A Sulphur Analogue of the Oxyporphyrins

By P. S. CLEZY* and G. A. SMYTHE

(*Department of Organic Chemistry, The University of New South Wales, P.O. Box 1, Kensington, N.S.W., Australia*)

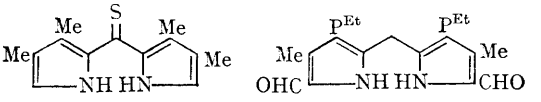
PREVIOUS communications from this laboratory[1,2] together with reports from other groups,[3-5] have described the synthesis and general properties of the oxyporphyrins (oxophlorins[6]). These compounds have exhibited interesting spectroscopic, magnetic, and tautomeric properties which have prompted an investigation of a sulphur analogue of the oxyporphyrins.

When an ethereal solution of a Grignard derivative of 3,4-dimethylpyrrole is treated at 0° with a benzene solution of thiophosgene, the thione (I) is obtained. A mixture of this thione (I) (0·1 mmole) and the diformyldipyrrylmethane (II) (0·1 mmole) when heated in acetic anhydride (5 ml.) containing HBr–acetic acid (45% w/v; 0·1 ml.) for 15 min. at 90° yields the porphyrin (IIIa), m.p. 260—262°, ν_{max} (Nujol) 3250 (NH), 1730 (CO_2Et), 1695 (SAc) cm.$^{-1}$; λ_{max} ($CHCl_3$) (log ϵ), 407 (5·09), 510 (4·02), 547 (3·89), 584 (3·69), 635 (3·69) mμ; τ ($CDCl_3$), 0·35 (3H, methine protons), 5·9 (8H, m, $2CH_2{\cdot}CH_2{\cdot}CO_2{\cdot}CH_2{\cdot}CH_3$), 6·55 (12H, 4Me), 6·62 (6H, 2Me), 6·87 (4H, m, $2CH_2{\cdot}CH_2{\cdot}CO_2{\cdot}CH_2{\cdot}CH_3$), 7·94 (3H, SAc), 8·89 (6H, t, $2CH_2{\cdot}CH_2{\cdot}CO_2{\cdot}CH_2{\cdot}CH_3$), *ca.* 14·0 (2H, NH).

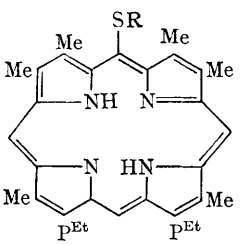
Treatment of the porphyrin (IIIa) with ethanolic sulphuric acid (10% v/v) under reflux for 5 hr. cleaved the thiol ester group to give another porphyrin, m.p. >300°, λ_{max} ($CHCl_3$) (log ϵ), 393 (4·91), 510 inflect. (4·02), 590 (3·99), 648 inflect. (3·62), 662 (3·70)mμ; τ ($CDCl_3$) −0·08 (1H, methine proton), 1·41 (2H, methine protons), 5·53 (4H, m, $2CH_2{\cdot}CH_2{\cdot}CO_2{\cdot}CH_2{\cdot}CH_3$), 5·78 (4H, $2CH_2{\cdot}CH_2{\cdot}CO_2{\cdot}CH_2{\cdot}CH_3$), 6·56 (6H, 2Me), 6·63 (4H, m, $2CH_2{\cdot}CH_2{\cdot}CO_2{\cdot}CH_2{\cdot}CH_3$), 7·88 (6H, 2Me), 8·79 (12H, t, $2CH_2{\cdot}CH_2{\cdot}CO_2{\cdot}CH_2{\cdot}CH_3$ plus 2Me; addition of 30% C_6H_6 to the $CDCl_3$ solution caused a shift of the latter resonance 0·12 p.p.m. downfield from the triplet revealing the signal associated with these two methyls as a sharp singlet), *ca.* 14·0 (2H, NH).

The n.m.r. spectrum of this tetrapyrrole is indicative of a symmetrical molecule with pairs of methyls at τ 6·56, 7·88, and 8·79. Only the first resonance occurs in the region normally associated with porphyrin ring methyls, the other methyls being clearly more shielded.

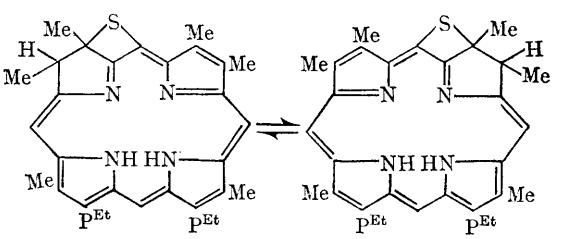
An explanation of these observations is that this tetrapyrrole in chloroform solution is best described as an equilibrium mixture of the tautomers (IVa) and (IVb). Providing this equilibrium is maintained rapidly enough this would explain the symmetry of the molecule, indicated by the n.m.r. spectrum, as well as the fact that the methyls at τ 8·79 appear as a singlet.



(I) $P^{Et}=CH_2{\cdot}CH_2{\cdot}CO_2Et$ (II)



(IIIa) R=Ac
(IIIb) R=H



(IVa) (IVb)

In $CF_3{\cdot}CO_2D$ solution in which the tetrapyrrole is protonated, an n.m.r. spectrum typical of other members of the porphyrin series is obtained and the compound probably exists as the di-cation of the thiol (IIIb); τ ($CF_3{\cdot}CO_2D$), −0·61 (3H, methine protons, 5·54 (4H, m, $2CH_2{\cdot}CH_2{\cdot}CO_2{\cdot}CH_2{\cdot}CH_3$) 5·82 (4H, q, $2CH_2{\cdot}CH_2{\cdot}CO_2{\cdot}CH_2{\cdot}CH_3$), 6·40 (6H, 2Me), 6·75 (6H, 2Me), 6·83 (4H, m, $2CH_2{\cdot}CH_2{\cdot}CO_2{\cdot}CH_2{\cdot}CH_3$), 6·89 (6H, 2Me), 8·86 (6H, t, $2CH_2{\cdot}CH_2{\cdot}CO_2{\cdot}CH_3{\cdot}CH_3$).

The mass spectra of these porphyrins differ from most other porphyrins in that their molecular ion is observed only as a very minor peak. In both the acetate (IIIa) and its hydrolysis product

the base peak is at 594 while the molecular ion in each case has a relative abundance of less than 1%. Presumably the loss of the sulphur substituent to give a *meso*-unsubstituted porphyrin is a very favoured fragmentation.

It is noteworthy that, unlike the oxyporphyrins, this sulphur analogue does not give an e.s.r. signal.

The tautomeric nature of this tetrapyrrole is being investigated further and will be reported in full elsewhere.

(*Received, October 27th*, 1967; *Com.* 1157.)

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