# Surprising Electrochemical Reduction Product from a Dihydrodiazepinium Salt

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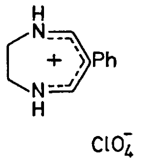
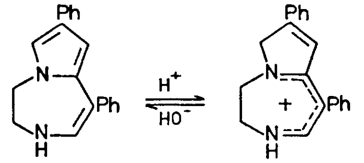
*Summary* Electrochemical reduction of 6-phenyldihydrodiazepinium perchlorate provides unexpectedly, in high yield, a pyrrolodiazepine; an interesting base–salt equilibrium between pyrrole and dihydrodiazepinium systems is observed.

Electrolytic reduction of the 6-phenyl-2,3-dihydrodiazepinium salt (I) provides an unexpected product, the pyrrolodiazepine (II). The reduction was carried out at a mercury pool electrode in a two-compartment cell, in dimethylformamide with 0·05M tetra-n-propylammonium perchlorate as a supporting electrolyte, at −1·6 V against an aqueous Ag–AgCl reference. The number of electrons consumed per mole was 1. The product was isolated in $> 80\%$ yield by pouring the reduced solution into water.[1] Similar results were obtained using a platinum cathode. The structure of (II) was proved by an *X*-ray crystallographic analysis,[1] and is consistent with observed i.r., n.m.r., and mass spectra and elemental analysis. A plausible explanation of the formation of (II) involves dimerisation of an initially formed radical followed by intramolecular displacement of ethylenediamine.



(I)



(II) (III)

The base (II) may be converted, reversibly, into a yellow salt by dilute hydrochloric acid. The structure of the resultant cation (III) has been confirmed by *X*-ray analysis of the crystalline perchlorate.[1] This acid-base equilibrium thus represents the interconversion of two distinct stabilised delocalised systems, a pyrrole and a dihydrodiazepinium salt, each having resonance energies of *ca.* 20 kcal $mol^{-1}$.[2] A similar product to (II), but with an *N*-methyl group, is isolated from the reduction of the mono-*N*-methyl derivative of (I).

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[1] Details of the electrolytic reduction (D. L., C.A.V., and D.J.W.) and *X*-ray analysis (J.P.D., G.G., and M. V. M.) will be published separately.

[2] D. Lloyd and D. R. Marshall, *Chem. and Ind.*, 1972, 335.