# On the Water and Methanol Adducts of the Propentdyopent System

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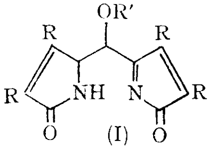
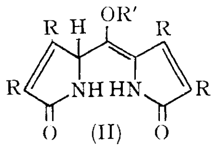
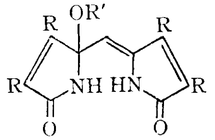
THE chemistry of the propentdyopents and their derivatives, which occur naturally in gall stones and in pathological urine,[1] and which have been regarded as catabolic products of the bile pigments,[2] has been investigated for the past thirty years or so, notably by von Dobeneck and his colleagues at Munich.[3] In 1962 structure (I; R′ = Me) was proposed[4] for the "methanol-propentdyopent" system (the adduct of methanol and the propentdyopent nucleus[4]). Recently[5] von Dobeneck and Schnierle have put forward a revised structure (III). Some of our results were mentioned by them, and we now present further evidence which, we believe, puts this structural proposal on a firmer basis.



(I)

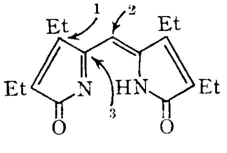


(II)



(III)

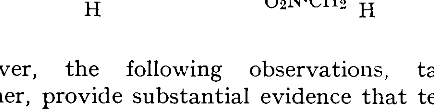
The tetraethyl system (R = Et) has been used throughout. Tetraethyl-water-propentdyopent, $C_{17}H_{24}N_2O_3$, was obtained both by degradation of octaethylhaemin ($H_2O_2$ –NaOMe–MeOH–$CHCl_3$ at −10°) and by oxidation of 3,3′,4,4′-tetraethyl-dipyrrolylmethane -5,5′-dicarboxylic acid. Treatment of the water adduct with refluxing methanol in the presence of a trace of acid gave tetraethyl-methanol-propentdyopent, $C_{18}H_{26}H_2O_3$. Either adduct on treatment with methanolic zinc acetate gave the orange zinc complex of tetraethylpropentdyopent, $(C_{17}H_{21}N_2O_2)_2Zn$: the n.m.r. spectrum suggested that this system was a symmetrical one, and that tetraethylpropentdyopent itself had structure (IV). Since the water (or methanol) adduct is regenerated from the zinc salt under acidic conditions in the appropriate solvent, the problem became that of locating the preferred position for nucleophilic attack (by water, or methanol) in the conjugate acid of this system.



(IV) Tetraethyl-propentdyopent

The n.m.r. spectrum of tetraethyl-methanol-propentdyopent showed that addition had not occurred at a $\beta$-position (*e.g.* 1 in IV). Thus in $CDCl_3$ at 100 MHz all the methylene groups appeared as a multiplet at $\tau$ 7·7, and the methyl groups at $\tau$ 8·9 (m), while the methoxyl methyl appeared at $\tau$ 6·84 (s). Three low-field signals, each representing one proton, were observed: a sharp singlet at $\tau$ 5·30 and two broad signals at $\tau$ 3·96 and 1·74. In the presence of $D_2O$ the last two signals disappeared at comparable rates, but the rest of the spectrum was unaffected. The infrared spectrum of the deuteriated product showed strong bands due to N–D stretching modes, but no absorption due to C–D stretching. Evidently two NH functions were present and structure (I) was untenable.

The alternatives favoured were: (II), which formally arises by the nucleophilic process 2 in (IV)[6] followed by tautomerisation; and (III), which arises by attack[7] at a valley position (*e.g.* 3). von Dobeneck has argued[5] that the ready elimination of methanol (for example, in the formation of the zinc complex of the propentdyopent) provides evidence against the former structure. We do not find this evidence compelling since system (II) is potentially tautomeric with (I), and elimination from the latter is readily envisaged. Examples of reactions occurring apparently *via* a tautomeric structure are known in related systems *e.g.*:[8]



However, the following observations, taken together, provide substantial evidence that tetraethylmethanol-propentdyopent has structure (III; R = Et, R′ = Me).

(i) Tetraethyl-water-propentdyopent (R = Et, R′ = H) reacted with methanol under acidic conditions to give the corresponding methanol derivative, but did not react with diazomethane under conditions[9] which favour the *O*-methylation of $\beta$-diketones. This result tends to favour the bis-allylic tertiary alcohol structure (III; R′ = H) since in the alternative (II; R′ = H) the hydroxylic hydrogen, as part of a vinylogous carbamic acid system, would be expected to be appreciably acidic.

(ii) On the basis of chemical shift, the signal at $\tau$ 5·30 does not distinguish between structures (II) and (III). However, this signal was a very sharp singlet and double irradiation experiments at −30° revealed no detectable coupling with either of the NH signals at lower field.

(iii) Treatment of zinc tetraethylpropentdyopent with MeOD containing a trace of $CF_3 \cdot CO_2D$ gave a deuteriated tetraethyl-methanol-propentdyopent. N.m.r. spectroscopy showed the two imino-functions had been deuteriated, but the signal at $\tau$ 5·30 still corresponded to one proton. Process 2 → (II) necessarily results in the introduction of deuterium at the valley position, whereas process 3 does not necessarily lead to *meso*-deuteriation. It is therefore concluded that the latter process occurred and that (III; R = Et, R′ = Me) is the structure of tetraethyl-methanol-propentdyopent.

Structure (III) does not account in a simple additive way for the u.v. spectrum [*e.g.* (III), $\lambda_{max.}$ 280 m$\mu$; 3,4-dimethyl-5-methylene-3-pyrrolin-2-one,[7] $\lambda_{max.}$ 260 m$\mu$; 5-methoxymethyl-ene-3,4-dimethyl-3-pyrrolin-2-one,[10] $\lambda_{max.}$303 m$\mu$]. It is presumed that the bathochromic shift with respect to the model chromophore arises partly by a substituent effect and partly by orbital overlap between the two chromophores present.

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[1] B. J. Stokvis, *Maandblad voor Naturwetenschappen*, 1870, No. 5; 1871, No. 2. The work is referred to by J. Myers, *Ber.*, 1872, **5**, 583.

[2] *E. g.*, H. Fischer and H. von Dobeneck, *Z. physiol. Chem.*, 1940, **263**, 125.

[2] H. von Dobeneck, E. Brunner, and U. Deffner, *Z. Naturforsch.*, 1967, **22b**, 1005, and earlier papers.

[4] H. von Dobeneck, E. Hägel, and W. Graf, *Z. physiol. Chem.*, 1962, **329**, 182. Here we employ the trivial nomenclature introduced in this paper.

[5] H. von Dobeneck and F. Schnierle, *Annalen*, 1968, **711**, 135.

[6] *Cf.* nucleophilic attack at the *meso*-position in the dipyrromethene-5,5′-dicarboxylate system: K. J. Brunings and A. H. Corwin, *J. Amer. Chem. Soc.*, 1944, **66**, 337.

[7] *Cf.* nucleophilic attack at the valley position in the 5-methylene-3-pyrrolin-2-one system: H. Plieninger, U. Lerch, and A. Tapia, *Annalen*, 1966, **698**, 191.

[8] I. Felner, A. Fischli, A. Wick, M. Pesaro, D. Bormann, E. L. Winnacker, and A. Eschenmoser, *Angew. Chem. Internat. Edn.*, 1967, **6**, 864.

[9] B. Eistert, F. Arndt, L. Loewe, and E. Ayca, *Chem. Ber.*, 1951, **84**, 156.

[10] J. H. Atkinson, R. S. Atkinson, and A. W. Johnson, *J. Chem. Soc.* (*C*), 1966, 40.