Electrochemical Reduction of the 5,7-Diphenyl-2,3-dihydro-1,4-diazepinium Cation

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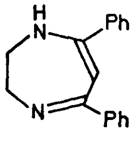
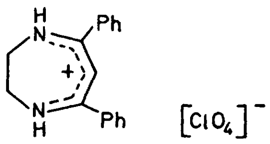
The 5,7-diphenyl-2,3-dihydro-1,4-diazepinium cation (II), dissolved in dimethylformamide, is reduced in two steps. The first wave, at −1.23 V with respect to an aqueous Ag–AgCl–KCl (saturated) reference, provides a radical which disproportionates to give the corresponding dihydrodiazepine base (I) and a tetrahydrodiazepine (IV). The second wave is at −2.00 V and produces the anion (IV). The reduction was studied by polarography, cyclic voltammetry, and preparative electrochemistry. The dihydrodiazepine base is electroinactive to −2.1 V, whereat it displays an apparently two-electron reduction wave.

THE 2,3-dihydro-1,4-diazepines, *e.g.* (I), and their related cations, *e.g.* (II), are examples, respectively, of very stable vinamidines and vinamidinium salts.[1] The latter are of interest as electron-rich cations; the delocalised vinamidinium system has a resonance stabilisation energy approaching 80 kJ mol^{-1}.[2] Some polarographic studies of these salts in aqueous solution have been reported,[3] and other electrochemical studies have been undertaken.[4]



(I)



(II)

In the present work a systematic investigation, involving polarography, cyclic voltammetry, and preparative electrochemistry of the electrolytic reduction of the base (I) and especially the salt (II) is reported.

EXPERIMENTAL

Materials.—The dihydrodiazepine and its perchlorate were prepared as described.[5]

Dimethylformamide (DMF) was spectroscopic grade, used without further purification. Dichloromethane was purified by distillation from calcium hydride. This procedure provided a solvent which was electroinactive from +1.0 to −1.7 V with 0.1 mol dm^{-3} tetra-n-propylammonium perchlorate (TPAP).

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.—Polarographic and cyclic voltammetric experiments were performed using an undivided cell (Amel; 494 Universal cell; 25 cm^3) with a three electrode system. The counter electrode was a platinum wire and the reference electrode an aqueous silver–silver chloride system separated from the cell solution by a salt bridge with low porosity sinter. Polarographic measurements were made using a capillary with natural drop time in the range 4—12 s. The height of the mercury column could be varied from 40 to 80 cm. At a standard height of 55 cm the mercury flow rate was 0.80 mg s^{-1}. Linear and cyclic scan experiments were made at a hanging mercury drop formed by microsyringe (Metrohm A1G E410), and at a platinum microelectrode formed by sealing a platinum wire into a glass tube and grinding and polishing to a flat surface. The measured mean cross section of the latter electrode was 1.97×10^{-3} cm^2. When this electrode was tested by reducing benzophenone in DMF containing 0.5 mol dm^3 TPAP the value for the diffusion coefficient was within 10% of the literature value (0.79×10^{-5} cm^2 s^{-1}).[6] It was therefore assumed that the electrochemical area was approximately the same as the geometric area in studies of the dihydrodiazepines.

The majority of polarographic and linear scan experiments used a potentiostat–sweep generator system constructed in this laboratory and based on solid state operational amplifiers in standard configurations. Data were recorded on an *x–y* recorder (Hewlett-Packard; Moseley 2D-4) equipped with a drive motor for *y–t* traces. Potential differences were measured using a digital voltmeter (Keithley, 190). High-speed scans, up to 100 V s^{-1}, were performed on a ' modular polarograph ' (Brüker, E 310) equipped for cyclic scanning. The cathode for such experiments was a dropping mercury electrode. The forced drop time was synchronised to the triggering of each scan and the current–voltage trace was recorded on sequential drops using a boxcar technique.

For all microscale experiments the electrolytic solution was 0.05 mol dm^{-3} TPAP in DMF. Solutions were degassed by purging with oxygen-free nitrogen which had been pretreated by passing through an aqueous vanadous chloride bubbler, then dried by passing through two towers containing activated molecular sieves (4A and 3A), and finally presaturated with dry electrolysis solvent.

Controlled-potential electrolyses were performed in a standard three compartment cell, using a high current potentiostat (Hermes Controls Ltd., SAS 50V 100) in a three-electrode mode. The surface of the mercury-pool cathode (area 10 cm^2) was stirred continuously by magnetic stirrer. An alternative cathode, consisting of a platinum-mesh cylinder with height and diameter of 2 cm gave similar results. Nitrogen was passed throughout the electrolysis and the cell was cooled in a water-bath. The quantity of electricity consumed was measured using an integrator (Hermes Controls Ltd., Int-2) and the current was monitored by *y–t* recorder (Bryans/Southern, 28000).

Some electrolyses were monitored by cyclic voltammetry. In these cases the main electrolysis potential was interrupted while scans were made at sweep rates of up to 500 mV s^{-1}, using a platinum microelectrode suspended in the catholyte, and the counter and reference electrodes already in place in the cell. Other electrolyses were followed by u.v. spectrometry. In these cases samples of catholyte were taken during electrolysis, without interruption of current. The samples were subsequently diluted to the required concentration with ethanol and spectra were recorded against a reference of ethanol–DMF in the same proportions.

When the electrolysis was completed the catholyte was worked up either by extraction with ether and aqueous washings or by addition of warm perchloric acid (60%) followed by washing with ether.

RESULTS

Polarography.—Reduction of the cation (II) showed two waves, with $E_{\frac{1}{2}}$ values of -1.23 and -2.00 V *versus* aqueous Ag–AgCl–KCl (saturated). The limiting currents of both waves varied linearly with depolariser concentration (in the range 5×10^{-3}—5×10^{-4} mol dm^{-3}) and with the square root of the height of the mercury column, and therefore fitted the criteria for diffusion control. The ratio of the limiting currents was 1.09, suggesting that the same number of electrons was involved in each step.

The first wave gave a linear plot of E *versus* log $(i_{\text{lim.}}\text{-}i)/i$ with a slope of 53 mV. The second wave gave a poorer line; the best estimate of the slope was 76 mV.

Insertion of the capillary characteristic into the Ilkovič equation provided a diffusion current constant of 1.935, from which a value of 0.75×10^{-5} cm^2 s^{-1} is obtained for the diffusion coefficient of (II), which is similar to the value for benzophenone.[6]

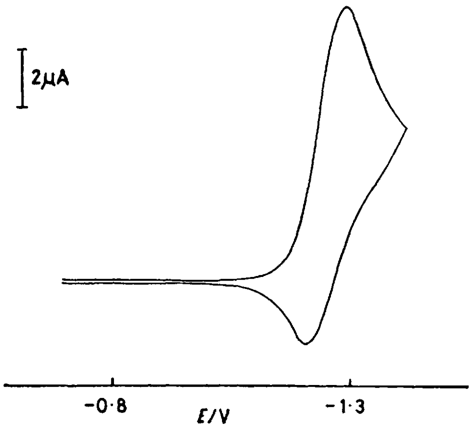


FIGURE 1 2.62×10^{-3} mol dm^{-3} solution of cation (II) in DMF containing 0.05 mol dm^{-3} TPAP. Potential scan at 50 mV s^{-1} at a hanging mercury drop electrode *versus* Ag–AgCl–Cl$^-$ (aqueous) reference electrode. Uncorrected for *iR* drop or charging current; cathodic followed by anodic sweep

Cyclic Voltammetry.—In experiments using a hanging mercury drop cathode, quasi-reversible behaviour was observed when the potential was scanned in the range -0.7 to -1.5 V at sweep rates greater than 50 mV s^{-1} (Figure 1), giving a standard potential for the couple of -1.24 V. Figure 2 shows a similar scan at 100 V s^{-1} where the reversibility is complete. On extending the scan to more cathodic potentials a persistent weak maximum was observed at -1.73 V (which may be an adsorption peak), and a second main wave, somewhat higher than the first (*ca.* 1.5 : 1), occurred at -2.13 V (Figure 3).

In quantitative experiments at a microplatinum electrode, similarly shaped voltammograms were obtained (Figure 4).

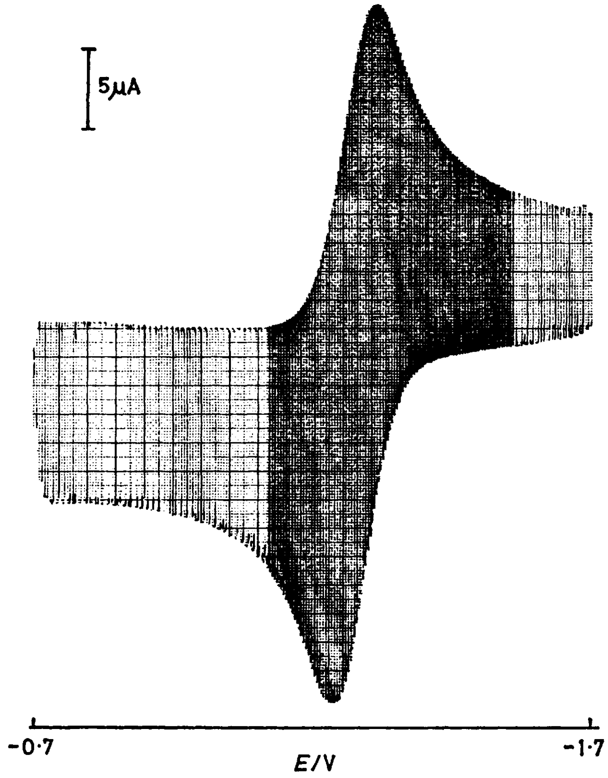


FIGURE 2 0.71×10^{-3} mol dm^{-3} solution of cation (II) in DMF containing 0.05 mol dm^{-3} TPAP. Potential scan at 100 V s^{-1} at a hanging mercury drop electrode *versus* aqueous calomel reference electrode using Brüker boxcar technique. Uncorrected for *iR* drop or charging current; cathodic followed by anodic sweep

(On occasion an irreversible cathodic wave was observed. This seemed to be due to a surface effect on the platinum cathode, since cleaning of the electrode in acetone and then DMF, followed by preliminary cycling of potential restored the reversible nature of the couple.)

Over a range of scans from 50 to 500 mV s^{-1} $(E_p)_c$ is -1.257 V and $(E_p)_a$ is -1.195 V [with respect to aqueous Ag–AgCl–KCl (saturated)] (corrected for *iR* drop), giving a value for ΔV of 62 mV, close to the value of 56 mV required for a reversible one-electron transfer. On switching the scans at -1.55 V the ratio $(i_p)_c/(i_p)_a$ was found to be within the range 1.1—1.3, and the current functions $(i/v^{\frac{1}{2}})$ for the

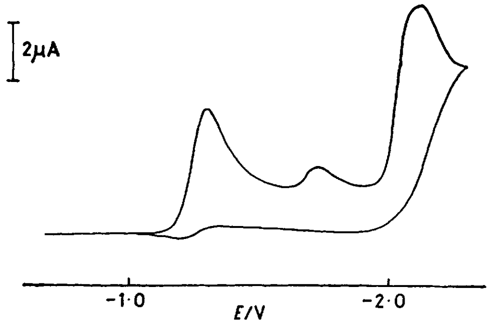


FIGURE 3 2.62×10^{-3} mol dm^{-3} solution of cation (II) in DMF containing 0.05 mol dm^{-3} TPAP. Potential scan at 100 mV s^{-1} at a hanging mercury drop electrode *versus* Ag–AgCl–Cl$^-$ (aqueous) reference electrode. Uncorrected for *iR* drop or charging current; cathodic followed by anodic sweep cathodic scans were between 4.0 × 10^{-6} and 4.09 × 10^{-6} A $s^{\frac{1}{2}}$ $V^{-\frac{1}{2}}$. Insertion of the data into the Randles–Ševčík equation leads to a value of the diffusion coefficient of the compound of 0.87 × 10^{-5} cm^2 s^{-1}.

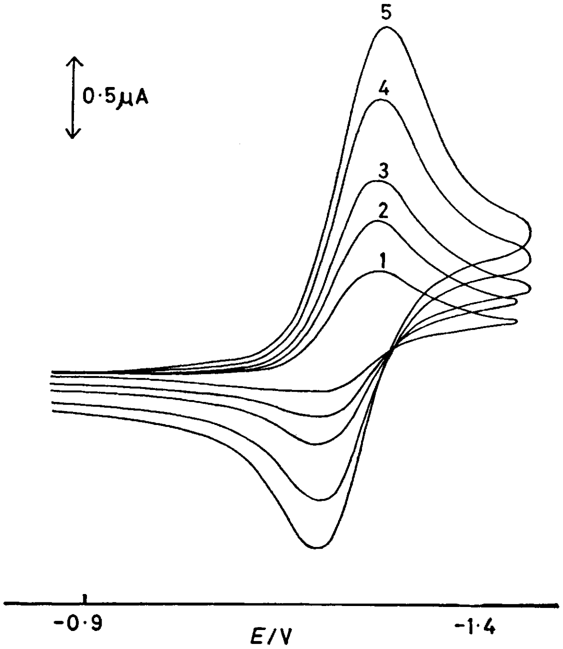


FIGURE 4 2.56 × 10^{-3} mol dm^{-3} solution of cation (II) in DMF containing 0.05 mol dm^{-3} TPAP. Potential scans at platinum microelectrode *versus* Ag–AgCl–Cl^- (aqueous) reference electrode. Uncorrected for *iR* drop or charging current; cathodic followed by anodic sweep in each case. 1, 30 mV s^{-1}; 2, 60 mV s^{-1}; 3, 100 mV s^{-1}; 4, 200 mV s^{-1}; 5, 300 mV s^{-1}

Preparative Electrolyses and Coulometry.—Controlled potential electrolyses (c.p.e.) were performed in 0.05 mol dm^{-3} TPAP in DMF, and in 0.1 mol dm^{-3} TPAP in dichloromethane, with initial concentrations of dihydrodiazepinium salt of 5.7—6.2 × 10^{-2} mol dm^{-3}. Electrolyses were carried out at the potential of the first wave, −1.5 V, at a mercury-pool cathode. In the case of solutions in DMF an aqueous reference electrode was used, but since this was not suitable for solutions in anhydrous dichloromethane, in these cases a platinum wire was used as a pseudoreference.

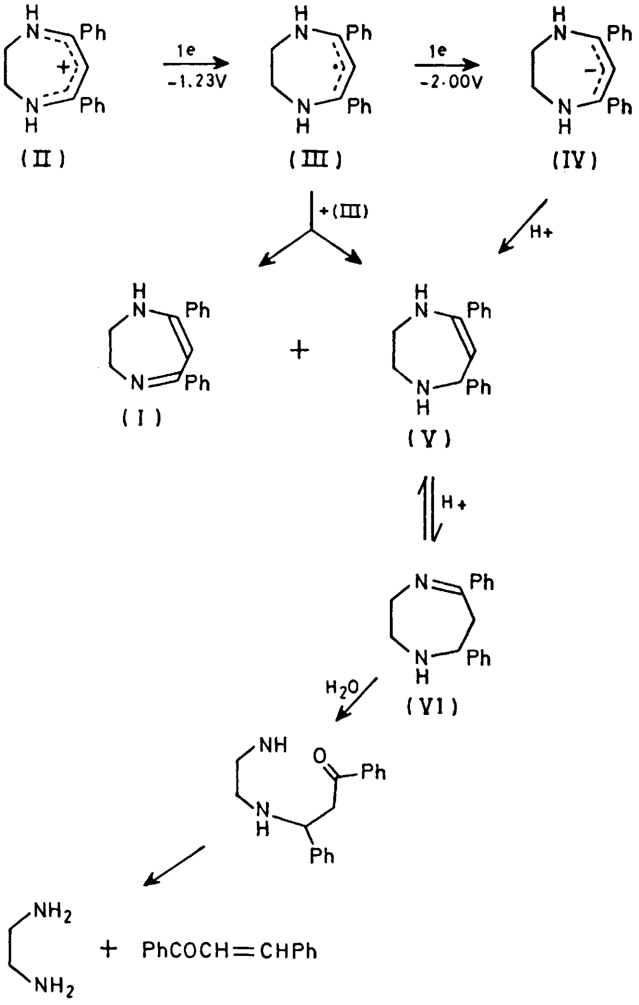
When a c.p.e. was monitored by cyclic voltammetry it showed a linear fall in the dihydrodiazepinium ion cathodic peak $(i_p)_c$ at the microelectrode with the number of coulombs consumed at the mercury pool. The final loss of dihydrodiazepinium cation occurred at 1 F mol^{-1}, and the normalised peak current was comparable to that obtained in a microscale experiment, suggesting that the same process occurs at both concentrations and at either the mercury or platinum cathodes. No peaks attributable to intermediates were observed in the potential range +1.0 to −2.0 V during the electrolysis, although a weak cathodic peak at −2.1 V was seen in the final solution after electrolysis.

Isolation of Products.—The final electrolysis solution from the c.p.e. was extracted with ether and the resulting solution was washed with water and dried. Evaporation of the solvent left a yellow oil which, on trituration with light petroleum, provided yellow crystals of the base (I) (47%), identical with an authentic sample. If, alternatively, this final electrolysis solution was warmed with an equal volume of perchloric acid (10%) in order to convert basic products into salts, and then extracted with ether, the ethereal solution when evaporated provided an oil, which partially solidified after distillation *in vacuo* and was benzylideneacetophenone (17%). Other oily products were not characterised.

DISCUSSION

Reduction of Cation (II).—The polarographic and cyclic voltammetric data indicate that the cation (II) undergoes two successive one-electron reductions.

It seems likely that at the first wave a 1,3-diphenylallyl radical (III) will be formed which, because of the delocalisation in this species, will have considerable stability. In the controlled potential electrolyses, at the potential of the first wave a deep green colour developed in the catholyte, which died away in a few minutes when the potential was switched off; it was noticeably more stable in dichloromethane than in DMF. This coloured species is likely to be the radical (III). The consumption of 1 F mol^{-1} at the potential of the first wave suggests that the radical reacts further by disproportionation, which may take place in a number of ways, *e.g.* by direct



SCHEME

hydrogen atom transfer between two radicals (III) or by electron transfer between two radicals (III) to give the cation (II) and anion (IV), followed either by deprotonation of (II) by (IV) or by hydride transfer from (IV) to (II). This would provide the base (I), which is isolated in *ca.* 50% yield in the preparative experiments, and a tetrahydrodiazepine (V). Isolation of benzylideneacetophenone from an aqueous acidic work-up of the preparative experiment provides evidence for the formation of this tetrahydrodiazepine. Hydrolysis of its tautomer (VI), which would be expected to be formed and hydrolysed under these conditions, followed by a retro-Michael-type reaction involving loss of ethylenediamine, would result in the formation of this enone.

Further corroboration of this scheme is provided by monitoring the electronic spectrum of a c.p.e. The absorption spectra of dihydrodiazepinium salts and their related bases are almost identical. When the cation (II) was reduced the intensity of its characteristic absorption peaks at $\lambda_{max.}$ 266 and 353 nm decreased linearly with the number of coulombs used until 1 F mol^{-1} had been passed, when the absorbance was 0.59 of its initial value. Addition of dilute aqueous sodium hydroxide to either this solution or to a solution of authentic base (I) led to identical changes in spectra with the appearance of maxima at $\lambda_{max.}$ 241 and 347 nm, *via* isosbestic points at 256, 295.5, and 331 nm. Furthermore no new absorption peaks >250 nm appeared in the course of the reduction.

The product after the passage of 1 F mol^{-1} at −1.5 V was electroinactive. In a cyclic voltammetric experiment undertaken with the base (I) this species was also found to be electroinactive in the region +1.0 to −1.9 V.

At the more strongly reducing potential of the second wave at −2.0 V, the first formed radical (III) is presumably converted into the anion (IV). This reacts further irreversibly and very quickly, very probably by abstraction of a proton from the solvent or substrate to provide the tetrahydrodiazepine (V). The second peak in the cyclic voltammogram, which occurs at the corresponding potential, is almost certainly a composite one, involving not only further one-electron reduction of the radical, but also two-electron reduction of some dihydrodiazepine base (I) which has been shown to be reduced at this potential, and which may be formed either from the radical (III) by disproportionation, or by removal of a proton from the cation (II) by interaction with the anion (IV).

Reduction of Base (I).—In a cyclic voltammetric experiment the dihydrodiazepine base (I) had a single irreversible cathodic wave at −2.1 V, associated with a weak oxidation wave at +0.2 V. The normalised cathodic current was nearly twice that for the cation (II) suggesting that this is a two-electron process if the diffusion coefficients of the two species are similar. Reduction of the imine bond to give a tetrahydrodiazepine is a likely reaction path.

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