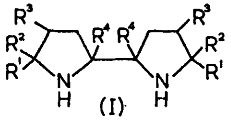
Ready Formation of the 2,2′-Bipyrrolidinyl System

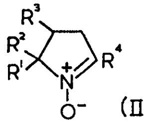
By J. B. BAPAT and D. ST. C. BLACK

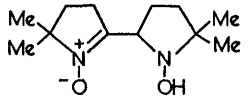
(Department of Chemistry, Monash University, Clayton, Victoria, Australia)

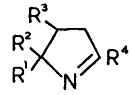
THE 2,2′-bipyrrolidinyl system (I), which is the parent of the A—D bicyclic moiety of the corrins, has been the object of various synthetic attempts, by Todd and his co-workers, involving dimerisation of a monomeric pyrroline derivative. Base-catalysed dimerisation[1] of 5,5-dimethyl-1-pyrroline 1-oxide (II: $R^1 = R^2 = Me$, $R^3 = R^4 = H$) produced the 2,2′-nitrone-hydroxylamine dimer (III), together with the corresponding 2,3′-dimer. Reduction of the dimer (III) successively with sodium borohydride and zinc and hydrochloric acid gave the 2,2′-bipyrrolidinyl (I: $R^1 = R^2 = Me$, $R^3 = R^4 = H$). The 1-pyrroline 1-oxide (II: $R^1 = R^2 = Me$, $R^3 = R^4 = H$) was also converted[2] in poor yield directly into the bis-hydroxylamine [identical with the borohydride reduction product of (III)], using sodium–potassium alloy in ethylene glycol dimethyl ether. However, all attempts by these workers[2] to prepare the system (I) by reductive dimerisation of 1-pyrrolines (IV), a process analogous to pinacol formation, were unsuccessful and resulted only in reduction to pyrrolidines.

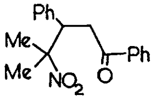
We have observed the very ready dimerisation of the 1-pyrroline (IV: $R^1 = R^2 = Me$, $R^3 = R^4 = Ph$), using aluminium amalgam or zinc and ammonium chloride at room temperature, to yield the bipyrrolidinyl (I: $R^1 = R^2 = Me$, $R^3 = R^4 = Ph$). Not only can the dimer be formed in this way, it is even more readily prepared from either the 1-pyrroline 1-oxide (II: $R^1 = R^2 = Me$, $R^3 = R^4 = Ph$) or its γ-nitro-ketone precursor (V), using zinc and ammonium chloride in aqueous tetrahydrofuran at 25°. Thus the γ-nitro-ketone (V) can give rise in high yield to either the usual nitrone, at temperatures less than 10° or the 2,2′-bipyrrolidinyl dimer at 25°, in one step. That the latter product was indeed the dimer and not the monomeric pyrrolidine was determined by the following evidence.


(I)


(II)


(III)


(IV)


(V)

Combustion analysis gave the empirical formula $C_{36}H_{40}N_2$, confirmed by molecular weight measurement. [Found: *M*(osmometric in benzene), 490. Calc.: *M*, 500]. The dimer was readily reconverted into the pyrroline (IV: $R^1 = R^2 = Me$, $R^3 = R^4 = Ph$) on pyrolysis above its melting point (200°) or photolysis in benzene. The infrared spectrum showed absorption at 3350 cm.$^{-1}$ ($>$NH) and other peaks characteristic of phenyl and *gem*-dimethyl groups, while only phenyl absorption was observed in the ultraviolet spectrum. The n.m.r. spectrum (in deuterochloroform) also confirmed the dimeric structure (I: $R^1 = R^2 = Me$, $R^3 = R^4 = Ph$) as singlets were obtained at τ 9·60 and 9·10 (methyl groups on C-5,5′), τ 7·65 (NH protons, exchanged on addition of D_2O), an ABX multiplet from τ 6·9—8·5 (methylene protons on C-3,3′ and methine protons on C-4,4′) and a complex multiplet from τ 2·2—3·2 (phenyl protons). The τ values for the methyl groups are significantly higher than those in monomeric systems, resulting from shielding by the 2-phenyl group on the adjacent pyrrolidine ring. For comparison, the n.m.r. spectrum of the pyrroline (I: $R^1 = R^2 =$ Me, $R^3 = R^4 =$ Ph) showed methyl singlets at τ 9·13 and 8·54. (By coincidence, the methylene protons at C-3 and methine proton at C-4 combined as a sharp singlet at τ 6·69.)

Although the formation of the 2,2′-bipyrrolidinyl dimer is undoubtedly facilitated[3] by the stability of the intermediate benzyl-type radical-ion resulting from addition of one electron to the pyrroline, 2-phenyl substitution does not appear to be critical and the generality of the reaction is under current investigation.

(*Received, November 7th,* 1966; *Com.* 858.)

[1] R. F. C. Brown, V. M. Clark, M. Lamchen, and Sir Alexander Todd, *J. Chem. Soc.*, 1959, 2116.

[2] V. M. Clark, B. Sklarz, and Sir Alexander Todd, *J. Chem. Soc.*, 1959, 2123.

[3] O. Anselmino, *Ber.*, 1908, **41**, 621; H. Thies and H. Schoenenberger, *Chem. Ber.*, 1956, **89**, 1918.