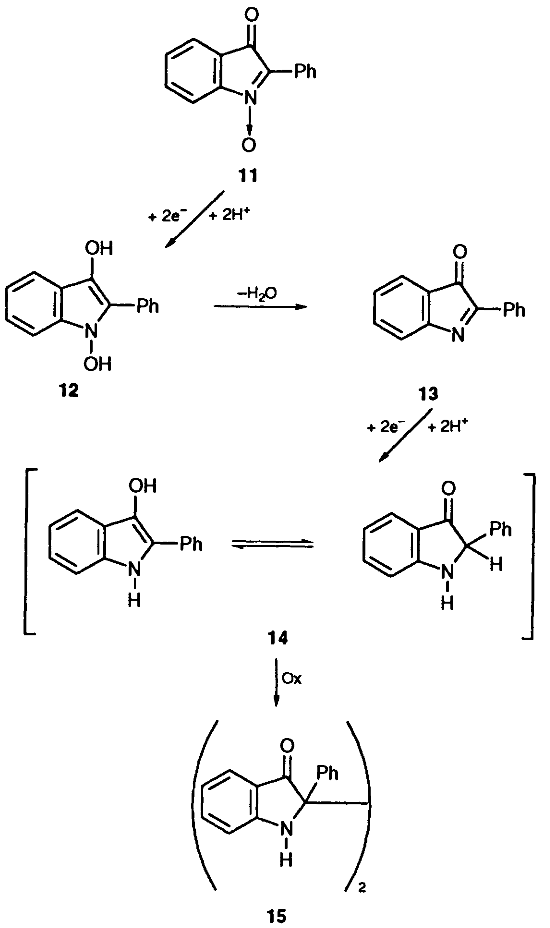


Fig. 2 EPR spectrum of **3c** resulting from a solution of quinone imine **1c** and $\mathrm{Bu^tOK}$ in THF–$\mathrm{Bu^tOH}$ (4:1 v/v) recorded at room temp.: (*a*) experimental; (*b*) computer simulated with the h.f.c. constants reported in Table 3.



the expected **6c**, owing to partial hydrolysis of the latter compound; when the reduction is carried out in the presence of molecular sieves or other water-absorbing agents no traces of the hydrolysis product are observed.

The loss of water from compounds **4** is also evident from the electrochemical experiments. As stated in the previous section, the electrochemical reduction of compounds **1a–e** in DMF affords compounds **6a–e**, but when the current falls to its background value, that is absorption of current ceases (100% conversion), the yield of the compounds **6** is only about 50%. The finding that current absorption resumes after allowing the reaction mixture to stand for a long time interval (overnight) may indeed be explained with formation of **5** (see Scheme 1) which may then react with **4** to give the products **6** and some starting material (**1a–e**) which can again be reduced; when the new current absorption ceases, the reaction is not however complete, and a new absorption takes place after some time.



After several cycles of this kind, a nearly quantitative yield of compounds **6a–e** is obtained. It also cannot be excluded that during the electrolytic reduction **5** is converted to some extent into **6**.

The polarographic and cyclic voltammetric studies on **1a–e** indicate that in an aprotic medium the reduction process begins with a mono-electronic reversible step leading to the anion radical **2a–e** (proved by EPR spectroscopy) followed by a second mono-electronic step leading to the formation of the corresponding di-anion. The irreversibility of the second electrode process, (as proved by the absence of the complementary second anodic peak) presumably derives from a reversible electron-transfer followed by a fast irreversible protonation reaction of the formed di-anion with any protonic source present in the medium, such as traces of water, the solvent itself, or the supporting electrolyte. The effect of a protonating agent like 3,4-dimethylphenol on the behaviour of **1a–e** provides a further support for this hypothesis: in the presence of 3,4-dimethylphenol, the second reduction wave shifts towards less negative potentials [Fig. 1, dotted curve (*a'*)]. A greater protonating power of the reaction medium (as in the case of chloroacetic acid) leads immediately to protonation of the radical anions at the electrode affording the corresponding neutral radicals. These are reduced at the potential of the first wave, which thus become bielectronic and irreversible.

Finally, it is important to note that the lower protonating ability of the reaction medium (the case of 3,4-dimethylphenol) only leads to the protonation of the radical anions in the bulk solution. Support for this statement can be found in the fact that in this case, the original reversible first voltammetric step is unaffected [Fig. 1, curve (*a*) and (*a'*)] while the electrolysis of the solution at the same potential leads to the EPR observation of the corresponding neutral aminoxyls **3a–e**.

We believe that the combined results from the different techniques provide a satisfying basis for the Scheme proposed for the overall reduction process.

Experimental

Apparatus.—M.p.s were measured on an Electrothermal Melting Point Apparatus and are uncorrected. IR spectra were recorded in Nujol on a Perkin-Elmer model 298 spectrophotometer, ^{1}H NMR spectra on a Varian Gemini 200 in $CDCl_3$ using Me_4Si as internal standard, mass spectra (EI$^+$ mode) on a Carlo Erba QMD 1000 spectrometer equipped with a direct probe apparatus, and EPR spectra on a Varian E4 and a Bruker ER 200 D spectrometer equipped with standard devices for field calibration and *g* factor determination. Voltammetric experiments were performed using a multipolarograph AMEL 472/WR coupled with a digital *x*/*y* recorder AMEL 863, and constant current, controlled-potential coulometries and EPR electrochemical reduction using a potentiostat-intentiostat AMEL 552 coupled with an integrator AMEL 731 and a recorder (OmniScribe).

Chemicals.—Compounds **1a–e** were prepared as reported in the literature.[1,20] Compound **6a** was identified by comparison with an authentic sample.[11] All other chemicals were purchased from Aldrich and used as such, with the exceptions of hydrazobenzene [$(PhNH)_2$] which was crystallized from cyclohexane, DMF (anhydr. 99+%, Aldrich) that had been purified according to a previously described protocol[21] and R_4NClO_4 which was recrystallized from water and dried *in vacuo* at 60 °C for three days.

Reactions.—Chemical reduction of **1** *with phenylhydrazine. General procedure.* A benzene solution (5 cm^3) of phenylhydrazine (108 mg, 1 mmol) was added dropwise to a benzene solution (10 cm^3) of compound **1** (0.5 mmol), and the mixture was stirred magnetically until complete disappearance of the substrate as monitored by TLC. The reaction mixture was concentrated under reduced pressure and chromatographed over SiO_2 preparative plates, eluting with benzene–acetone, 95:5. Product **6** was obtained in the following yields: **6a** = 80%; **b** = 85%; **d** = 75%; **e** = 87%.

In the case of **1c** the reaction was also carried out in the presence of 4 Å (Aldrich) molecular sieves obtaining product **6c** in 82% yield.

Chemical reduction of **1** *with hydrazobenzene in the EPR cavity. General procedure.* DMF solutions of compound **1** (1 mmol dm^{-3}) and of hydrazobenzene (0.5 mmol dm^{-3}) were introduced into the two legs of an inverted U cell,[22] degassed with nitrogen bubbling, and mixed. The cell was then placed in the EPR cavity and the spectra of radicals **3** were recorded.

Chemical reduction of **1** *with potassium* tert-*butoxide in the EPR cavity. General procedure.* Some crystals of Bu^{t}OK were introduced into a glass capillary tube (i.d. = 0.8 mm) together with some crystals of **1** then the capillary was filled with DMSO. For reduction in protic media, compound **1** and the butoxide were inserted into a glass tube (i.d. = 4 mm) and dissolved with 200 µl of a THF–Bu^{t}OH or THF–Bu^{t}OD (4:1 v/v) mixture. The resulting solution was then purged with nitrogen before recording the EPR spectra.

Electrochemical Measurements.—Polarographic and voltammetric studies. The electrochemical studies were carried out at room temp. in a three-electrode cell using nitrogen-purged DMF solutions of **1** (1×10^{-3} mol dm^{-3}), containing 0.1 mol dm^{-3} R_4NClO_4 (R = Et or Bu) and, in some of the experiments, 2×10^{-3} mol dm^{-3} of 3,4-dimethylphenol or chloroacetic acid as protonating agent, using the apparatus and the cell described elsewhere.[23]

In voltammetric experiments a long-lasting sessile-drop mercury electrode (LLSDME)[23] was used as working electrode and a platinum wire as the auxiliary electrode. Hg–Hg_2Cl_2,-NaCl(sat.aq.)–DMF–Et_4NClO_4/sintered glass disk[21] was used as reference electrode.

Electrochemical reduction. In analytical and large scale electrolysis a magnetically stirred mercury pool (apparent area *ca.* 20 cm^2) was the working electrode and a platinum gauze cylinder (placed on the inner wall of a glass tube and connected to the test solution *via* a methyl cellulose–DMF–Et_4NClO_4 plug/sintered glass-disk) was the auxiliary one, the electrolysed solution consisting of **1** (0.3 mmol; 3×10^{-3} mol dm^{-3}), Et_4NClO_4 (1.38 g, 6 mmol; 0.1 mol dm^{-1}) and chloroacetic acid (0.057 g, 0.6 mmol; 3×10^{-2} mol dm^{-3}) in DMF (60 cm^3).

EPR Studies.—For electrochemical EPR experiments a small platinum gauze was inserted into a commercial EPR flat cell, the reference and auxiliary electrodes being those used in the voltammetric experiments (working and auxiliary electrodes were separated by sintered glass disks). The radical anions were generated at constant current by electrolysis of DMF solutions of **1** (1.5×10^{-3} mol dm^{-3}) and Et_4NClO_4 (0.1 mol dm^{-3}). The corresponding neutral radicals were obtained by addition of 2,4-dimethylphenol (0.08 mol dm^{-3}).

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