The Electrochemical Reduction of the 6-Phenyl-2,3-dihydro-1,4-diazepinium Cation and its 1-Methyl and 5-Methyl Derivatives: Formation and Some Properties of Pyrrolodiazepines

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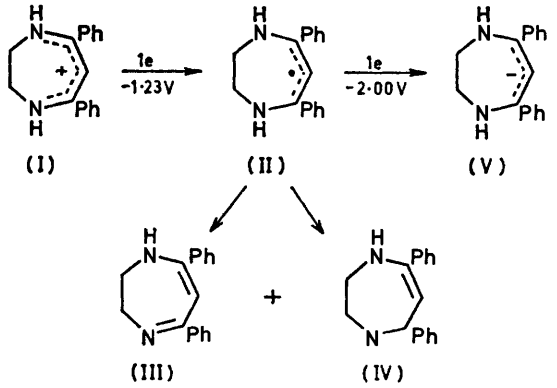
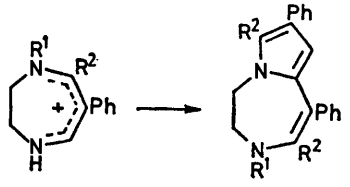
The 6-phenyl-2,3-dihydro-1,4-diazepinium cations (VIa—c), dissolved in dimethylformamide, undergo one-electron single reduction waves at −1.2 to −1.5 V. The reductions were studied by polarography, cyclic voltammetry, and preparative electrochemistry. Rapid chemical reactions follow the initial reduction and the isolated products are pyrrolodiazepines (VIIa—c). The latter compounds are reversibly protonated to provide pyrrolodihydrodiazepinium cations (IX) and appear to form dications and stable cation radicals when they are, respectively treated with triphenylmethyl perchlorate or oxidised electrochemically.

ELECTROCHEMICAL reduction of the 5,7-diphenyl-2,3-dihydro-1,4-diazepinium cation (I) proceeded in two steps, providing first a radical (II), which disproportionated to give the dihydrodiazepine base (III) and a tetrahydrodiazepine (IV), and at the second wave the anion (V).[1]



The 5,7-positions and the 6-position of the dihydrodiazepinium ring differ markedly in their properties because of the alternation of polarity along the conjugated vinamidinium chain,[2] and substituents at the different positions consequently have differing effects.[2,3] Hence it seemed desirable to compare the electrochemical



a; $R^1 = R^2 = H$
b; $R^1 = Me, R^2 = H$
c; $R^1 = H, R^2 = Me$

reduction of 6-phenyldihydrodiazepinium cations with that of the 5,7-diphenyl analogues. Not surprisingly completely different products were isolated, in high yield, for example the pyrrolodiazepine (VIIa) from the cation (VIa).[4]

EXPERIMENTAL

Materials.—The dihydrodiazepinium salt (VIa) was prepared as described,[5] and salts (VIb and c) were prepared by a similar procedure.[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.—Polarographic and cyclic voltammetric experiments were carried out in an undivided cell (Amel; 494 Universal cell) of volume 25 cm^3 with a three electrode system. The counter electrode was a platinum wire and the reference electrode was 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 span 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 (cross section 1.97×10^{-3} cm^{-2}) into a glass tube and grinding and polishing to a flat surface.

Polarographic and linear scan experiments used a potentiostat–sweep generator system constructed in this department and based on solid state operational amplifiers in standard configurations. Data were recorded on an x–y recorder (Hewlett–Packard, Mosley 2D-4) equipped with a drive motor for y–t traces. Potential differences were measured using a digital voltmeter (Keithley, 190).

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 it through an aqueous vanadous chloride bubbler and then dried by passing it through two towers containing activated molecular sieves (4A and 3A), and which was finally presaturated with dry electrolysis solvent.

Controlled potential electrolyses were carried out 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, 28 000).

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 monitored 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.

Work-up of Preparative Electrolyses.—When the electrolyses were completed, water was added to the catholytes and the products precipitated. Yields were the same using platinum or mercury cathodes. In the case of the dihydrodiazepinium salt (VIb) an alternative procedure was also used, involving ether extraction of the aqueous solution. This provided an oil from which fine golden scales were obtained on crystallisation from ethanol; addition of water to the ethanolic mother-liquors precipitated more product, the total yield of both fractions corresponding to the yield obtained by direct addition of water to the catholyte. The products obtained were as follows.

4,5-*Dihydro*-1,8-*diphenyl*-3H-*pyrrolo*[1,2-d][1,4]*diazepine* (VIIa).—This *diazepine* (92%) had m.p. 184° (decomp.), $\nu_{max.}$ (Nujol mull) 3 430 cm^{-1}, $\lambda_{max.}$ (ethanol) 258, 284, and 312 nm (ε 14 900, 10 600, and 10 700), $\lambda_{max.}$ (acidic ethanol) 321 and 401 nm (ε 8 500 and 10 000), τ(CD_2Cl_2–D_2O) 2.7 (10 H, m), 3.1 (1 H, d, *J* 1.8 Hz), 3.82 (1 H, s), 4.02 (1 H, d, *J* 1.8 Hz), 5.74 (2 H, t), and 6.48 (2 H, t), τ(CF_3CO_2H) 2.41 br (1 H, s), 2.52 (10 H, m), 3.28 (1 H, s), 4.80 (2 H, s), 5.77 (2 H, m), and 6.08 (2 H, m). It is poorly soluble and rather unstable in many organic solvents, but dissolves in dichloromethane to provide a stable solution (Found: M^+, 286.147. $C_{20}H_{18}N_2$ requires *M*, 286.148).

4,5-*Dihydro*-3-*methyl*-1,8-*diphenyl*-3H-*pyrrolo*[1,2-d]-[1,4]*diazepine* (VIIb).—This golden brown *diazepine* (55%) had m.p. 146° (decomp.), $\lambda_{max.}$ (ethanol) 256, 287, and 319 nm (ε 21 500, 14 800, and 17 000), $\lambda_{max.}$ (acidic ethanol) 324 and 408 nm (ε 12 100 and 16 100), τ($CDCl_3$) 2.5—2.82 (10 H, m), 3.15 (1 H, d, *J* 2.0 Hz), 4.00 (1 H, d, *J* 2.0 Hz), 4.10 (1 H, s), 5.79 (2 H, t, *J* 3.7 Hz), 6.57 (2 H, t, *J* 3.7 Hz), and 7.09 (3 H, s), τ(CF_3CO_2H) 2.39 (1 H, s), 2.58 (10 H, m), 3.33 (1 H, s), 4.82 (2 H, s), 5.78 (2 H, m), 6.05 (2 H, m), and 6.51 (3 H, s) (Found: M^+, 300.162. $C_{21}H_{20}N_2$ requires *M*, 300.164).

4,5-*Dihydro*-2,7-*dimethyl*-1,8-*diphenyl*-3H-*pyrrolo*[1,2-d]-[1,4]*diazepine* (VIIc).—This yellow *diazepine* (27%) was readily soluble but unstable in many organic solvents and had m.p. 130° (decomp.), $\nu_{max.}$ (Nujol) 3 430 cm^{-1}, $\lambda_{max.}$ (ethanol) 252 and 309 nm (ε 15 600 and 12 600), $\lambda_{max.}$ (acidic ethanol) 318 and 392 nm (ε 10 600 and 15 500), τ($CDCl_3$) 2.70, 2.76 (10 H, 2s), 4.79 (1 H, s), 5.80 (2 H, t), 6.4br (3 H), 7.68 (3 H, s), and 8.41 (3 H, s) (Found: M^+, 314.177. $C_{22}H_{22}N_2$ requires *M*, 314.180).

4,5-*Dihydro*-1,8-*diphenyl*-7H-*pyrrolo*[1,2-d][1,4]*diazepinium Perchlorate* (IX).—A solution of the diazepine (VIIa) in trifluoroacetic acid was added to excess perchloric acid (60—70%), whereat the green diazepinium perchlorate crystallised out and was recrystallised from acetone plus one drop of perchloric acid.

RESULTS

Polarography.—In potential scans at room temperature in DMF containing TPAP from −0.3 to −2.3 V (*versus* aqueous Ag–AgCl) the three dihydrodiazepinium cations (VIa—c) each displayed single reduction waves at values between −1.2 and −1.5 V (see Table 1). All three limiting currents varied linearly with both 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.

TABLE 1

Polarographic reduction of dihydrodiazepinium cations

Cation	$E_{\frac{1}{2}}$/V *	Slope mV	$i_{lim.}$/μA‡	D/cm^2 s^{-1}
(VIa)	−1.373	56.0 †	2 070	6.0×10^{-6}
(VIb)	−1.311	44.0 †	2 590	9.3×10^{-6}
(VIc)	−1.475	48.5 †	1 790	4.5×10^{-6}
(I)	−1.231	52.5	2 320	7.0×10^{-6}

[(VIb) also displays the beginning of a second wave at −2.4 V]

* *versus* aqueous Ag–AgCl. † Maxima make evaluation difficult. ‡ Normalised with respect to concentration.

The columns of Table 1 list, respectively, the half-wave potentials, the slopes of the plots of log $[(i_{lim.} - i)/i]$ against potential, the limiting currents normalised with respect to concentration, and the diffusion coefficients, which were calculated assuming the transfer of one electron per molecule. This assumption is reasonable because of coulometric measurements described below, and since the results are comparable with those previously obtained with cation (I),[1] which are also included in Table 1. Cation (I) undergoes a reversible one-electron reduction and is of similar size to the cations (VI). Data for the cations (VI) were recorded at *ca.* 3×10^{-4} mol dm^{-3}, the low concentration being necessary to minimise interference from persistent maxima, which increases with concentration, but at 10^{-3} mol dm^{-3} for (I) since this compound does not suffer from the interference of polarographic maxima, even at higher concentrations. These maxima caused some difficulty in evaluating the slopes for cations (VI).

Cyclic Voltammetry.—Each of the 6-phenyl substituted cations (VIa—c) showed similar traces at sweep speeds up to 600 mV s^{-1} in the potential range +0.9 to −2.5 V in DMF containing TPAP at a microplatinum electrode (Figure 1). A single totally irreversible reduction wave occurred in the region −1.0 to −1.4 V, associated with a subsequent irreversible oxidation wave in the region +0.4 to +0.7 V; the latter wave was dependent upon a previous reduction having taken place. 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 reduction 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 coefficients calculated from the Randles–Ševčík

equation. All the scans reported in Table 2 were recorded at 400 mV s^{-1} and started at −0.3 V (*versus* aqueous Ag–AgCl). Diffusion coefficients were again calculated assuming one-electron transfer per molecule. The good agreement between these values and those reported in Table 1 may be noted.

All concentrations were in the range 3×10^{-3}—7×10^{-3} mol dm^{-3}. For comparison, data from the reversible one-electron reduction of the 5,7-diphenyl substituted cation (I) at the same electrode is also included in Table 2.

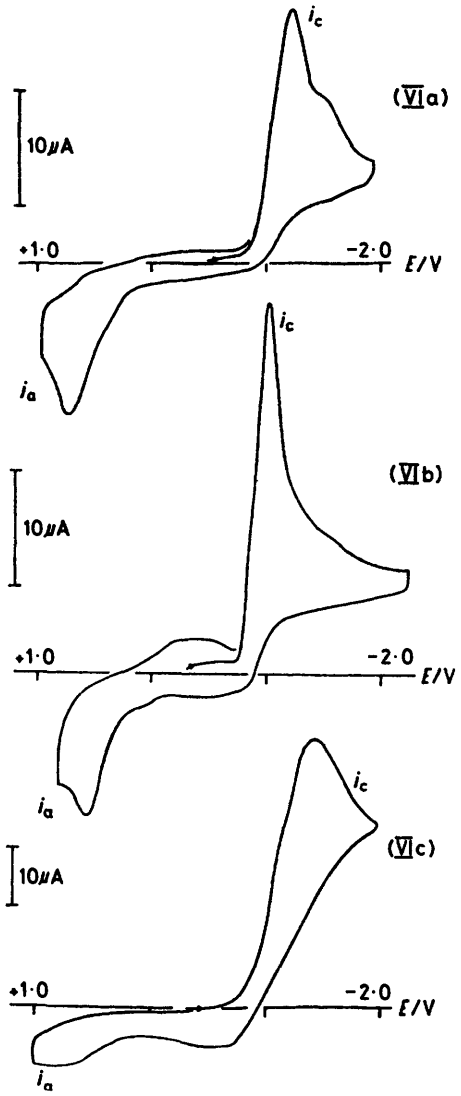


FIGURE 1 Cyclic linear scan voltammograms for 6-phenyl substituted cations (VIa—c) at a platinum microelectrode at a scan rate of 500 mV s^{-1}, in 0.05 mol dm^{-3} TPAP–DMF. Ag–AgCl–Cl^- (aqueous saturated) reference. Uncorrected for iR drop or charging current. (VIa) 0.824 g dm^{-3}; (VIb) 2.132 g dm^{-3}; (VIc) 0.780 g dm^{-3}

The *N*-methyl cation (VIb) also displays a second wave at the scan limit of −2.5 V, with a similar limiting current to the first wave. This reflects a second electron transfer but was not investigated further.

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.

There was no appearance of partial reversibility for the reduction of (VIa or b) at the faster rates, and even at the high rate of 100 V s^{-1}, recorded on an oscillosope, no trace of a return peak was observed for (VIa). Thus the chemical steps which follow the initial reduction appear to be extremely fast.

Cation (VIc) does show a weak return peak at −1.0 V at 600 mV s^{-1}, which may indicate a trace of partial reversibility, though its behaviour with change of scan rate was not consistent. This cation also shows a weaker oxidation wave at *ca.* +0.7 V than do cations (VIa and b). If the scan is initiated at −1.17 V, beyond the reduction wave,

TABLE 2

Cyclic voltammetry of dihydrodiazepinium cations

Cation	E_{pc}/ V	E_{ox}/ V	I_{pc}/ μA mol^{-1}	$I_{pc}v^{\frac{1}{2}}$/ μA $V^{\frac{1}{2}}$	D/ cm^2 s^{-1}
(VIa)	−1.18	+0.75	743	1 175	5.4×10^{-6}
(VIb)	−1.04	+0.6	957	1 513	8.2×10^{-6}
(VIc)	−1.42	+0.7 *	545	862	4.2×10^{-6}
(I)	−1.19		792	1 250	5.7×10^{-6}

* The oxidation wave is very broad.

and run anodically, a much stronger and sharper oxidation wave is found at +0.2 V and the return peak at −1.0 V no longer appears.

Coulometry.—Similar results were obtained at both mercury-pool and platinum-basket electrodes with stirred solutions in DMF containing TPAP at 20°. Electrolyses were performed at potentials on the plateaux of the reduction waves, typically between −1.6 and −1.8 V (*versus* aqueous Ag–AgCl). 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}. Cations (VIa and b) consumed exactly 1 F mol^{-1}. Cation (VIc) consumed 1.1 F mol^{-1} at mercury and 1.3 F mol^{-1} at platinum. In the latter case an erratic current–time trace was obtained due to fouling of the solid electrode and, although no visible film could be detected on the surface, cleaning of the electrode was necessary for the reaction to proceed to completion. During the electrolyses the initially pale yellow solutions became lighter in colour.

Monitoring of Electrolyses.—Electrolyses of cations (VIa and b) were monitored by cyclic voltammetry and by u.v. spectroscopy. The former was carried out 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 for voltammetry were the same ones used for the electrolyses. Scans were initiated at −0.3 V, run cathodic first, and switched at −2.3 and at +1.0 V. Loss of the cation reduction waves was found to be linear with respect to the number of coulombs passed, total loss occurring after the passage of 1 F mol^{-1}. An irreversible oxidation wave at +0.3 V for (VIa) and at +0.6 V for (VIb) became more intense during the electrolysis and was associated with a subsequent irreversible reduction, on the second cycle, at a potential close to that of the original cation. This was particularly noticeable in the final electrolysis solution where there is no dihydrodiazepinium reduction on the first cycle, yet a peak appears at the same voltage on the second cycle. The intensities of the oxidation wave and the second reduction wave are comparable, but both are less than the initial dihydrodiazepinium reduction wave at the beginning

of the electrolysis. These results clearly reflect the reduction of a species produced by oxidation of the main electrolysis product, there being an intervening chemical step after the oxidation which is not reversible.

For u.v. spectroscopic monitoring, samples were withdrawn by pipette from the electrolysis cell without interruption of the current and were diluted with ethanol to the requisite concentration. A linear loss of absorption due to the diazepinium 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 the passage of 1 F mol^{-1}. The product species gave characteristic spectra in neutral ethanol and the spectra of the final product solutions after electrolysis closely resembled those of the isolated products, in neutral, acidic, and basic solutions.

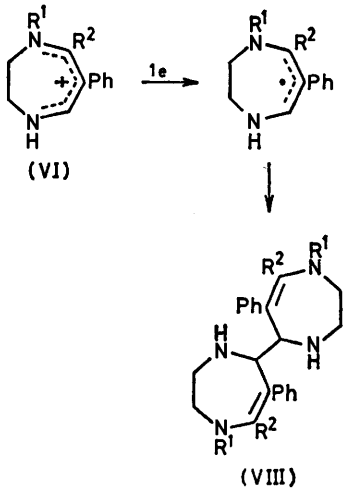
Identification of the Isolated Products.—The identity of product (VIIa) rests ultimately upon an *X*-ray analysis.[4,7] Spectroscopic evidence concurs; thus the i.r. spectrum shows a sharp N–H stretching peak, while ^1H n.m.r. shows two suitably coupled doublets for the protons attached to the pyrrole ring and a singlet and two triplets for the hydrogens attached to carbon atoms of the diazepine ring. The spectra of products (VIIb and c) clearly show that they have the same fundamental structure as (VIIa) (see Experimental section).

DISCUSSION

Both polarographic and cyclic voltammetric data suggest that the dihydrodiazepinium cations (VIa and b) undergo one-electron reductions which are followed by rapid chemical reactions leading to species which are oxidised at small positive potentials. Coulometry also supports the consumption of one electron per molecule. The products isolated from preparative electrolyses are oxidised at slightly different potentials from those observed in cyclic voltammetry, and the oxidation is semi-reversible (see also below). These differences in oxidation characteristics suggest that further chemical reactions ensue after the initial ones, in a time interval outwith the time scale of cyclic voltammetry. Dihydrodiazepinium salt (VIc) shows similar behaviour, but the data from polarography and cyclic voltammetry is less comparable. The lower isolated yield in this case suggests that an alternative reaction pathway may be competing. Steric interference between the vicinal methyl and phenyl groups in this cation is known to affect its shape and chemical behaviour [6] and this may also be a factor in its electrochemical behaviour.

The 6-phenyldihydrodiazepinium cations (VI) are all reduced less readily than is the 5,7-dihydrodiazepinium cation (I). The allylic radical (II) formed from (I) will have far more stabilisation due to the terminal phenyl groups than will be afforded by the phenyl group attached to the central carbon atom of the corresponding radicals produced from (VI), and this may be reflected in the difference of reduction potentials. In the case of (VIc) the reduced stabilisation afforded by the 6-phenyl group is further diminished since it is forced out of coplanarity with the seven-membered ring by the neighbouring methyl group; this is again reflected in the reduction potential of this cation.

The radical (II) formed by reduction of the 5,7-disubstituted cation (I) does not dimerise, presumably because of the sterically hindering 5,7-substituents. There is no such inhibiting feature in the case of the cations (VI). A logical route for the formation of the isolated products (VII) involves dimerisation of the first formed radical to give a bi(tetrahydrodiazepinyl) (VIII). Similar dimers have been isolated from the reduction of 1,4,6-trisubstituted dihydrodiazepinium cations.[8]

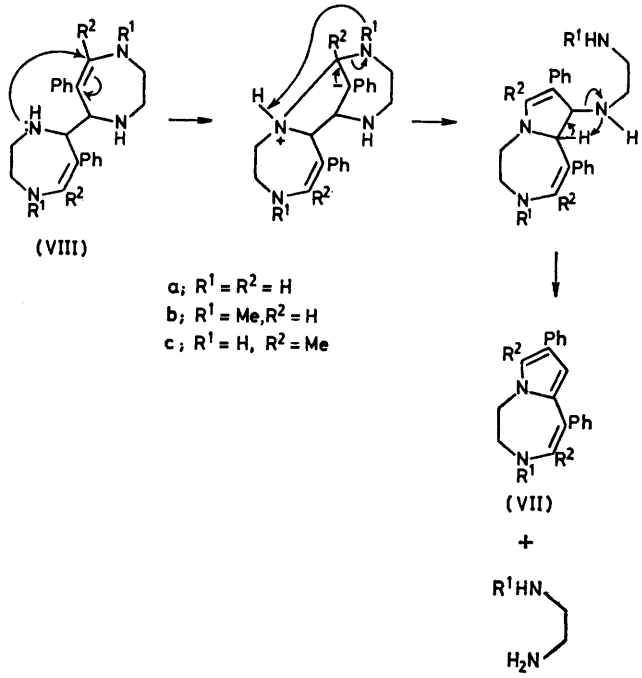


Succeeding steps must involve attack by the NH group of one ring onto the 5-position of the other ring, followed by extrusion of ethylenediamine (or its *N*-methyl derivative) from this second ring. Plausible mechanistic routes, for example the one shown in the Scheme, can be drawn but no evidence is presently available concerning the detailed reaction path.

The lower yield of (VIIb) is in accord with the proposed pathway. Formation of (VIIb) depends upon which sites are involved in the dimerisation of the intermediate radicals, which are not symmetrically substituted. For steric reasons dimerisation *via* the sites next to NH seems likely to be preferred to involvement of the sites next to NMe, and this produces the requisite dimer to provide (VIIb), but some of the isomeric dimers may also be formed. Formation of (VIIb) requires that the pyrrole nitrogen atom must derive from the unmethylated nitrogen atom of (VIb).

The Scheme also accounts for the formation of (VIIc) from (VIc). Dimerisation in this case would almost certainly proceed preferentially at the unsubstituted positions of the diazepinyl radicals, providing (VIII; $R^1 = H$, $R^2 = Me$). The low yield obtained is thus probably associated with some other factors. It has been found [9] that when the 5,7-dimethyldihydrodiazepinium cation is reduced electrochemically a fast chemical reaction follows the one-electron reduction. Since 5,7-methyl groups consistently impede attack at these positions of the ring,[10] it seems most likely that

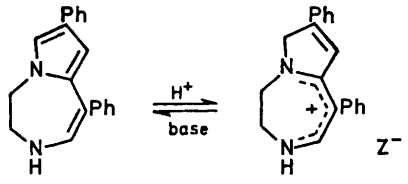
dimerisation at the 5,7-positions is not involved in this case, and that reaction involving the methyl groups may ensue. It is possible that the methyl group of the radical derived from (VIc) may take part in some similar



SCHEME

alternative reaction, thus providing competition to the formation of (VIIc) and lowering its yield.

Properties of Pyrrolodiazepines.—Acid–base equilibria. When ethanolic solutions of the pyrrolodiazepines were acidified they became yellow and their spectra showed marked bathochromic shifts (see Experimental section), which were reversed when the solution was neutralised again. Similarly quite different n.m.r. spectra were obtained from solutions in trifluoroacetic acid compared with solutions in deuteriochloroform or dideuteriodichloromethane. A perchlorate of pyrrolodiazepine (VIIa) was obtained by adding perchloric acid to a solution of (VIIa) in trifluoroacetic acid. An *X*-ray analysis of this salt showed it to be a pyrrolodihydrodiazepinium salt (IX; Z = ClO_4).[4,7] The n.m.r. spec-



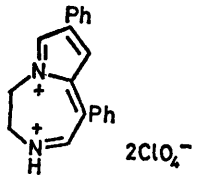
(VIIa) (IX)

trum (see Experimental section) is also consistent with this structure, showing that the same species is present in the solid and in solution. The two coupled 1-H signals of the pyrrole are replaced by two singlets representing 1 H and 2 H respectively, and a singlet at τ 2.41, a chemical shift characteristic of the 5(7)-positions of dihydrodiazepinium cations,[3] replaces a singlet at τ 3.82 observed for (VIIa).

Similar spectroscopic changes are observed when solutions of (VIIb and c) are acidified, and must indicate the formation of analogous protonated species.

These acid–base equilibria represent the interconversion of two distinct stabilised delocalised systems, a pyrrole and a dihydrodiazepinium cation. Calculations of the resonance energies of these two systems from p*K* data indicated that each should have resonance energies of *ca.* 20 kcal mol^{-1},[11] and the present results, showing their ready interconversion, tally nicely with the conclusion that they should be of simliar stability.

Reaction with triphenylmethyl perchlorate. When the pyrrolodiazepines (VIIa and b) were treated with two molar equivalents of triphenylmethyl perchlorate in dichloromethane the solutions became deep green, and after a short time fine yellow-green powders precipitated. These solids were stable in air, insoluble in non-polar solvents, and their solutions in solvents of high polarity rapidly lost their colour. They were however sufficiently soluble and stable enough in acetone to permit an n.m.r. spectrum to be accumulated overnight. A characteristic multiplet at τ 5.3—5.9 indicated that the



(X)

two methylene groups of the seven-membered ring were still present. Apart from the phenyl groups, other singlets were observed at τ 3.07 and 3.47. I.r. spectra showed strong perchlorate bands, and in the case of (VIIa) a broad NH absorption at 3 300 cm^{-1}. Electronic spectra in trifluoroactic acid showed a structured absorption centred at 413 nm, *i.e.* at longer wavelength than for either the pyrrolodiazepines or their monoprotonated species. Analyse were approximately but not accurately in accord with the dication structure (X) (errors: C, 1.4; H, 0.6; N, 0.14%) but clearly indicated the presence of two perchlorate ions.

Structure (X) is tentatively assigned to this salt; it is a vinylogue of the dihydrodiazepinium dications which are formed in strong acid.[3] To form such a dication triphenylmethyl perchlorate is acting as an electron transfer reagent rather than a hydride transfer reagent. Such a role is supported by the isolation of bistriphenylmethyl peroxide from the reaction mixture, since this is known to be formed from the resultant triphenylmethyl radical. (The initial perchlorate was free from any peroxide.)

Electro-oxidation of Pyrrolodiazepines.—Cyclic voltammetry experiments on the pyrrolodiazepines (VIIa and b) [platinum microelectrode, DMF containing 0.05M-TPAP (*versus* aqueous Ag–AgCl) or CH_2Cl_2 containing

0.1M-TPAP (*versus* platinum wire pseudoreference); 200 mV s^{-1}; start at −0.3 V; anodically; limits +0.8 and −1.3 V] showed almost reversible couples at *ca.* +0.3 V, with a subsequent irreversible reduction wave at *ca.* −0.6 V (Figure 2).

In preparative runs, using dichloromethane containing 0.1M-TPAP at a platinum basket electrode, at potentials at the peak of the oxidation wave, both pyrrolodiazepines consumed exactly 1 F mol^{-1}, and the solutions became dark green-black.

No product could be isolated satisfactorily from (VIIb) but from (VIIa) a dark blue-black fine powdery precipitate was obtained. Its i.r. spectrum showed the presence of N–H bonds and of perchlorate anions ($\nu_{max.}$ 3 280 and 1 100 cm^{-1}). It was insoluble in solvents of low polarity, but dissolved in protic and polar aprotic solvents with loss of colour. It formed a brilliant blue solid. These signals were still observable after the solutions had been kept for a week. On the basis of the e.s.r. spectra, which will be further investigated, the mass spectrum, and its mode of formation, the structure (XI) is tentatively suggested for this product, which is apparently a stable radical cation.

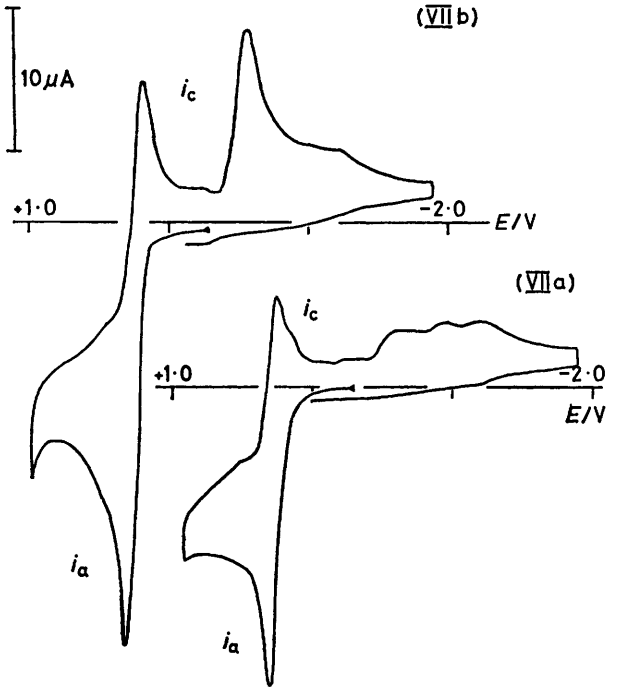
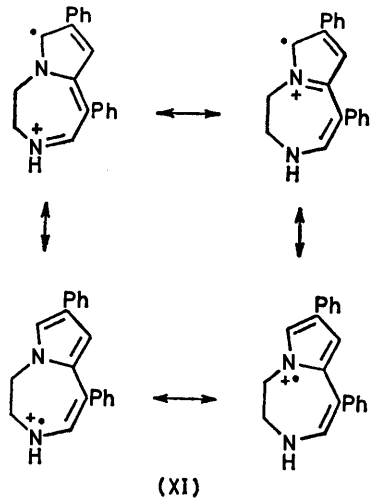


FIGURE 2 Cyclic linear scan voltammograms for pyrrolodiazepines (VIIa and b) at a platinum microelectrode at a scan rate of 200 mV s^{-1}, in 0.05 mol dm^{-3} TPAP–DMF. Ag–AgCl–Cl^- (aqueous saturated) reference. Uncorrected for *iR* drop or charging current. (VIIa) 0.712 g dm^{-3}; (VIIb) 0.968 g dm^{-3}

solution in concentrated nitric acid with $\lambda_{max.}$ 624—644 nm. It shrivelled but did not melt at 300°. Under normal operating conditions it was too involatile to provide a mass spectrum, but at high temperature showed a small peak at *m/e* 286. The electrolysis solutions gave strong e.s.r. spectra, as did the isolated



(XI)

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