

Surprising Electrochemical Reduction Product from a Dihydrodiazepinium Salt

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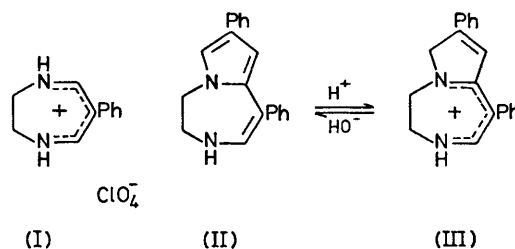
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Summary Electrochemical reduction of 6-phenyldihydrodiazepinium perchlorate provides unexpectedly, in high yield, a pyrrolo-diazepine; an interesting base-salt equilibrium between pyrrole and dihydrodiazepinium systems is observed.

ELECTROLYTIC reduction of the 6-phenyl-2,3-dihydrodiazepinium salt (I) provides an unexpected product, the pyrrolo-diazepine (II). The reduction was carried out at a mercury pool electrode in a two-compartment cell, in dimethyl-formamide 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.



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.