Chemical and Electrochemical Reduction of *ortho*-Nitroanilides. A Combined Chemical, Polarographic and EPR Study

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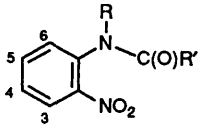
The acetyl and benzoyl *o*-nitroanilines **1a** and **1b** and the acetyl and benzoyl *o*-nitrodiphenylamines **1c** and **1d** have been reduced chemically (Bu^{t}OK/DMSO) and electrochemically inside the cavity of an EPR spectrometer. For all compounds the EPR signal of the radical anions could be recorded and interpreted. In DMSO the radical anions $\mathbf{1c}^{\bullet -}$ and $\mathbf{1d}^{\bullet -}$ evolved to the phenazine radical anion within 1 h. The polarographic study showed that the four compounds are reduced in two different steps, the first being monoelectronic and reversible, as demonstrated by cyclic voltammetric experiments.

Compounds **1a–d** were reduced with Fe/AcOH to the benzimidazoles **5a–d**. The catalytic reduction of **1a** gave the hydroxy-2-methylbenzimidazole **7a** together with the azoxy derivative **6a**. The macroscale electrolysis of **1c** and **1d** may be regarded as a convenient synthetic method of preparing benzimidazoles **5c** and **5d**, while the catalytic reduction may be considered the best route to benzimidazole *N*-oxides **4c** and **4d**.

Benzimidazoles have been synthesized by chemical and electrochemical reduction of *ortho*-nitroanilides and their derivatives.[1–4] In particular, it has been recently shown that 1-phenylbenzimidazole 3-oxides **4c** and **4d** can be conveniently prepared by catalytic hydrogenation of *N*-acetyl- (or *N*-benzoyl-) *N*-phenyl-*o*-nitroaniline (**1c** and **1d**); on the other hand, *N*-benzoyl-*o*-nitroaniline (**1b**) under similar conditions fails to cyclize and affords the corresponding hydroxylamine **2b**.[5]

Despite the substantial body of work concerning the reduction of *ortho*-nitroanilides, the available information appeared rather confusing. We have therefore carried out a systematic investigation of the reduction of four *ortho*-nitroanilides under different conditions. In particular, we have studied the electrochemical, catalytic (H_2/Pd) and chemical (Fe/AcOH) reduction of **1a–d** under synthetic conditions. In order to identify some of the species involved in these processes we have also carried out an EPR investigation of the electrochemical and chemical (Bu^{t}OK/DMSO) reduction of these compounds, together with a study of their polarographic behaviour.



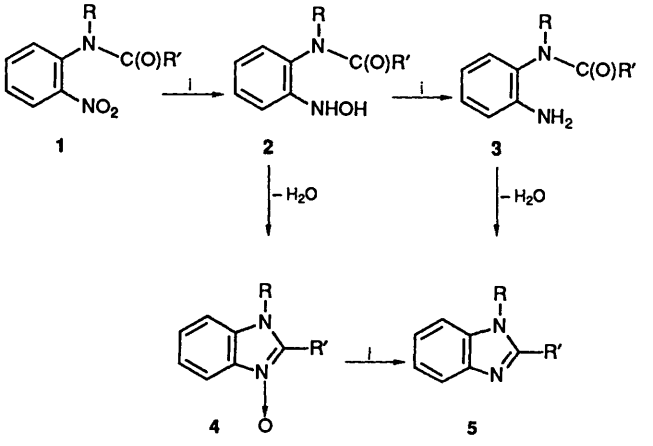
	R	R'
1a	H	Me
b	H	Ph
c	Ph	Me
d	Ph	Ph

Results and Discussion

The reduction of *ortho*-nitroanilides **1a–d** may lead to the benzimidazole *N*-oxides **4**, the benzimidazoles **5**, or the substituted amines **3** as exemplified in Scheme 1, the resulting products strongly depending on the nature of the starting compounds and the operating conditions.

Macroscale Reductions.—(a) *Reduction with* Fe/AcOH. Treatment of compounds **1a–d** in boiling acetic acid with iron powder for 30–60 min afforded the four benzimidazoles **5a–d** in good yield (70–80%). The identification of these benzimidazoles was based on their mass and ^{1}H NMR spectra, and was further confirmed by the fact that these products proved to be identical with those obtained by similar (Fe/AcOH) reduction of the corresponding benzimidazole *N*-oxides **4a–d**.

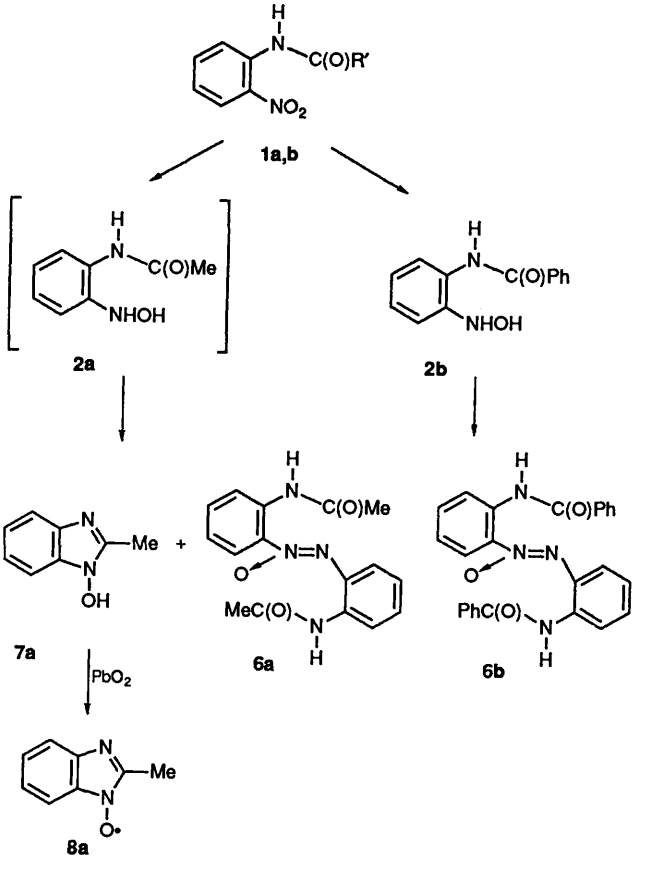
No intermediate products could be isolated in these reductions. Although reductive cyclization of *ortho*-nitro amines in hot acetic acid has been reported,[6] it seems likely that this occurs through the formation and subsequent reduction of the *ortho*-hydroxylaminoacetamides **2**.



Scheme 1 *Reagents:* i, Reduction

(b) *Catalytic reduction* (H_2/Pd). Compounds **1a–d** show a different behaviour towards catalytic reduction. The two *N*-

phenyl-*ortho*-nitroanilides **1c** and **1d** afford, as previously reported, the corresponding benzimidazole *N*-oxides **4c** and **4d**, while compounds **1a** and **1b** do not. In fact, catalytic reduction of **1b** leads to the isolation of the hydroxylamine **2b** which, under the reaction conditions, is partially converted to the azoxyderivative **6b**; on the other hand, in the catalytic reduction of compound **1a** only the azoxyderivative **6a** and the cyclic hydroxylamine **7a** are isolated (see Scheme 2).[7] The identity of the latter compound was confirmed by the observation of the



Scheme 2

EPR spectrum from nitroxide **8a** upon its oxidation with lead dioxide.* The recovery of **7a** and the failure to isolate **2a** are considered to be a consequence of the fact that the acetyl group undergoes condensation much more readily than the benzoyl group.

(c) *Electrochemical reduction.* The electrochemical reduction at constant current of compound **1a** in acetic acid–water afforded the corresponding benzimidazole **5a** in almost quantitative yield. In contrast, the electrochemical reduction of compound **1b** led to the amino derivative **3b**. The behaviour of **1a** and **1b** parallels that already observed under electrolytic conditions in different media,[2] while the electrolytic reduction of **1c** and **1d** had not been investigated before. Reduction of **1c** leads directly to benzimidazole **5c**, whilst reduction of **1d** affords the amine **3d**, which, if left in the reaction medium, is converted to the benzimidazole **5d**. In all cases there is no evidence of the intervention of hydroxylamines **2** in the reduction process, but these compounds may represent a common intermediate to the formation of both amines **3**, *via* further reduction, and benzimidazoles **5**, *via* condensation of the hydroxylamines to benzimidazole *N*-oxides **4** followed by reduction (see Scheme 1). Benzimidazole **5**, on the other hand, may also originate from direct condensation of the amines **3**.

* By simulating the EPR spectrum of **8a** we found the following spectral parameters: $a(N_1)$ 5.15, a(Me) 0.25, $a(N_3)$ 1.74, $a(H_{4,6})$ 0.25 and 0.49, $a(H_5)$ 2.42, a (H_7) 2.13, g 2.0061_1, which are somewhat different from those reported in the literature. H. G. Aurich and W. Weiss, *Chem. Ber.*, 1973, **106**, 2845.

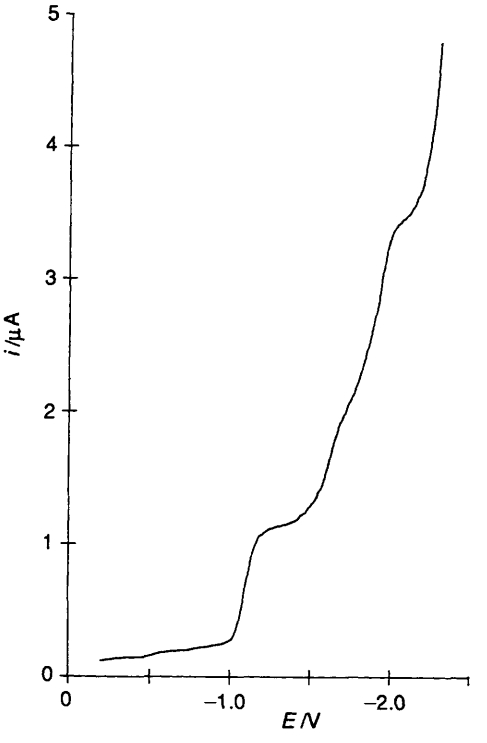


Fig. 1 Sampled polarogram of **1b** (6.2×10^{-4} mol dm^{-3}) in DMF/Bu_4NClO_4 (0.1 mol dm^{-3}). (Sweep rate, 5 mV s^{-1}, drop time, 1 s.)

Polarographic Studies.—The electroreduction of *ortho*-nitroanilides **1a–d** at either a mercury or a platinum electrode in dimethylformamide (DMF) with Bu_4NClO_4 (or Et_4NClO_4) as supporting electrolyte involves two polarographic stages (a typical polarogram for compound **1c** is shown in Fig. 1).

The first stage exhibits a very well defined polarographic wave, whose half-wave potential lies between -1.0 and -1.1 V (see Table 1). Cyclic voltammetric experiments on **1a–d** in DMF/Bu_4NClO_4 in the sweep rate range 0.5–2.0 V s^{-1} at a potential corresponding to the first polarographic wave yield fully reversible voltammograms (i'_{pc}/i'_{pa} is approximately unity at all scan rates), with a 60–70 mV difference between the anodic and cathodic peak potentials and a current function ($i'_{pc}/v^{1/2}$) invariant with changes in v.

These results suggest that in the examined concentration range (10^{-3}–10^{-4} mol dm^{-3}) the first reduction stage of **1a–d** in aprotic media is a reversible, diffusion-controlled monoelectronic transfer leading to a radical anion species which is stable during the voltammetric experiments. The second reduction stage involves two unresolved waves in the potential range -1.5 to -2.0 V (see Fig. 1), the total height being 3–4 times that of the first.

According to some literature evidence[8] it can be assumed that these unresolved waves correspond to the formation of a dianion (the first, monoelectronic step) followed by formation of the hydroxylamino derivative of the initial compound (the second, bielectronic step).

To gain further insight into the reduction process of **1a–d**, we also investigated the effect of protonating agents on the voltammograms. When increasing amounts of benzoic acid are added to the DMF/Bu_4NClO_4 solutions of **1a–d**, the first reduction stage increases its height at the expense of the second, and shifts slightly to less negative potentials ($\Delta E_{1/2}$ 30–70 mV).

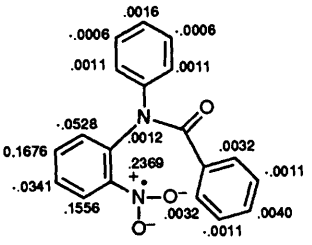


Fig. 2 Spin-density distribution computed for **1c**

For molar ratios (benzoic acid/substrate) > 7, all voltammograms show a single reduction step, whose height is *ca.* four times that of the first step measured in aprotic media.

EPR Studies.—The four *ortho*-nitroanilides have been reduced either chemically or electrochemically and the resulting paramagnetic species have been investigated by means of EPR spectroscopy.

The electrochemical reduction was carried out at constant current within an electrolytic cell placed inside the cavity of the EPR spectrometer (see Experimental). When current was circulated through deoxygenated DMF solutions of the four *ortho*-nitroanilides containing some tetraethyl ammonium perchlorate 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. In all cases the spectra indicated the presence of a single radical species, which persisted for several minutes even when the circulation of the current was interrupted, and could be satisfactorily simulated with the hfs constants collected in Table 2. For all four anions the spectral parameters indicated coupling of the unpaired electron with four protons and with the nitrogens of the amidic and nitro groups, and that the amidic function acts as a conjugation insulator. The assignment of the coupling constants to the different positions was based on spin-density calculations carried out by the McLachlan method (see Experimental) using compound **1d** as a general model, which gave results in very good agreement with experiment (Fig. 2); they indicate that the proton splittings should be assigned in decreasing order to the protons in positions 5, 3, 4 and 6, respectively, predict a rather small coupling for the amidic nitrogen, and little, if any, involvement of the benzoyl moiety in the delocalization of the unpaired electron.

Table 1 Half-wave reduction potentials of compounds **1a–d**

Compound	Concentration/ mmol dm^{-3}	$-E'_{1/2}$/V	i'/μA	Slope/mV
1a	0.67	0.96	0.74	75
1b	0.58	0.91	0.77	65
1c	0.62	1.09	0.79	65
1d	0.53	1.10	0.68	70

Our present results are in good agreement with those from previous EPR studies by Volanschi *et al.*,[9,10] who investigated the radical anions of some *para*-nitroanilides. These authors also found that the nitro group, rather than the amidic function, dictates the spin density distribution over the molecular framework.

Calculations also predict little spin-density on the *N*-phenyl ring. This is consistent with the number of observed proton couplings, but does not explain why substitution of a phenyl ring for the amidic hydrogen should lead to such a marked decrease of $a_N(NO_2)$ coupling constants. This finding is probably to be explained on the basis of steric effects. The lower $a_N(NO_2)$ and the greater a_{5-H} values exhibited by the anions of **1c** and **1d** with respect to those from **1a** and **1b** suggest that in the two former species the nitro group is closer to the plane of the aromatic ring, thus favouring delocalization of the unpaired electron onto it.

The four *ortho*-nitroanilides were also reduced in dimethyl sulphoxide (DMSO) with potassium *tert*-butoxide (Fig. 3). Although in all cases the radical anions could be observed (see Table 2), under these conditions they were much less persistent. Moreover, the spectra of the two *N*-phenyl derivatives **1c** and **1d** were soon contaminated by a signal from an adventitious species, which, after *ca.* 30 min replaced the original spectrum completely. The species responsible for this new signal was the same for both **1c** and **1d** and persisted for several days in the absence of oxygen. It showed coupling of the unpaired electron with two sets of four equivalent protons (a_{4H} = 1.60 and a_{4H} = 1.84 G) and a set of two equivalent nitrogens (a_{2N} = 5.20 G) and had a *g* factor of 2.0037. These spectral parameters are not consistent with the cyclized products that one might have expected to form on the basis of the chemical studies, but rather have led us to identify this species with the radical anion of phenazine. Indeed reduction of an authentic sample of phenazine in DMSO/Bu^{t}OK led to an EPR spectrum identical with that eventually observed upon similar reduction of compounds **1c** and **1d**. The fact that, despite the detection of its radical anion, phenazine was not one of the isolated reaction products indicates that it must be produced in very small quantities; it should in fact be borne in mind that the high sensitivity of the EPR technique allows the detection of species present in very low concentrations. Moreover, the fact that only paramagnetic species are detected makes it possible that species which are not on the main reaction co-ordinate are observed, while other diamagnetic molecules involved in the main reaction process are not.

The formation of phenazine is not easily rationalized; the fact that it is only formed with the two *N*-phenyl derivatives implies that it must proceed through an intramolecular cyclization involving that aromatic ring. Two alternative routes to phenazine may be envisaged. One (Scheme 3) involves deoxygenation of the nitro to the nitroso anion, followed by loss of the $RC(O)^-$ group with formation of an aminyl radical. This conjugated radical could attack the nitroso group *via* a position of high spin-density leading to a cyclic nitroxide, whose

Table 2 EPR spectral parameters (hfs constants in Gauss = 10^{-4} T) for the radical anions from **1a–d**

Compound	$a_N(NO_2)$	a_{3-H}	a_{4-H}	a_{5-H}	a_{6-H}	$a_N(NH)$	$a_H(NH)$	g
1a[a]	12.25	3.30	1.15	3.38	0.79	0.87	—	2.0046_8
1a[b]	10.97	3.53	1.30	3.91	0.83	0.41	0.41	—
1b[a]	13.16	3.74	*c*	2.95	*c*	*c*	—	2.0048_8
1b[b]	10.80	3.50	1.12	3.80	0.96	0.60	—	—
1c[a]	9.10	3.30	1.18	4.12	1.14	0.70	—	2.0048_4
1c[b]	8.70	3.24	1.20	4.18	1.08	0.72	—	—
1d[a]	9.22	3.58	1.15	4.07	1.15	0.66	—	2.0048_8
1d[b]	8.71	3.30	1.25	3.85	1.10	0.77	—	—

[a] Generated in DMSO/Bu^{t}OK. [b] Generated by cathodic reduction in DMF. [c] Not resolved.

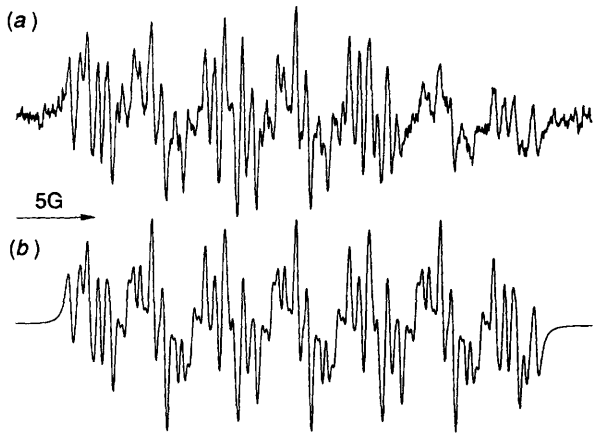
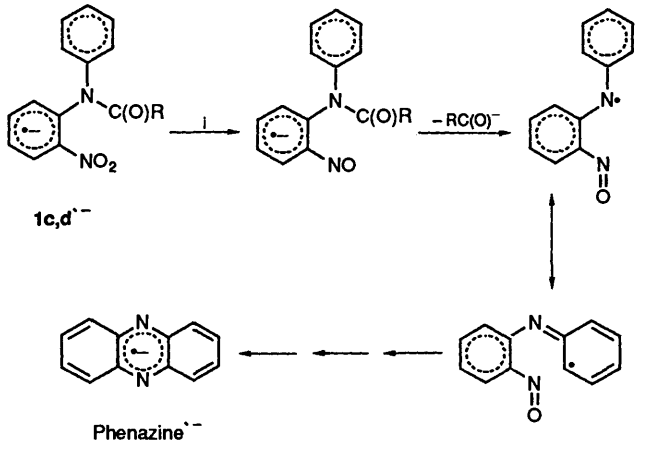


Fig. 3 Experimental (*a*) and simulated (*b*) EPR spectra observed by reduction of **1c** with Bu'OK in DMSO. The spectrum is due to the radical anion **1c**$^{\bullet -}$, and contamination from the radical anion of phenazine is not yet evident.



Scheme 3 *Reagents:* i, Reduction

deoxygenation would eventually afford phenazine. Alternatively, reduction of the nitro group may lead to a nitrene, which could attack the *N*-phenyl ring and subsequently lose $RC(O)^-$.

In no case could the radical anions of the cyclized products recovered in the macroscale experiments be observed.

As a last point, it should be noted that the nitrogen coupling constants in the radical anions of **1a–d** vary with the nature of the solvent, being smaller in DMF than in DMSO. This effect is not large for the anions of the *N*-phenyl nitroanilides **1c** and **1d** (0.4–0.5 G), but becomes very pronounced for the anions of **1a** and **1b**. Although slight variations of the nitrogen hfs constants with the relative permittivity of the solvent are not unexpected, the significant increase observed for a_N in **1a**$^{\bullet -}$ and **1b**$^{\bullet -}$ when going from DMF to DMSO suggests that hydrogen bonding between the amidic hydrogen and the solvent is important, the interaction being stronger in the more polar DMSO.

Experimental

Compounds **1a**,[11] **1b**,[12] **1c**[5] and **1d**[5] were prepared as described in the literature. Melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer, ^{1}H NMR spectra were recorded on a Gemini 200 Varian spectrometer using tetramethylsilane (TMS) as internal standard and liquid chromatography was performed with a Perkin-Elmer (series 2) HPLC.

Macroscale Reductions.—Reduction of **1a–d** *with* Fe/AcOH. Compounds **1a–d** (0.003 mol) and iron powder (0.5 g) were refluxed in acetic acid (10 cm^3) for 30 min. The reaction mixture was filtered, the filtrate diluted with water, and the solution, neutralized with sodium carbonate, was extracted four times with dichloromethane. The organic layer, dried on sodium sulphate and evaporated to dryness, gave benzimidazoles **5a–d** in 70–80% yield. Compounds **5a**, **b** were checked against commercial samples, while compound **5c** exhibited physical properties identical to those reported in the literature.[13] 1,2-*Diphenylbenzimidazole* (**5d**): m.p. 111–112 °C (ligroin); ν_{max}(Nujol)/cm^{-1} 1610, 1595, 1525, 1490; δ_H($CDCl_3$) 7.23–7.63 (m, 12 H_{arom}), 7.95 (d, 2 H_{arom}); (Found: C, 84.1; H, 4.8; N, 10.45%. Calc. for $C_{19}H_{14}N_2$: C, 84.5; H, 5.2; N, 10.3).

Catalytic reduction of **1a–d** *with* H_2 *on* Pd/C. Compound **1a** (0.01 mol) in pyridine (50 cm^3) was hydrogenated in a Parr apparatus in the presence of 5% palladium/carbon (0.2 g) for 15 min. The catalyst was filtered and the filtrate evaporated to dryness. After chromatographic separation (silica gel cyclohexane–ethyl acetate 1:1) of the residue, **6a** (30% yield)* and **7a** (63% yield) were obtained. 2′,2″-*Azoxyacetanilide* (**6a**): m.p. 270–272 °C; ν_{max}(Nujol)/cm^{-1} 3305, 1660, 1590; δ_H($CDCl_3$) 2.31 (s, 6 H_{methyl}), 7.12–7.75 (m, 8 H_{arom}), 8.69 (s, 1 H_{NH}); (Found: C, 62.1; H, 4.7; N, 17.9. Calc. for $C_{16}H_{16}N_4O_3$; C, 61.5; H, 5.1; N, 18.0). 1-*Hydroxy*-2-*methylbenzimidazole* (**7a**): m.p. 178–180 °C; ν_{max}(Nujol)/cm^{-1} 3320, 1695, 1660, 1610, 1590; δ_H($CDCl_3$) 2.2 (s, 6 H_{methyl}), 7.14–7.88 (m, 4 H_{arom}), 8.39 (bs, 1 H_{OH} or $_{NH}$), 8.47–8.69 (m, 4 H_{arom}), 9.86 (bs, 1 H_{OH} or $_{NH}$); (Found: C, 64.6; H, 6.0; N, 18.3. Calc. for $C_8H_8N_2O$: C, 64.9; H, 5.4; N, 18.9.)

A similar procedure using **1b** gave two products: **6b** (9% yield) and **2b** (77% yield). The physical properties of the latter compound matched those reported in the literature.[5] 2′,2″-*Azoxybenzanilide* (**6b**): m.p. 194 °C; ν_{max}(Nujol)/cm^{-1} 3395, 3320, 1675, 1595, 1587; δ_H($CDCl_3$) 7.18–7.67 (m, 10 H_{arom}), 7.83–8.03 (m, 6 H_{arom}), 9.36 (bs, 1 H_{NH}), 11.10 (bs, 1 H_{NH}); (Found: C, 72.0; H, 4.7; N, 12.6. Calc. for $C_{26}H_{20}N_4O_3$: C, 71.6; H, 4.6; N, 12.8).

Catalytic reduction of **1c** and **1d** is known to afford benzimidazole *N*-oxides.[5]

Electrochemical reduction. A magnetically-stirred mercury pool (apparent area *ca.* 20 cm^2) was used as working electrode while a platinum gauze cylinder, placed on the inner wall of a glass tube and connected to the test solution *via* a methylcellulose–DMF–Bu_4NClO_4 plug/sintered glass disc, was used as auxiliary electrode. In a typical experiment the *ortho*-nitroanilide (0.6 mmol) was dissolved in 9:1 acetic acid–water (60 cm^3) and the current was maintained at 200–250 mA. After the time interval corresponding to the consumption of 6 Faradays per mole of substrate, the catholyte was evaporated to dryness, taken up with chloroform and water, neutralized with sodium hydrogencarbonate, dried on sodium sulphate and evaporated to dryness. Compound **1a** gave product **3a**[14] (67% yield) which led to **5a** upon boiling in acetic acid; compound **1b** gave the amine **3b**[15] in a 94% yield. Compound **1c** gave **4c**[5] and **5c**[4] in 68 and 31% yields (as determined by HPLC: eluent, MeOH–H_2O 80:20; flow, 1.0 cm^3 min^{-1}; *T*, 55 °C; column, nucleosil-R C-18 5μm), respectively. Compound **1d** gave **5d** in a 74% yield.

Polarographic Studies.—The electrochemical studies were carried out at room temperature in a three-electrode cell using nitrogen (99.99% pure) purged DMF (spectrophotometric grade) solutions containing Bu_4NClO_4 (0.1 mol dm^{-3}) which had been recrystallized from water and dried *in vacuo* at 60 °C

* Compounds **6a** and **7a** had already been described in an old paper,[7] but, according to our present results, their melting points have been exchanged.

for two days. Constant current and controlled-potential electrolysis were performed using a potentiostat–intensiostat (Amel 552) coupled with an integrator (Amel 558) and a recorder (Leeds & Northrup Speedomax W). In voltammetric experiments a long-lasting sessile-drop mercury electrode[16] or a pulsed platinum disc[17] (Amel 492, φ = 1 mm) were used as working electrodes, while the auxiliary electrode was provided by a platinum wire. A $Hg–Hg_2Cl_2, NaCl_{(sat.aq.)}$–DMF–$Bu_4NClO_4$/sintered glass disc[18] was used as reference electrode.

EPR Studies.—All EPR spectra were recorded with a Bruker ER 200 D spectrometer equipped with standard devices for field calibration and *g* factor determinations. Compounds **1a–d** were reduced by treatment with potassium *tert*-butoxide in DMSO. The electrochemical reduction was carried out in DMF/Bu_4NClO_4 using as working electrode a small platinum net placed inside a commercial EPR flat cell, the auxiliary electrode being that used in voltammetric experiments.

McLachlan spin density calculations were carried out using the following parameters: $h_N(NO_2)$ 2.2, $k_{NO}(NO_2)$ 1.67, $k_{CN}(CNO_2)$ 1.2, $h_O(NO_2)$ 1.4,[19] $h_N(NH)$ 1.5, $k_{CN}(CNH)$ 0.8,[9] $h_O(CO)$ 1.5, $k_{CO}(CO)$ 1.6.[19]

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