Electrochemical Reduction of 1,1-Diaryl-substituted Ethenes in Dimethylformamide

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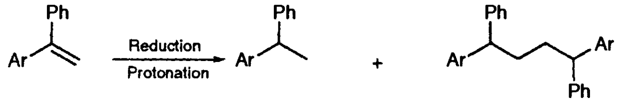
The cathodic behaviour of 1,1-diaryl-substituted ethenes (Ar)PhC=CH$_2$ (where Ar = phenyl-, 2-naphthyl-, 2-pyridyl-, 2-thienyl-, 2-furyl-) at a Hg cathode in *N,N*-dimethylformamide (DMF) and 0.1 mol dm^{-3} tetraethylammonium tetrafluoroborate (TEAF), was investigated by cyclic voltammetry and controlled potential electrolysis experiments. In cyclic voltammetry, at a potential scan rate of 0.2 V s^{-1}, all substrates showed an irreversible reduction peak [($E_{p,c}$) between −2.27 and −2.54 V *vs.* saturated calomel electrode (SCE)]. Controlled potential coulometries indicated that the apparent charge number of the process involved ranges from 1 to 2. The reduction products were characterised as (Ar)PhCH–Me (1-aryl-1-phenylethanes) and (Ar)PhCH–[CH$_2$]$_2$–CHPh(Ar) (1,4-diaryl-1,4-diphenylbutanes). The charge number of the process and the ratio between the two different reduction products depended strongly on the structure and concentration of the substrate. Exhaustive electrolyses performed in the presence of variable amounts of D$_2$O or in [^{2}H$_7$]DMF allowed us to suggest that two distinct pathways are involved in the reduction process, leading to the monomeric and dimeric product, respectively. Hypotheses on the nature of the two reduction mechanisms are discussed.

Recently, we reported that treatment of some 1,1-diaryl-substituted ethenes with Na metal in *N,N*-dimethylformamide (DMF) afforded 4,4-diaryl-*N,N*-dimethyl-2-hydroxybutanamides.[1] This reaction represents the first example of insertion of two DMF units into a carbon–carbon double bond occurring under reductive conditions; as a likely hypothesis, the reaction is triggered by the electron transfer from metal to substrate. Since DMF is widely used as a solvent in cathodic reductions, we felt it worth studying which reduction mechanisms actually occur at the electrode.† We have therefore undertaken the investigation of the cathodic behaviour of various 1-aryl-1-phenylethenes, coupled with an accurate characterisation of the products of exhaustive electroreduction. A further aim of this work was to get preliminary information on the intermediates involved in the reduction process.

While there are literature reports on the cathodic behaviour of 1,1-diphenylethene, due to the work of Wawzonek,[3] Elving,[4,5] Funt[6] and Baizer's[7] groups, no literature data are available for other 1-aryl-1-phenylethenes. On the other hand, there is a wealth of literature data on the electrochemical reduction of olefins mono- and di-substituted with electron-withdrawing (activating) groups,[8] with particular attention being paid to the reaction of electrohydrodimerisation (electrochemically induced hydrodimerisation). After early patents by Baizer[9] on the hydrodimerisation of vinylpyridines at a Hg cathode, significant contributions were given by the research groups of Bard,[10] Savéant,[11,12] Parker[13] and Guidelli;[14] as a typical example, the synthesis of adiponitrile by electrohydrodimerisation of acrylonitrile was the subject of many papers[8,14–17] and patents.[8]

We report here the results obtained on the reduction at a Hg cathode in DMF of 1,1-disubstituted ethenes **1–5**. According to the general Scheme 1, in all cases the reaction products resulted from simple reduction and/or hydrodimerisation of the substrate.



1–5 **6–10** **11–15**

1,6,11 Ar = Ph
2,7,12 Ar = 2-Naphthyl
3,8,13 Ar = 2-Pyridyl
4,9,14 Ar = 2-Thienyl
5,10,15 Ar = 2-Furyl

Scheme 1

Results

Cyclic Voltammetric Experiments under Anhydrous Conditions.—Two cathodic responses are obtained in cyclic voltammetric tests performed on solutions of compounds **1–5**. A typical example of the cathodic portion of the voltammograms obtained is reported in Fig. 1.

With the exception of **2**, no backward anodic response is associated directly to the less cathodic peak at scan rates up to 100 V s^{-1}. At a scan rate of 50 V s^{-1}, **2** shows a coupled backward anodic peak; the value of the anodic current, however, never reaches that of the cathodic current, even at scan rates as high as 100 V s^{-1}.

The values of the cathodic peak potential for the first cathodic response, $(E_{p,c})_1$, together with estimates of the 'halfwave potential', $(E_{\frac{1}{2}})_2$, for the more cathodic systems, obtained for substrates **1–5** under the reported conditions of concentration and potential scan rate, are summarised in Table 1. By comparison with voltammetric tests performed for solutions of

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† The involvement of DMF and other solvents as reagents in cathodic reductions has been discussed; see ref. 2.

Table 1 Voltammetric data for substrates **1–5**

Compound	$(E_{p,c})_1/V^a$	$(E_{\frac{1}{2}})_2/V^a$	$(E_{p,c})_1/V^b$ (lit. data)
1	−2.52	−2.55	−2.56[c]; −2.43[d]
2	−2.30	−2.56	
3	−2.27	−2.74[e]	
4	−2.33	−2.60	
5	−2.48	−2.55	

[a] Substrate concentration: 5×10^{-3} mol dm^{-3}; working electrode: Hg–Au; potential scan rate: 0.2 V s^{-1}; reference electrode: SCE. [b] Reference electrode: SCE. [c] Ref. 6. [d] Ref. 7. [e] Ill-defined cathodic reduction, close to the solvent discharge.

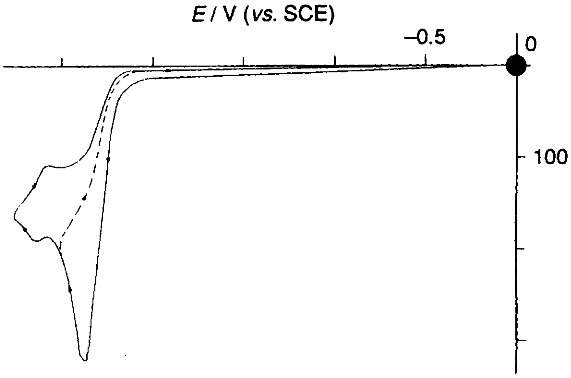

Fig. 1 Cyclic voltammetric curves recorded for a 8.4×10^{-3} mol dm^{-3} solution of substrate **4** in DMF containing 0.1 mol dm^{-3} TEAF, Hg working electrode, 0.2 V s^{-1} potential scan rate; ● starting potential for the initial cathodic scans

pure dimeric products, it was established that the more cathodic, quasi-reversible system could be attributed to the reduction of the dimeric product.

Cyclic Voltammetric Experiments in the Presence of Water.—The voltammograms of solutions of **1–5** containing an increasing amount of water show an increase of the cathodic current of the first peak, that, however, never becomes as high as twice the current observed in the absence of water. This behaviour suggests that, at the potentials of the first cathodic peak, at least two reduction mechanisms of different charge number are operative. The reduction consuming more electrons should indeed be favoured by the presence of a proton donor in the reaction medium.

Controlled Potential Coulometries.—The exhaustive reduction of substrates **1–5** was carried out on a Hg pool electrode at a potential *ca.* 0.1 V less cathodic than the relevant $(E_{p,c})_1$. Using a substrate concentration of 8×10^{-3} mol dm^{-3} the values of apparent charge number, *n*, were always between 1 and 2 (Table 2), thus confirming that different concomitant pathways of reduction take place also on the longer time scale proper of these tests.

In each case the analysis of the reaction mixtures revealed the presence of two distinct products that, after proper isolation and purification, were characterised as arylphenylethanes **6–10** and 1,4-diaryl-1,4-diphenylbutanes **11–15** (Scheme 1). As limiting cases, under the conditions reported in Table 2, only 1,1-diphenylethane **6** (the simple reduction product) is formed from **1**, whereas only 1,4-diphenyl-1,4-di(2-pyridyl)butane **13** (the product of hydrodimerisation) is formed from **3**. Mixtures of variable amounts of both types of products are obtained from the other substrates. It has to be pointed out that formation of reduction products **6–10** requires two electrons per molecule of substrate, [eqn. (1)], whereas formation of the hydrodimerisation products **11–15** requires only one electron per molecule [eqn. (2)].

Table 2 Controlled potential electrochemical reduction of 1,1-diaryl-substituted ethenes **1–5** in DMF, 0.1 mol dm^{-3} TEAF at various concentrations

Compound	Concentration/ mmol dm^{-3}	*n*	Product ratio (%)[a,b]	
			Monomeric	Dimeric
1	8	1.97	**6** (100)	**11** (0)
1	40	1.66	**6** (57)	**11** (43)
2	8	1.37	**7** (34)	**12** (66)
2	40	1.32	**7** (21)	**12** (79)
3	8	0.93	**8** (0)	**13** (100)
3	40	1.01	**8** (0)	**13** (100)
4	8	1.63	**9** (61)	**14** (39)
4	40	1.51	**9** (52)	**14** (48)
5	8	1.77	**10** (71)	**15** (29)
5	40	1.60	**10** (61)	**15** (39)

[a] Determined by integration of the ^{1}H NMR spectrum of the reaction mixtures prior to flash column chromatography; estimated error *ca.* 2%. [b] Total yields were in all cases higher than 95%.

$$\mathbf{1\text{–}5} + 2e^- + 2H^+ \longrightarrow \mathbf{6\text{–}10} \qquad (1)$$

$$2\,\mathbf{1\text{–}5} + 2e^- + 2H^+ \longrightarrow \mathbf{11\text{–}15} \qquad (2)$$

Considering that the fractional number of electrons stoichiometrically consumed in the reduction of one molecule of depolariser can result from the concomitant occurrence of one- and two-electrons processes, the values of *n* reported in Table 2 fit well the composition of the reduction mixture.

It is also noteworthy that the 'apparent charge number' of the whole reduction process for the different substrates increases as the absolute value of the reduction potential, as measured by $(E_{p,c})_1$,* is increased. As a consequence, the relative amount of products **6–10** in the reaction mixtures increases with the same trend.

Cyclic voltammetry curves recorded after exhaustive electrolysis, using a Hg working electrode, only exhibit the more cathodic peak system observed for the starting solution, reversible for **1**, **2**, **4** and **5** [$(E_{\frac{1}{2}})_2$ between −2.55 and −2.65 V] and irreversible for **3** [$(E_{p,c})_1 = -2.74$ V]. In the anodic portion of the voltammetric curves, working with a Pt electrode, only a broad, irreversible oxidation peak at a potential between 1.0 and 1.3 V is observed for all reduction mixtures.

Exhaustive Electrolyses at Different Substrate Concentrations.—In order to obtain qualitative information on the influence of the concentration of substrate on the composition of the reduction mixture, coulometric tests at two different concentrations were carried out; the results are reported in Table 2. It was thus possible to recognise a general trend, more or less evident for the various substrates, according to which an increase of concentration corresponds to an increase of the relative amount of dimeric product. However, owing to the limited range of concentrations taken into consideration, particular caution should be exerted in generalising these results.

Exhaustive Electrolyses in the Presence of Deuterium Oxide.—Controlled potential electrolyses were carried out in the

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* It must be stressed that such values were not obtained from responses relative to reversible uncomplicated electron transfers; therefore they lack precise thermodynamic significance.

Table 3 Controlled potential electrochemical reduction of 1,1-diaryl-substituted ethenes **1–5** in DMF, 0.1 mol dm^{-3} TEAF, in the presence of D_2O[a]

Compound	D_2O : substrate molar ratio	n	Product ratio (%)[b,c]			
			ArCH(Ph)Me	ArCD(Ph)CH$_2$D	ArCH(Ph)[CH$_2$]$_2$CH(Ph)Ar	ArCD(Ph)[CH$_2$]$_2$CD(Ph)Ar
1	0	1.97	**6** (100)		**11** (0)	
1	50	1.97	**6** (0)	100	**11** (0)	
1	100	1.99	**6** (0)	100	**11** (0)	
2	0	1.37	**7** (17)		**12** (83)	
2	30	1.57	**7** (0)	63	**12** (0)	37
2	50	1.77	**7** (0)	70	**12** (0)	30
2	100	1.94	**7** (0)	88	**12** (0)	12
3	0	0.93	**8** (0)		**13** (100)	
3	100	1.63	**8** (0)	65	**13** (0)	35
3	200	1.88	**8** (0)	90	**13** (0)	10
4	0	1.63	**9** (61)		**14** (39)	
4	30	1.65	**9** (0)	75	**14** (0)	25
4	50	1.72	**9** (0)	82	**14** (0)	18
4	100	1.75	**9** (0)	97	**14** (0)	3
5	0	1.77	**10** (71)		**15** (29)	
5	30	1.75	**10** (0)	75	**15** (0)	25
5	50	1.89	**10** (0)	90	**15** (0)	10
5	100	1.80	**10** (0)	100	**15** (0)	0

[a] Substrate concentration: 8 × 10^{-3} mol dm^{-3}. [b] Determined by ^{1}H NMR spectroscopy; estimated error *ca.* 2%. [c] See footnotes to Table 2.

presence of variable amounts of D_2O, up to 200 : 1 with respect to the substrate. D_2O was chosen (*i*) as a 'proton' donor, possibly able to induce a preferred path of reduction (see above) and (*ii*) to allow us to make hypotheses on the protonation site(s) of the basic species involved as intermediates in the reduction process. The results obtained are reported in Table 3. It is noteworthy that the amount of the monomeric reduction products increases with increasing the ratio D_2O : substrate. Compound **3** requires the highest amounts of D_2O in order to force the reduction towards the monomeric product.

Inspection of the reduction mixtures by ^{1}H NMR spectroscopy permitted us to ascertain that the monomeric products were 1,1-diaryl-1,2-dideuterioethanes, *i.e.*, products **6–10** deuteriated both at the 1- and at the 2-position, and that the dimeric products were 1,1,4,4-tetraaryl-1,4-dideuteriobutanes, *i.e.*, products **12–15** deuteriated both at the 1- and at the 4-position (Table 3).

Exhaustive Electrolyses in Deuteriated DMF.—Controlled potential electrolyses were carried out in [$^2H_7$]DMF and 0.1 mol dm^{-3} TEAF, only for substrates **1–4**, under conditions somewhat different from those used in the previous experiments (5 cm^3 cell; substrate concentrations: 2 × 10^{-2} mol dm^{-3}). The small amount of substrate used permitted us to isolate only the reductions' products formed in the highest amount: these were the monomer **6** in the case of **1** and the dimers **12** and **13** in the case of **2** and **3**, respectively. In the case of **4**, a mixture of products **9** and **14** in the ratio of 1 : 3 was obtained. Deuterium incorporation was complete in the 1-position of **6** and **9**; no deuterium was found in the 2-position of **6** and **9**, nor in any position of dimers **12–14**.

Identification of Products.—The mixtures of products of exhaustive electrolysis were purified by flash chromatography on silica gel and the single products identified by spectroscopic techniques, mostly ^{1}H NMR. For comparison purposes, in some cases authentic samples of the reduction products were prepared.

The position of the deuterium atom(s) and the amount of deuterium incorporation were determined by careful comparison of the ^{1}H NMR spectra of deuteriated products with the spectra of non-deuteriated products.

Discussion

The main features of the results may be summarised as follows: (*i*) very negative reduction potentials, more negative than −2.3 V *vs.* SCE, are observed for all the substrates investigated. In cyclic voltammetry, the first cathodic peak is, in general, chemically irreversible, except for substrate **2**, which shows a reversible behaviour only at quite high potential scan rates; (*ii*) the reaction products formed are in all cases the monomers **6–10** and the dimers **11–15**, with an overall charge number of the process in good agreement with their relative amounts; (*iii*) the ratio between the two different reduction products depends on the structure of the substrate and is affected by the concentration of substrate and by the amount of added proton donor (H_2O or D_2O); (*iv*) the deuteriation experiments show that the formation of the monomeric reduction products under 'anhydrous' conditions occurs through a first protonation at the very basic 1-position by DMF and a second protonation at the much less basic 2-position by water, possibly present in traces or added during quenching; under the same conditions, formation of the dimeric reduction products occurs through double protonation by water at the two diaryl-substituted carbon atoms. In the presence of added water, the formation of both monomeric and dimeric reduction products occurs *via* protonation by water rather than by DMF.

(*i*) The very negative values of reduction potential of substrates **2–4** are in accord with the value reported in the literature for substrate **1**, as measured both by polarographic and voltammetric techniques.[3,7] In addition, our data show that the substitution of one of the aryl groups of the substrate with a group which presents, in principle, a higher possibility of charge delocalisation than phenyl, *i.e.*, 2-naphthyl, or with an electron-withdrawing aromatic group, *i.e.*, 2-pyridyl, affects only marginally the reduction potential of the substrates. Such a levelling effect makes it difficult to draw a correlation between the value of the reduction potential and the structure of the substrate. Furthermore, different conformations of the aryl groups of the various substrates may induce differences in the energy level of the relevant LUMO, leading to differences in the reduction potentials.*

(*ii*) Careful checking of the reaction mixtures of the exhaustive electrolyses allows us to exclude the presence of

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* See preceding footnote.

products of insertion of DMF (or fragments of it) among the reaction products. This suggests that the previously reported formation of 4,4-diarylbutanamides in the reduction of substrates **1**–**5** by Na metal has to be imputed to the particular conditions of such reaction,[1] rather than to intrinsic properties of the intermediates involved in the process.

(*iii*) Although the values of $(E_{p,c})_1$ of substrates **1**–**5** are quite close to one another, a rough correlation can be drawn between the reduction potential and the monomer : dimer ratio, where similar concentrations of substrates are used; indeed, increasing relative amounts of the monomeric product are formed from less easily reducible substrates. Inspection of Table 2 shows that, as extreme cases, at both the concentrations used, the dimeric reduction product **8** is exclusively formed from **3** $[(E_{p,c})_1 = -2.27$ V], whereas the monomeric reduction product **6** is exclusively formed from **1** $[(E_{p,c})_1 = -2.52$ V] at the lowest concentration used. As stressed above, this is in agreement with an overall mechanism in which two different reduction products are formed through two distinct pathways.

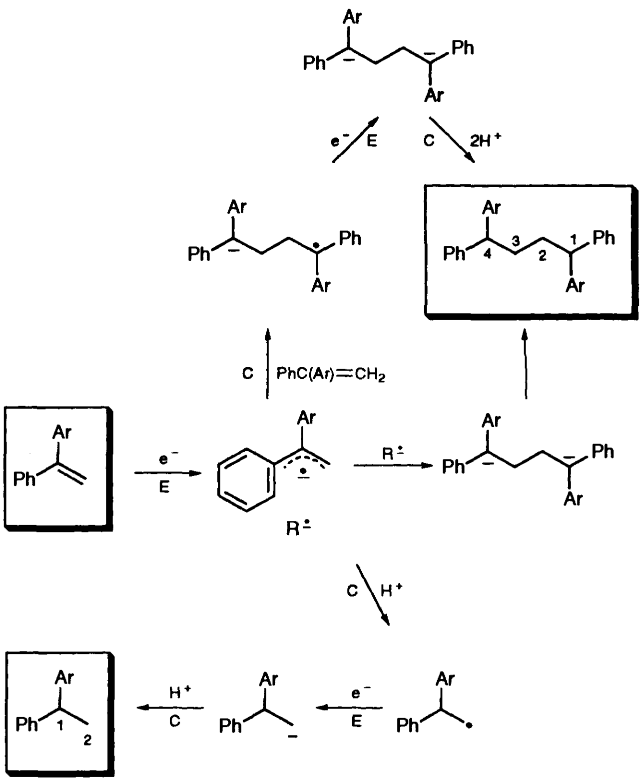
(*iv*) The correlation found between the monomer : dimer ratio and the amount of added proton donor, such that increasing amounts of monomeric reduction products are formed as the relative amount of proton donor is increased, indicates that the protonation step has a deep influence on the subsequent path of the reaction. The fact that protonation by DMF occurs only on the intermediate(s) leading to the monomeric product and does not occur on the intermediate(s) leading to the dimeric product suggests that the protonation reaction is not a common step of the two pathways. In addition, the direct intervention of DMF in the protonation step requires strongly basic intermediates.* Indeed, intervention by $[^2H_7]$DMF occurs quantitatively in the case of **1**, *i.e.*, the substrate having the most negative $(E_{p,c})_1$, leading to the exclusive formation of monodeuteriated **6**. Under the same conditions **4**, *i.e.*, a substrate having a less negative $(E_{p,c})_1$ than **1**, leads to the preferential formation of dimeric **14** over monomeric **9**, suggesting in this case a less basic character of the intermediate species undergoing protonation by DMF.

All of the results allow us to offer a possible rationale, based on the hypothesis that the differentiation between the two different reaction pathways occurs at the level of a radical anion formed at the electrode in the first elemental one-electron transfer step. Reasonable hypotheses for the evolution of this radical anion to monomeric and/or dimeric reduction products may then be advanced (Scheme 2). For simplicity, disproportionation reactions that are possible in principle but were not checked by us, are omitted in Scheme 2.

According to Scheme 2, electrohydrodimerisation can occur either by (*i*) anion radical—anion radical coupling, to give a stable dimeric dianion which is subsequently protonated (mechanism Dim1, according to the classification of Savéant and coworkers)[19] or (*ii*) reaction of the radical anion with a molecule of substrate to give a dimeric radical anion, that first undergoes a second one-electron transfer and then protonation (mechanism Dim2, ECE).[19]

As to the formation of dimeric products, we can rule out, for the reductions performed in 'anhydrous' DMF, all mechanistic pathways involving protonation of the monomeric radical anion. On the other hand, a possible pathway of formation of the monomeric product is an ECEC mechanism, where the radical anion is first protonated, then one-electron reduced and subsequently further protonated.

Further work devoted to better define from both a qualitative and, possibly, quantitative point of view the reduction mechanisms by voltammetric techniques at varying substrate concentrations and under different experimental conditions is in progress in our laboratories.



Scheme 2 E: Electrode charge transfer; C: chemical step

Experimental

M.p.s and b.p.s are uncorrected. ^{1}H NMR (300 MHz) spectra of $CDCl_3$ solutions were recorded using a Varian VXR 300s spectrometer. The chemical shifts are reported in ppm downfield from internal Me_4Si; *J* values are given in Hz. Mass spectra were performed using a mass spectrometer Hewlett Packard model 5988. Elemental analyses were performed at the Microanalytical Laboratory of the *Dipartimento di Chimica, Sassari.*

Materials.—*N*,*N*-Dimethylformamide (DMF) (Aldrich, anhydrous, 99+%, Gold Label, water < 0.005%, packaged under nitrogen) was used in all experiments without further purification. Tetraethylammonium tetrafluoroborate (TEAF) (Fluka, *purissimum*, > 99%) supporting electrolyte was stored under reduced pressure and dried overnight at 50 °C at a pressure lower than 5 Torr (1 Torr = 133.322 Pa) before use. Hg Electrode material (Aldrich, triply distilled, 99.99+%) was used as received.

1,1-Diphenylethene **1** was obtained commercially (Aldrich, 97%) and was purified by distillation under reduced pressure. The following starting materials were prepared according to literature procedures: 1-phenyl-1-(2-naphthyl)ethene **2**,[20] 1-phenyl-1-(2-pyridyl)ethene **3**,[21] 1-phenyl-1-(2-thienyl)ethene **4**[22] and 1-phenyl-1-(2-furyl)ethene **5**.[23]

Electrochemical Tests.—An Amel System 5000 computerised instrument was used as the potential waveform generator, potentiostat and coulometer in all the electrochemical experiments. This instrument is suitable for storing data collected in relatively high scan rate voltammetric tests (up to 100 V s^{-1}) and subsequently for using an XY recorded (Amel model 863) to plot the current/potential data sequences. Cyclic

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* DMF is known to lose the aldehydic proton in the presence of strong bases such as lithium diisopropylamide.[18]

Table 4 Physical constants and analytical data for compounds **6–15**

Compound (formula)	M.p./°C (b.p./°C)	Found (%) (required)				m/z (M^+)
		C	H	N	S	
6	(146–148)[a]					
($C_{14}H_{14}$)						
7	36–38[b]					
($C_{18}H_{16}$)						
8	(121–123)[c]					183
($C_{13}H_{13}N$)						
9	(*ca.* 140)[d]	76.3	6.45		17.2	
($C_{12}H_{12}S$)		(76.55)	(6.4)		(17.0)	
10	(*ca.* 140)[d,e]	83.4	6.85			
($C_{12}H_{12}O$)		(83.7)	(7.0)			
11	121–122[f]					362
($C_{28}H_{26}$)						
12	*g*	93.6	6.6			
($C_{36}H_{30}$)		(93.45)	(6.55)			
13	*g*	85.75	6.7	7.6		364
($C_{26}H_{24}N_2$)		(85.7)	(6.65)	(7.7)		
14	*g*	77.0	5.8		17.35	
($C_{24}H_{22}S_2$)		(76.95)	(5.9)		(17.1)	
15	*g*	84.05	6.75			
($C_{24}H_{22}O_2$)		(84.2)	(6.5)			

[a] At 15 Torr (lit.,[25] b.p. 148 °C at 15 Torr). [b] Colourless crystals (from MeOH) (lit.,[26] m.p. 37–38 °C). [c] At 5 Torr (lit.,[27] b.p. 122 °C at 5 Torr). [d] Bath temperature during bulb to bulb distillation at 5 Torr. [e] Lit.,[28] colourless oil; in ref. 28 the ^1H NMR spectra of **10** at 200 MHz was reported, but no b.p. and no analytical data. [f] Colourless crystals (from EtOH) (lit.,[29] m.p. 120–121.6 °C). [g] Solid product; being a mixture of diastereoisomers, the m.p. was not determined nor separation of the components attempted.

Table 5 ^1H NMR data for compounds **6–15**

Compound	1-H	2-H	Aromatic H	Heteroaromatic H
6	4.12 (q, *J* 7.50)	1.62 (d, *J* 7.50)	7.06–7.28 (10 H, m)	
7	4.30 (q, *J* 6.67)	1.72 (d, *J* 6.67)	7.06–7.82 (12 H, m)	
8	4.28 (q, *J* 7.50)	1.70 (d, *J* 7.50)	7.00–7.60 (8 H, m)	8.46 (1 H, d, *J* 4.60)
9	4.38 (q, *J* 7.30)	1.74 (d, *J* 7.30)	6.98–7.60 (5 H, m)	6.82 (1 H, d, *J* 2.5); 6.95 (1 H, dd, *J* 2.5 and 4.6), 7.10 (1 H, d, *J* 4.6)
10	4.10 (q, *J* 6.60)	1.58 (d, *J* 6.60)	7.13–7.63 (6 H, m)	5.96–6.09 (1 H, m), 6.23–6.30 (1 H, m)
	1,4-H	2,3-H	Aromatic H	Heteroaromatic H
11	3.82–3.95 (m)	1.95–2.05 (m)	7.09–7.27 (20 H, m)	
12[a]	4.01–4.16 (m)	2.07–2.15 (m)	7.06–7.82 (24 H, m)	
13[a]	4.02–4.16 (m)	1.96–2.28 (m)	7.00–7.60 (16 H, m)	8.52 (2 H, d, *J* 5.00)
14[a]	4.14–4.22 (m)	2.05–2.18 (m)	6.98–7.60 (12 H, m)	6.70–6.75 (2 H, m); 6.82–6.87 (2 H, m)
15[a]	3.82–4.00 (m)	1.75–2.18 (m)	7.10–7.33 (12 H, m)	5.96–6.09 (2 H, m); 6.23–6.30 (2 H, m)

[a] Mixture of diastereoisomers in the ratio of *ca.* 1 : 1.

voltammetries (at potential scan rates lower than 0.5 V s^{-1}) and controlled potential coulometric tests were all carried out in H-shaped cells. The working electrode compartment was separated from auxiliary and reference electrodes by low-porosity frits. In the cyclic voltammetric experiments the working electrode was either a Hg electrode prepared by covering a gold disk (2 mm diameter) or a platinum electrode with similar dimensions. In exhaustive electrolyses, the working electrode was a large Hg pool. In low scan rate voltammetric tests and in controlled potential coulometries the auxiliary electrode was a Hg pool. In all experiments the potentials are referred to a saturated calomel electrode (SCE). This reference electrode was connected to the working electrode compartment by a salt bridge containing the same solvent–electrolyte medium. High scan rate (up to 100 V s^{-1}) voltammetric experiments were performed in a geometrically suitable cell,[24] that minimises the *i*R drop between working and reference electrodes. Either a Hg covered gold disk or a platinum disk (2 mm diameter) were also in this case used as the working electrode; the auxiliary electrode was a coiled platinum wire surrounding the tip of the working electrode, and the reference electrode was a SCE connected to the working electrode by a Luggin capillary.

All measurements were performed at room temp.; the solutions were carefully deaerated by bubbling 99.999% pure argon through; the same gas flowed over the solution during the experiments. No difference in the results could be obtained by taking additional care to perform the tests inside a glove box.

Isolation and Identification of Reaction Products.—The reduction products were isolated, after quenching of the electrolysis mixtures with ice–water and standard work up,[25] by flash chromatography on silica gel (230–400 mesh), with hexane–diethyl ether 1 : 1 as eluent; this permitted us to separate the products of simple reduction (**6–7** and **9–10**) from the products of hydrodimerisation (**11–15**) and to exclude the formation of secondary reaction products. Products **6**, **7**, **10** and **11** were known compounds and were identified by comparison with literature data (Table 4). 1-Phenyl-1-(2-pyridyl)ethane **8**, which was not formed in the electrochemical reduction, was prepared in almost quantitative yield by catalytic hydrogenation of **3** on Pd on carbon. Products **9** and **12–15** were characterised by elemental analyses and in few cases by mass spectroscopy (Table 4); all products were further characterised by ^{1}H NMR spectroscopy (Table 5).

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References

1 C. Botteghi, S. Gotta, M. Marchetti and G. Melloni, *Tetrahedron Lett.*, 1992, **33**, 5601.
2 F. Maran, E. Vianello, F. D'Angeli, G. Cavicchioni and G. Vecchiati, *J. Chem. Soc., Perkin Trans. 2*, 1987, 33; F. D'Angeli, G. Cavicchioni, G. Catellani, P. Marchetti and F. Maran, *Gazz. Chim. Ital.*, 1989, **119**, 471, and ref. cited therein. See also F. Maran, E. Vianello, F. D'Angeli and G. Cavicchioni, presented at the Journées d'Electrochimie, Firenze, 1985, and ref. cited therein.
3 S. Wawzonek, E. W. Blaha, R. Berkey and M. E. Runner, *J. Electrochem. Soc.*, 1955, **102**, 235.
4 P. G. Grodzka and P. J. Elving, *J. Electrochem. Soc.*, 1963, **110**, 225.
5 P. G. Grodzka and P. J. Elving, *J. Electrochem. Soc.*, 1963, **110**, 231.
6 B. L. Funt and D. G. Gray, *J. Electrochem. Soc.*, 1970, **117**, 1020.
7 T. Troll and M. M. Baizer, *Electrochim. Acta*, 1974, **19**, 951.
8 M. M. Baizer, *Organic Electrochemistry*, ed. H. Lund and M. M. Baizer, Marcel Dekker, New York, 1991, ch. 22, pp. 908–925.
9 M. M. Baizer, US Pat. 3 218 245, 1965 (*Chem. Abstr.*, **64**, 17554f); M. M. Baizer and E. J. Prill, US Pat. 3 218 246, 1965 (*Chem. Abstr.*, 1966, **64**, 17554h).
10 M. J. Hazelrigg Jr. and A. J. Bard, *J. Electrochem. Soc.*, 1975, **122**, 211; J.-M. Nigretto and A. J. Bard, *J. Electrochem. Soc.*, 1976, **123**, 1303.
11 L. Nadjo and J. M. Savéant, *J. Electroanal. Chem.*, 1976, **73**, 163, and ref. cited therein.
12 C. Amatore, R. Guidelli, M. R. Moncelli and J. M. Savéant, *J. Electroanal. Chem.*, 1983, **148**, 25, and ref. cited therein.
13 V. D. Parker, *Acta Chem. Scand. B*, 1983, **37**, 393, and ref. cited therein.
14 M. R. Moncelli, R. Guidelli and M. Carlà, *J. Electroanal. Chem.*, 1991, **313**, 313, and ref. cited therein.
15 A. N. Haines, I. F. McConvey and K. Scott, *Electrochim. Acta*, 1985, **30**, 291.
16 P. J. Kinlen and C. H. J. King, *J. Electroanal. Chem.*, 1991, **304**, 133.
17 K. Scott, I. F. McConvey and J. Henderson, *J. Appl. Electrochem.*, 1987, **17**, 329.
18 B. Banhidai and U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, 1972, **12**, 836.
19 C. Amatore, *Organic Electrochemistry*, ed. H. Lund and M. M. Baizer, Marcel Dekker, New York, 1991, ch. 4, p. 221.
20 K. Maruyama, T. Otsuki and K. Mitsui, *J. Org. Chem.*, 1980, **45**, 1424.
21 R. Schubert and H. F. Grützmacher, *J. Am. Chem. Soc.*, 1980, **102**, 5323.
22 N. R. Krishnaswamy, Ch. S. S. R. Kumar and S. R. Prasanna, *J. Chem. Res. (S)*, 1991, 166.
23 K. Maruyama, T. Otsuki, K. Mitsui and M. Tojo, *J. Heterocycl. Chem.*, 1980, **17**, 695.
24 Southampton Electrochemistry Group, *Instrumental Methods in Electrochemistry*, Ellis Horwood Ltd, Chichester, UK, 1985.
25 G. Farnia, F. Marcuzzi, G. Melloni, G. Sandonà and M. V. Zucca, *J. Am. Chem. Soc.*, 1989, **111**, 918.
26 A. Spilker and W. Schade, *Ber. Dtsch. Chem. Ges.*, 1932, **65**, 1686.
27 B. R. Brown and D. Ll. Hammick, *J. Chem. Soc.*, 1948, 1395.
28 U. Azzena, G. Chelucci, G. Delogu, S. Gladiali, M. Marchetti, F. Soccolini and C. Botteghi, *Gazz. Chim. Ital.*, 1986, **116**, 307; A. J. Canty and N. J. Minchin, *Aust. J. Chem.*, 1986, **39**, 1063.
29 S. S. Hall and S. E. Farahat, *J. Heterocyc. Chem.*, 1987, **24**, 1205.
30 K. Scholtis, *Liebigs Ann. Chem.*, 1945, **557**, 82; see also: C. B. Wooster and J. F. Ryan, *J. Am. Chem. Soc.*, 1934, **56**, 1133; H. Gilman and J. C. Bailie, *J. Am. Chem. Soc.*, 1943, **65**, 267.

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