The Electrochemical Reduction of *NN'*-Disubstituted 6-Phenyl-2,3-dihydro-1,4-diazepinium Salts: Formation of Bis(tetrahydrodiazepinyls) and a Di-imidazolidinylbutadiene

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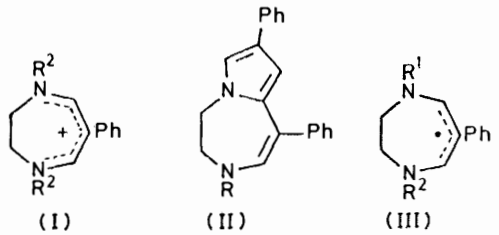
The *NN'*-disubstituted 6-phenyl-2,3-dihydro-1,4-diazepinium cations (Ia—c), in solution in dimethylformamide, undergo one-electron single reduction waves at −0.9 to −1.3 V with respect to Ag–AgCl–KCl (saturated). The reductions were studied by polarography, cyclic voltammetry, and constant potential electrolysis. Rapid chemical reactions follow the initial reduction and isolated products were the bis(tetrahydrodiazepinyls) (IV) and (VI) and a di-imidazolidinylbutadiene (V). These products were hydrolysed by concentrated hydrochloric acid to give the corresponding *NN'*-disubstituted ethylenediamine dihydrochloride and also, in the case of (V), 2,5-diphenylhexa-2,4-diene-1,6-dial. The *meso*-isomer (IVa) was converted into its racemic isomer (IVb) when heated in dimethylformamide. Compound (IVb) was quantitatively converted into the diene (V) in a cold mixture of chloroform and ethanol. Cyclic voltammetry studies of (IV) indicated that they were oxidised to bis(dihydrodiazepinium) cations, and that (V) was reduced, with similar behaviour to the reduction of 1,4-diphenylbuta-1,3-diene.

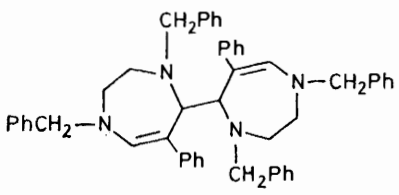
ELECTROCHEMICAL reduction of the 6-phenyl-2,3-dihydro-1,4-diazepinium cation (Id), or of its mono-*N*-methyl derivative (Ie), in dimethylformamide at a mercury or a platinum electrode, surprisingly gave as products tetrahydropyrrolo[1,2-*a*]diazepines (II; R = H or Me).[1,2] Formation of (II) probably involves dimerisation of an initially formed radical (III). A similar radical appears to be formed when the 5,7-diphenyl-2,3-dihydro-1,4-diazepinium cation (VII) is reduced electrochemically, but in that case it disproportionates to give a dihydrodiazepine and a tetrahydrodiazepine.[3,4]

If both nitrogen atoms in (I) are substituted formation



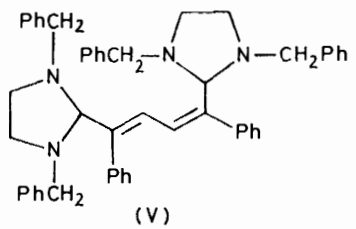
(I) (II) (III)

a; $R^1 = R^2 = PhCH_2$
b; $R^1 = R^2 = Me$
c; $R^1 = R^2 = Ph$
d; $R^1 = R^2 = H$
e; $R^1 = H, R = Me$

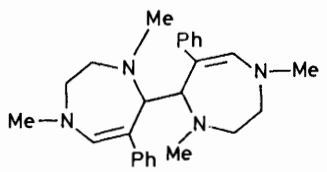


(IV)

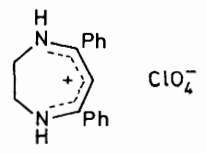
a; *meso*
b; racemic



(V)



(VI)



(VII)

of a pyrrolodiazepine is prevented and alternative reaction paths must ensue. This is found to be so. Electrochemical reduction of (Ia), under similar conditions to those used in the other studies, provides three products, in a total yield of 85—90%, namely the *meso* and racemic isomers (IV) of the dimer of the radical (III) and another unexpected rearrangement product, the di-imidazolidinylbutadiene (V).[5] Reduction of (Ib) also provided a bis(tetrahydrodiazepinyl) (VI), but no definable products were isolated from the reduction of (Ic).

EXPERIMENTAL

Materials.—Dihydrodiazepinium salts (I) were prepared as described.[6] Dimethylformamide (DMF) was spectroscopic grade, used without further purification. Tetra-n-propylammonium perchlorate (TPAP) was prepared by neutralisation of the corresponding hydroxide (10% aqueous solution) with aqueous perchloric acid (60—70%) and purified by recrystallisation from aqueous acetonitrile (20%).

Electrochemical Apparatus and Procedure.—Apparatus and procedure were as described in a previous paper.[2]

Work-up of Preparative Electrolyses.—During the reduction of (Ia) a fine powder precipitated. This was filtered off and proved to be the *meso*-bistetrahydrodiazepinyl (IVa). Water was added to the filtrate, and it was extracted with ether. Removal of ether left an orange oil which, on trituration with hot ethanol, provided granular crystals consisting of the racemic bistetrahydrodiazepinyl (IVb) and the butadiene (V). These were separated by repeated careful crystallisation from ethanol. Overall yields were 85—90%. This was made up of *ca.* 35% of (IVa) and 60% of the mixture of (IVb) and (V). The amount of (IVa) was effectively constant in a series of reductions but the ratio of (IVb) to (V) varied in different reductions. The amount of (V) [which has been shown to be a rearrangement product of (IVb); see below] was greatest in electrolyses in which the catholyte had been contaminated by small amounts of solution leaking from the anode compartment through the coarse sinters. If particular care was taken to minimise diffusion, and the cell was cooled to −10°, very little compound (V) was formed. The same products were also obtained from a reduction carried out in dry methanol–DMF (4 : 1). Products (IVa and b), plus a small amount of (V), precipitated out in the course of the electrolysis, and more of (V) was obtained by an aqueous ether work-up procedure, as above.

meso-7,7′-*Bis*-(1,4-*dibenzyl*-6-*phenyl*-1,2,3,4-*tetrahydro*-1,4-*diazepinyl*) (IVa).—This *diazepine* had m.p. 158°, $\nu_{max.}$ (Nujol) 1 641s and 1 595 cm^{-1}, τ ($CDCl_3$) 2.5—3.0 (30 H, m), 3.59 (2 H, s), 5.28 (2 H, s), 5.83—6.28 (q) and 6.0 (s) (8 H), and 7.1—7.9 (8 H, m) (Found: C, 84.95; H, 7.4; N, 7.8%; *m/e*, 353.210. $C_{50}H_{50}N_4$ requires C, 84.9; H, 7.1; N, 7.95%; *M*/2, 353.206).

Racemic 7,7′-*Bis*-(1,4-*dibenzyl*-6-*phenyl*-1,2,3,4-*tetrahydro*-1,4-*diazepinyl*) (IVb).—This *diazepine* had m.p. 147°, $\nu_{max.}$ (Nujol) 1 642, 1 625, and 1 594 cm^{-1}, τ ($CDCl_3$) 2.6—3.05 (m) and 2.72 (s) (30 H), 3.98 (2 H, s), 5.10 (2 H, s), 6.06 (4 H, s), 6.11 (4 H, s), and 6.3—7.6 (8 H, m) (Found: C, 84.8; H, 7.5; N, 7.9%; *m/e*, 353.210. $C_{50}H_{50}N_4$ requires C, 84.9; H, 7.1; N, 7.95%; *M*/2, 353.206).

1,4-*Bis*-(NN′-*dibenzyl*-2-*imidazolidinyl*)-1,4-*diphenylbuta*-1,3-*diene* (V).—This *diene* had m.p. 162°, $\nu_{max.}$ (Nujol) 1 595w and 2 780s cm^{-1}, τ ($CDCl_3$) 2.14—2.85 (32 H, complex), 5.59—7.00 (14 H, complex), and 7.6br (4 H) (Found: C, 84.85; H, 7.4; N, 7.8%; M^+, 706. $C_{50}H_{50}N_4$ requires C, 84.9; H, 7.1; N, 7.95%; *M*, 706).

Acid Hydrolyses of Compounds (IVa *and* b) *and* (V).—Addition of a drop of concentrated hydrochloric acid to solutions of either of these compounds rapidly produced deep red solutions from which fine precipitates deposited, in the case of (V) in 90% yield, but less from (IVa and b). These were NN′-*dibenzylethylenediamine dihydrochloride*, m.p. 298° (Found: C, 60.85; H, 7.1; N, 8.75. $C_{16}H_{22}Cl_2N_2$ requires C, 61.3; H, 7.05; N, 8.95%), identical with a sample prepared from *NN*′-dibenzylethylenediamine and hydrochloric acid (2 equiv.) in DMF. Partition of the product from (V) between water and ether also gave, from the washed (dilute NaOH, dilute NaCl), dried ethereal solution, 2,5-*diphenylhexa*-2,4-*diene*-1,6-*dial* (52%), an orange powder, which was washed with cold ethanol–methanol, m.p. 167°, $\lambda_{max.}$ (ethanol–ether) 341.5 nm (ε 14 400), $\nu_{max.}$ (Nujol), 1 670vs cm^{-1}, τ ($CDCl_3$) 0.04 (2 H, s) and 2.4—2.8 (6 H, m) (Found: C, 81.1; H, 5.3%, M^+, 262. $C_{18}H_{14}O_2$ requires C, 82.4; H, 5.3%; *M*, 262).

7,7′-*Bis*-(1,4-*dimethyl*-6-*phenyl*-1,2,3,4-*tetrahydro*-1,4-*diazepinyl*) (VI).—This *diazepine*, which precipitated from the electrolysis solution, had m.p. 156°, $\nu_{max.}$ (Nujol) 1 638s and 1 591s cm^{-1}, τ ($CDCl_3$) 2.6—2.9 (10 H, m), 4.07 (2 H, s), 5.85 (2 H, s), and 7.38 (s), 7.58 (s), and 7.3—7.6 (m) (20 H) (Found: C, 77.2; H, 8.85; N, 13.95%; *m/e*, 201.139. $C_{26}H_{34}N_4$ requires C, 77.55; H, 8.45; N, 13.95%; *M*/2, 201.142).

RESULTS

Polarography.—The 1,4-dibenzyl-6-phenyl- (Ia), 1,4-dimethyl-6-phenyl- (Ib), and 1,4,6-triphenyl- (Ic) dihydrodiazepinium cations, in DMF containing 0.05M-TPAP at room temperature, all displayed single reduction waves in the potential region −0.3 to −2.3 V [*versus* aqueous Ag–AgCl–KCl (saturated)]. The limiting currents varied linearly with the depolariser concentrations (between 10^{-4} and 10^{-3} mol dm^{-3}), and with the square root of the height of the mercury column, thereby fitting the criteria for diffusion control.

In Table 1 are listed the half-wave potentials ($E_{\frac{1}{2}}$), the slopes of the plots of log $[(i_{lim} - i)/i]$ against potential, the limiting currents normalised with respect to concentration (i_{lim}), the diffusion current constant (I_D) (calculated from the capillary characteristics), and the diffusion coefficients (D), which were calculated assuming the transfer of one electron per molecule. This is reasonable because of their agreement with coulometric measurements described below, and because the present results are comparable with those previously obtained with 5,7-diphenyl-2,3-dihydro-1,4-diazepinium perchlorate (VII) at the same capillary,[4] which are also included in Table 1.

TABLE 1

Polarographic reduction of dihydrodiazepinium cations

Cation	$E_{\frac{1}{2}}$/V *	Slope/mV	i_{lim}/μA dm^3 mol^{-1}	I_D	10^6 D/cm^2 s^{-1}
(Ia)	−1.262	38 †	2 057	1.67	5.6
(Ib)	−1.287	40 †	2 790	2.24	7.5
(Ic)	−0.900	38 †	1 950	1.56	4.8
(VII)	−1.231	52.5	2 320	1.87	7.0

* *Versus* aqueous Ag–AgCl–KCl (saturated). † Affected by maxima; may be artificially low.

Cyclic Voltammetry.—Each of the cations (Ia—c) showed similar traces at sweep speeds of up to 600 mV s^{-1} in the potential range +0.9 to −2.5 V in DMF containing 0.05M-TPAP at a microplatinum electrode (Figures 1 and 2). A

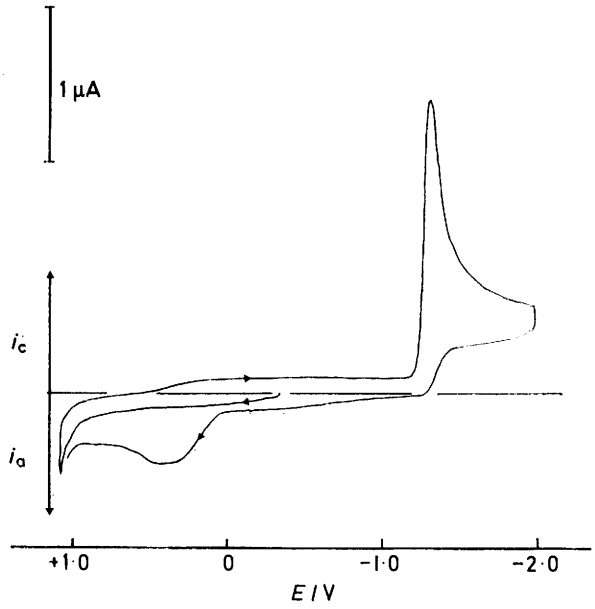


FIGURE 1 1,4-Dibenzyl-6-phenyl-2,3-dihydro-1,4-diazepinium perchlorate (Ia): 2.16 mol dm^{-3} in DMF containing 0.05 mol dm^{-3} TPAP. Cyclic voltammogram at Pt using 200 mV s^{-1} scan rate, *versus* aqueous Ag–AgCl–Cl^- reference: uncorrected for *i–R* drop. Initial sweep in anodic direction

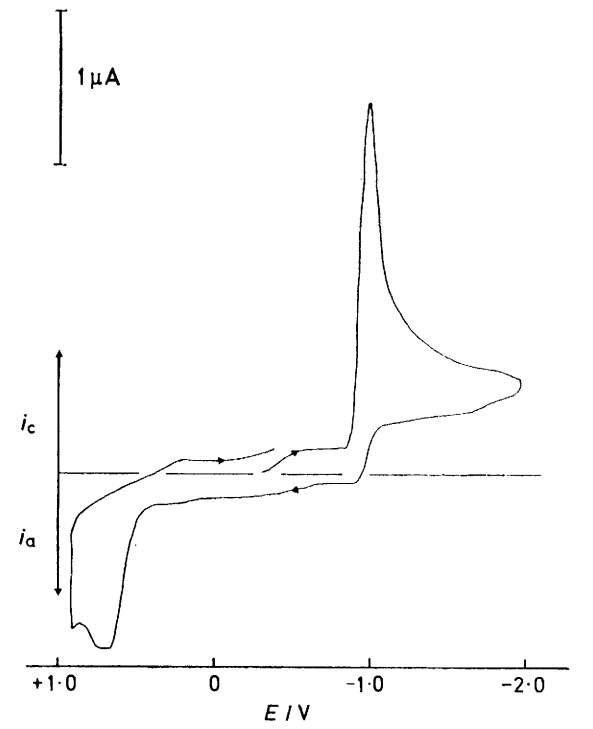


FIGURE 2 1,4,6-Triphenyl-2,3-dihydro-1,4-diazepinium perchlorate (Ic): 3.30 mol dm^{-3} in DMF containing 0.05 mol dm^{-3} TPAP. Cyclic voltammogram at Pt using 400 mV s^{-1} scan rate, *versus* aqueous Ag–AgCl–Cl^- reference; uncorrected for *i–R* drop. Initial sweep in cathodic direction

single totally irreversible reduction wave at *ca.* −1.0 V was observed, associated with a subsequent irreversible oxidation wave in the region of *ca.* +0.5 V. The peak currents I_{pc} of the reductions varied linearly with depolariser concentration in the range 10^{-3}—10^{-2} mol dm^{-3}. The oxidation currents were broader and weaker. This, and the great difference in potential between the waves, suggests that the oxidation refers to a species produced by a chemical reaction of the initially formed product.

Data from cyclic voltammetry are detailed in Table 2, namely the reduction potentials (E_{pc}) and approximate oxidation potentials (E_{ox}), the reduction currents normalised with respect to concentration, ($I_{pc}v^{-\frac{1}{2}}$) (v = scan rate), and the diffusion constants calculated from the Randles–Ševčík equation (*D*). All the scans reported in Table 2 were recorded at 400 mV s^{-1} and started at −0.3 V [*versus* aqueous Ag–AgCl–KCl (saturated)]. Diffusion constants were again calculated assuming one-electron transfer per molecule. Concentrations were in the range 2×10^{-3}–7×10^{-3} mol dm^{-3}. For comparison, data from the reversible one-electron reduction of the 5,7-diphenyl substituted cation (VII) are also included in Table 2.

TABLE 2

Cyclic voltammetry of dihydrodiazepinium cations

Cation	E_{pc}/V	E_{ox}/V	I_{pc}/μA dm^3 mol^{-1}	$I_{pc}v^{-\frac{1}{2}}$/μA dm^3 mol^{-1} $V^{-\frac{1}{2}}$ $s^{\frac{1}{2}}$	10^6 D/cm^2 s^{-1}
(Ia)	−1.29	+0.48	1 022	1 610	8.8
(Ic)	−0.99	+0.70	881	1 395	6.0
(VII)	−1.19		792	1 250	5.7

Cation (Ic) showed a weak peak at −1.7 V, which may be due to adsorption.

The data in Table 2 refer to one scan rate only, but only minor changes in the current function were introduced by varying the scan rate from 30 to 600 mV s^{-1}, and no change in the shape of the trace was observed, apart from a broadening, attributed to convection, at the slowest speeds.

The irreversibility of the reduction suggests that the chemical steps which follow the initial reduction are very fast.

Coulometry.—Similar results were obtained at both mercury pool and platinum basket electrodes with stirred solutions in DMF containing 0.05M-TPAP at 20°. Electrolyses were performed at potentials on the plateaux of the reduction waves, typically between −1.3 and −1.8 V [*versus* aqueous Ag–AgCl–KCl (saturated)]. Initial current densities at mercury were in the range 2.5—5 mA cm^{-2}, and at platinum in the range 8—14 mA cm^{-2}. In all the electrolyses the cations consumed 1 F mol^{-1}.

Monitoring of Electrolyses.—Electrolyses were monitored by cyclic voltammetry and by u.v. spectroscopy. The former was carried out for cation (Ia) by suspending a platinum microelectrode in the catholyte. The electrolysis current (at a mercury pool cathode) was interrupted while sampling was done. The secondary and reference electrodes were the same ones used for the electrolyses. The initial dihydrodiazepinium salt concentration was 0.15 mol dm^{-3}. Loss of the cation reduction wave was found to be linear with respect to the number of coulombs passed, total loss occurring after the passage of 1 F mol^{-1}. The slope of the graph of current *versus* dihydrodiazepinium ion concentration was 910 μA mol^{-1}. This may be compared with the value of 1 022 μA mol^{-1} obtained at the same electrode and at the same sweep rate, but in the much more dilute con-

centration of cyclic voltammetry (see Table 2). The similarity of these values suggests that similar processes take place in both dilute and concentrated solutions. At the end of the electrolysis an irreversible oxidation wave at +0.6 V was present. It was less intense than the initial dihydrodiazepinium cation reduction wave, and was associated with a subsequent reduction wave, which was very broad and weak, at *ca.* −1.3 V. If the scan was extended to −2.7 V a new series of waves appeared, which did not interfere with the other waves, and which were presumably due to a second reduction product. There was a double wave at −2.2 and −2.4 V. The first of these waves appeared to be partly reversible and clipping the scan between the waves, at −2.3 V, restored much of the reversible nature of this first wave. This double peak at quite strongly negative conditions was subsequently shown to be characteristic of one of the isolated reaction products, while the irreversible oxidation wave at +0.6 V was shown to be characteristic of another of the isolated reduction products.

Reductions of cations (Ia—c) were monitored by u.v. spectroscopy. For this purpose samples were withdrawn by pipette from the electrolysis cell without interruption of the current and were diluted with ethanol to the requisite concentration. Spectra were recorded against a reference of ethanol–DMF in the appropriate proportions. A linear loss of absorption due to the dihydrodiazepinium cation and a concomitant rise in absorption due to the products, with good isosbestic points, were observed. Both changes in absorption were linear with the number of coulombs consumed in the electrolyses and total loss of absorption due to the dihydrodiazepinium cation occurred after passage of 1 F mol^{-1}. The spectra of the final product solutions after electrolysis closely resembled those of the isolated products. In the case of (Ia) there was loss of absorption at 252.5 and 375 nm (ε 15 200 and 13 705) and rise of a broad absorption at 300 nm. Clean isosbestic points at 276 and 334 nm were obtained, despite the formation during the electrolysis of an insoluble precipitate which was also insoluble in the solution diluted with ethanol for u.v. spectroscopy. With (Ib) there was loss of absorption at 253.5 and 379 nm (ε 11 600 and 11 100) with increase of a broad absorption at 296 nm. In this case also formation of insoluble material did not interfere with clean isosbestic points, at 272 and 335 nm. For (Ic) there was a loss of absorption at 408 nm (ε 24 140) and rise of a broad peak at 305—312 nm with an isosbestic point at 353 nm.

Identification of the Isolated Products.—The identity of products (IVa and b) and (V) rest ultimately upon *X*-ray analyses.[5,7] Spectroscopic evidence, especially n.m.r. spectra, concur. Thus, in their ^{1}H n.m.r., both (IVa and b) show, in addition to aryl and methylene signals, two singlets due, respectively, to the 5- and 7-hydrogen atoms. In the ^{13}C n.m.r. spectra the complexity of the sp^2 carbon portions of the spectra prevented reasoned assignment of the signals in this region, save for signals at δ 120.26 (s) [(IVa)] and 117.58 (s) [(IVb)], which are assigned to C(6) of the diazepine rings. (All values are expressed as p.p.m. downfield from Me_4Si; spectra were recorded in $CDCl_3$.) Other signals were as follows: (IVa), δ 47.67 (t) and 49.76 (t) [C(2,3)], 59.01 (t) and 62.12 (t) (PhCH_2), and 65.90 (d) [C(7)]; (IVb), δ 46.89 (t) and 47.06 (t) [C(2,3)], 56.81 (t) and 62.24 (t) (PhCH_2), and 61.48 (d) [C(7)]. There is a notable difference in the shifts shown by the carbon atoms which link the two seven-membered rings in the *meso* and racemic isomers. Signals for sp^3 atoms of (V) appear at δ 50.30 (t) and 50.49 (t) (NCH_2CH_2N), 57.19 (t) and 57.31 (t) (PhCH_2), and 84.39 (d) and 92.76 (d) (1 : 1, NCN). The appearance of two signals representing the 2-imidazolidinyl carbon atoms confirms the *cis–trans*-isomerism of the butadiene moiety. The structure of product (VI) is inferred from the similarities of its ^{1}H n.m.r. spectrum with those of (IV).

Cyclic Voltammetry Experiments on Products (IV) *and* (V).—A saturated solution of compound (IVa) (1.43 × 10^{-3} mol dm^{-3}) in DMF containing 0.05M-TPAP, at a platinum microelectrode and at 200 mV s^{-1}, showed an irreversible oxidation wave at +0.35 V [*versus* aqueous Ag–AgCl–KCl (saturated)], associated with a subsequent irreversible sharp reduction wave at −1.34 V, of a similar current intensity (Figure 3). I_{ox}, normalised, was 1 260 μA dm^3 mol^{-1},

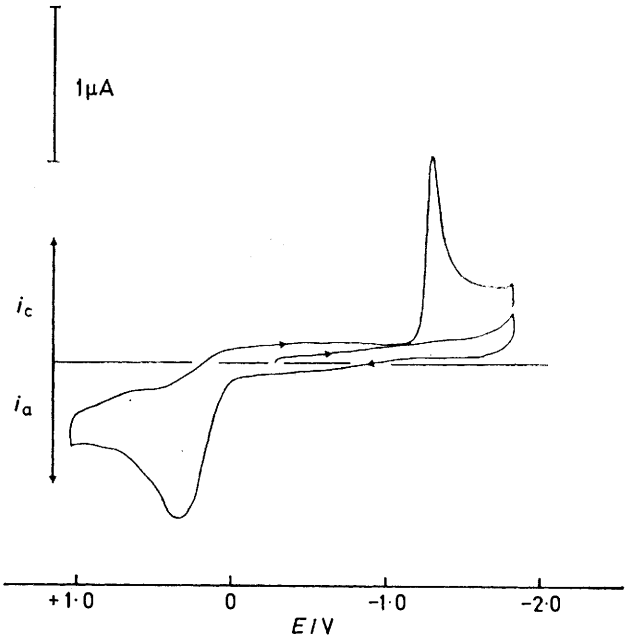


FIGURE 3 *meso*-7,7′-Bis-(1,4-dibenzyl-6-phenyl-1,2,3,4-tetrahydro-1,4-diazepinyl) (IVa): 1.43 × 10^{-3} mol dm^{-3} (saturated) in DMF containing 0.05 mol dm^{-3} TPAP. Cyclic voltammogram at Pt using 200 mV s^{-1}, *versus* aqueous Ag–AgCl–Cl$^-$ reference; uncorrected for *i*–*R* drop. Initial sweep in cathodic direction

giving values for the diffusion coefficient (*D*) of 1.13 × 10^{-5} cm^2 s^{-1}, assuming one-electron transfer (*N* 1) or of 2.8 × 10^{-6} cm^2 s^{-1} assuming two-electron transfer (*N* 2). For the reduction wave $I_{norm.}$ = 1 050 μA dm^3 mol^{-1}, *D* = 7.15 × 10^{-6} cm^2 s^{-1} (*N* 1) or 1.96 × 10^{-6} cm^2 s^{-1} (*N* 2). Because of the large size of this molecule (*M* = 706), and especially since it might react with one electron in each tetrahydrodiazepine moiety, the diffusion coefficients obtained assuming two-electron transfer are reasonable. Compound (IVb) behaved very similarly.

Compound (V), in DMF containing 0.05M-TPAP, at platinum, and at 400 mV s^{-1}, showed no oxidation wave out to +1.0 V and no reduction wave until −2.1 V, whereafter a double peak apeared at −2.14 and −2.30 V [*versus* aqueous Ag–AgCl–KCl (saturated)] [Figure 4(a)]. If the scan was clipped at −2.25 V partial reversibility appeared in the first peak.

A very similar trace was obtained, under identical conditions, with 1,4-diphenylbuta-1,3-diene (3.44 × 10^{-3} mol

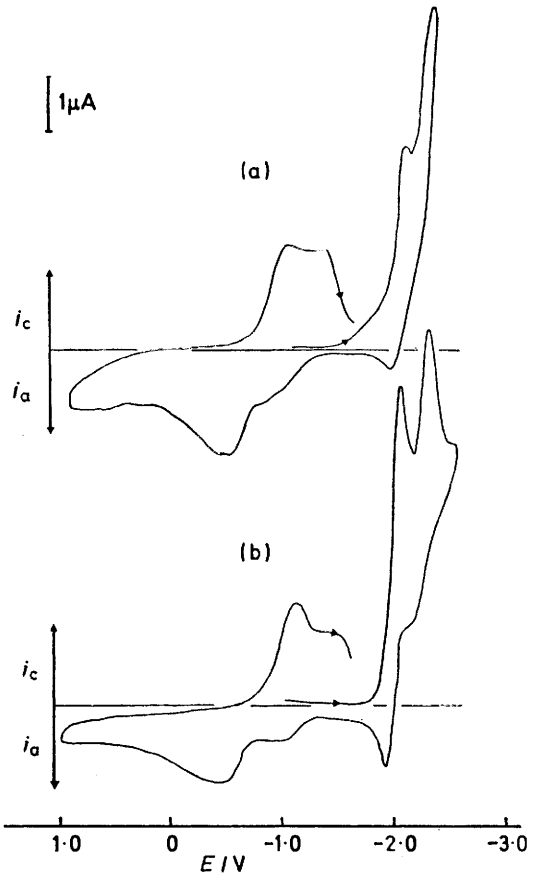


FIGURE 4 (a) 1,4-Bis-(*NN'*-dibenzyl-2-imidazolidinyl)-1,4-diphenylbuta-1,3-diene (V): 3.50×10^{-3} mol dm^{-3} in DMF containing 0.05 mol dm^{-3} TPAP. Cyclic voltammogram at Pt using 400 mV s^{-1}, *versus* aqueous Ag–AgCl–Cl$^-$ reference; uncorrected for *i–R* drop. (b) 1,4-Diphenylbutadiene: 3.44×10^{-3} mol dm^{-3} in DMF containing 0.05 mol dm^{-3} TPAP. Cyclic voltammogram at Pt using 400 mV s^{-1}, *versus* aqueous Ag–AgCl–Cl$^-$ reference; uncorrected for *i–R* drop. Initial sweep in cathodic direction

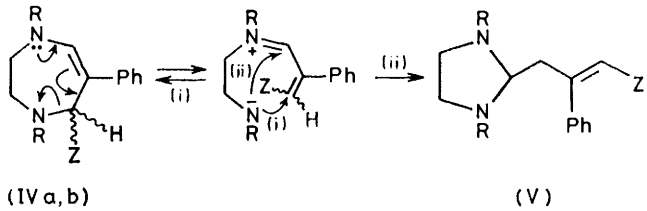
dm^{-3}) [Figure 4(b)]. Twin peaks occurred at −2.02 and −2.30 V, and partial reversibility was shown by a return peak at −1.85 V. This reversibility was improved by clipping the scan at −2.2 V, where I_{pc}/I_{pa} becomes close to 1. For the first peak, I_{pc}, normalised, is 1 453 μA, giving $D = 1.9 \times 10^{-5}$ cm^2 s^{-1} (*N* 1) or 4.7×10^{-6} cm^2 s^{-1} (*N* 2). These values suggest a two-electron transfer.

DISCUSSION

The electrochemical data indicate that the dihydrodiazepinium cations (I) undergo one-electron reductions which are followed by rapid chemical reactions to give species which are oxidised at small positive potentials. Coulometry also supports the consumption of one electron per molecule. Reduction of cations (I) proceeds more readily in the sequence (Id) < (Ie) < (Ib) < (Ia) < (Ic). As previously found for cations (Id and e),[2] [but not (VII)],[4] cations (Ia—c) provide radicals which dimerise providing, in the case of (Ia, b), isolable bis(tetrahydrodiazepinyls).

Rearrangement Reactions of Products.—The *meso*-isomer (IVa) separated out as a solid from the electrolysis solution in *ca.* 35% yield. The racemic isomer (IVb) and the butadiene (V) are more soluble in organic solvents but are obtained in subsequent work-up. From studies of the isolated products it appears that (IVa) may be converted into (IVb), which in turn may be converted into (V). The conversion of the *meso*-product (IVa) into the racemate (IVb) is effected by heating the former in dimethylformamide at 100°. Solution of the racemate in a cold mixture of chloroform and ethanol provides, as the solvents evaporate, a quantitative yield of the butadiene (V). The mixture of solvents is necessary; (IVb) remains unchanged in chloroform and may be recrystallised from hot ethanol with only a trace of rearrangement product being formed.

Presumably both of these rearrangements, (IVa) to (IVb), and (IVb) to (V), must in the first place involve a retro-Michael reaction (see Scheme 1). Attack of the



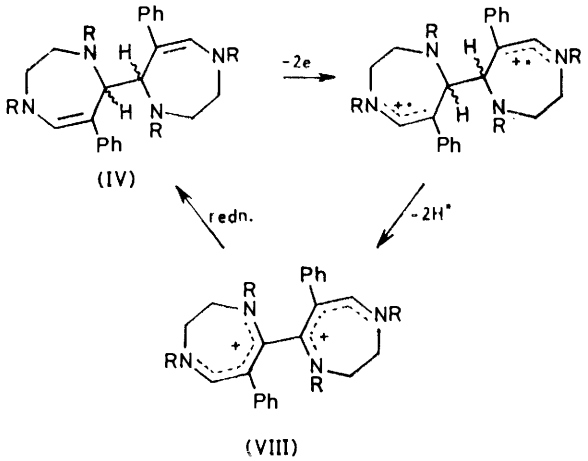
SCHEME 1 Z = other half of molecule

resultant nitrogen anion at the carbon atom it has left, but in an opposite steric sense, provides the alternative stereoisomer (IVb). Alternatively attack of the nitrogen atom at the iminium group leads to formation of the diimidazolidinyldiene. The role of the mixed solvent may be for the chloroform, or hydrogen chloride contained therein, to promote ring-opening by protonating a nitrogen atom, and for the ethanol to promote formation of the intermediate by solvating it. The diene is not reconverted into the bisdiazepinyls but there is evidence from n.m.r. spectra that a solution in chloroform is very slowly converted into a geometric isomer, which seems most likely to be the *trans–trans*-isomer. This conversion is promoted by addition of traces of acid.

Acid Hydrolysis of Reduction Products.—Solutions of the three reduction products (IVa and b) and (V) in DMF all give deep red solutions from which, after a few minutes, precipitates separated, which were shown to be *NN'*-dibenzylethylenediamine dihydrochloride, by comparing them with an authentic sample made from the free amine in DMF and two molar equivalents of concentrated hydrochloric acid. Work-up of the solution from (V) also provided 2,5-diphenylhexa-2,4-diene-1,6-dial. These products obviously arose from hydrolytic cleavage of the heterocycles.

Cyclic Voltammetry Experiments on Products (IV) *and* (V).—Not surprisingly, because of their different structures, products (IV) and (V) showed very different electrochemical behaviour. In each case results indicate two-electron transfer, which is entirely reasonable in view of the two identical halves in each of the molecules.

In the case of (IV) an irreversible oxidation wave is associated with a subsequent irreversible sharp reduction wave. The similarity of this reduction wave to that observed for the initial dihydrodiazepinium cation (Figures 1 and 3) suggests that oxidation of the tetrahydrodiazepine may well be leading to a bis(dihydrodiazepinium) cation (VIII) (Scheme 2), which may in turn be reduced again to (IV).



SCHEME 2 R = $PhCH_2$

In the case of (V) there is no oxidation wave but reduction occurs showing a double peak. The close similarity of the data obtained to that obtained from 1,4-diphenylbuta-1,3-diene (see Results section) indicates that the reduction may involve the butadiene portion of the molecules, since this feature is common to both. The reversibility of the initial reduction step indicates the formation of a stable radical anion, and shows that fast reductive dimerisation, a common behaviour of conjugated molecules, does not follow, perhaps inhibited by steric crowding. Similarly fast protonation of the radical anion is excluded, but the dianion is not stable and formation of a 2-monoene may occur *via* this entity.

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