Reaction of Cobalt(II) Octaethylporphin with Ethyl Diazoacetate

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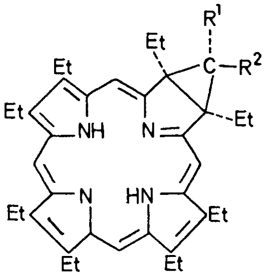
Summary Reaction of ethyl diazoacetate with cobalt(II) octaethylporphin yields a cobalt(III) salt (III) as the primary adduct; reactions of (III) include rearrangement with chromous chloride to the chlorocobalt(II) complex of *N*-ethoxycarbonylmethyloctaethylporphin (IV) and with ethanolic hydrogen chloride to the metal-free, *NN*-bridged compound (V; $R^3 = CO_2Et$).

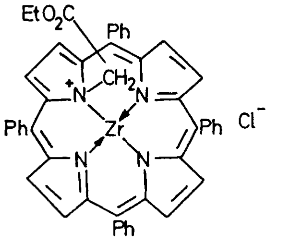
RECENT papers have described the reactions of ethyl diazoacetate with copper(II) octaethylporphin which gives some *meso*-substitution but mainly addition to the $\beta\beta$-double bonds, to form the isomeric chlorins (Ia, b) after removal of the metal,[1] and with zinc *meso*-tetraphenylporphin when reaction at nitrogen was observed yielding (II), together with some $\beta\beta$-addition.[2] We now report that the reaction of ethyl diazoacetate with cobalt(II) octaethylporphin yields a novel type of product (III), showing that the nature of the product from metal porphins with ethyl diazoacetate is dependent on the nature of the co-ordinating metal.



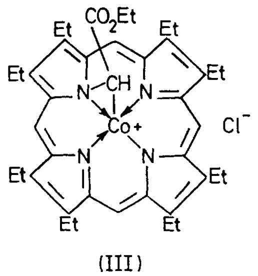
(I)

a; $R^1 = H$, $R^2 = CO_2Et$

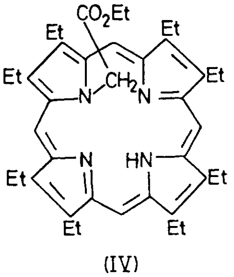
b; $R^1 = CO_2Et$, $R^2 = H$



(II)



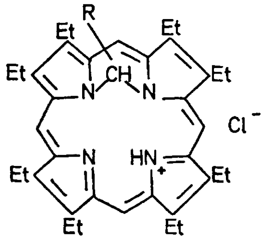
(III)



(IV)

Structure (III) is supported by the results of elemental analysis, polarography [cobalt(III) complex], electrophoresis, and n.m.r., which showed that the four *meso*-hydrogens remained and that the eight β-ethyl groups were roughly equivalent. In C_5D_5N a high-field signal corresponding to a single carbene methine proton (τ 12·25) was observed, and in the mass spectrum there was a weak signal at *m/e* 677 corresponding to $C_{40}H_{50}CoN_4O_2$ (loss of anion). The carbene fragment was readily eliminated from the adduct, *e.g.* by heating an ethanolic solution with sodium acetate when cobalt(II) octaethylporphin was obtained together with diethyl fumarate and a little dimethyl maleate.

Further support for structure (III) has been derived from chemical transformations. Chromous chloride reduction gave the neutral chlorocobalt(II) complex of *N*-ethoxycarbonylmethyloctaethylporphin (IV), and this structure was confirmed by demetallation with acids to the free porphin, the hydriodide of which has been defined by *X*-ray crystallography.[3] The porphin (IV) has been synthesised in low yield from octaethylporphin by reaction with ethyl bromoacetate,[4] the main product from this reaction being the *trans*-21,22-bisethoxycarbonylmethyl derivative. The action of concentrated sulphuric acid on the adduct (III) gave some (IV) as well as *ca.* 40% octaethylporphin.



(V)

When (III) was treated with ethanolic hydrogen chloride, a crystalline cobalt-free chloride was obtained. Analysis of the corresponding bromide indicated the molecular formula $C_{40}H_{51}BrN_4O_2$ (*m/e*, 618; *M*—HBr) corresponding to an adduct of octaethylporphin and ethoxycarbonylcarbene (+ bromide). A signal (1H) at τ 15·78 in the n.m.r. spectrum of a $CDCl_3$ solution corresponded to the methine hydrogen and from the spectrum it was evident that the four *meso*-protons were present as a 1:2:1 set and that no addition had occurred at the β-positions. The visible spectrum also suggested a porphin rather than a chlorin nucleus. Accordingly structure (V; $R = CO_2Et$), where the carbene fragment bridges N-21 and N-22, has been assigned to this compound. This is the first example of a 21,22-*cis*-disubstituted porphin.

The related structure (V; R = H) has been prepared in low yield by reaction of octaethylporphin with methylene iodide in presence of potassium carbonate at 100° for 10 days. In this case a broad singlet at τ 18·0 in the n.m.r. spectrum was associated with the hydrogens of the methylene bridge.

Compounds derived from the formal addition of two equivalents of ethoxycarbonylcarbene to the porphin have also been isolated from the reaction of cobalt(II) octaethylporphin and ethyl diazoacetate and the structures of these will be discussed later.

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[2] H. J. Callot, *Bull. Soc. chim., France*, 1972, 4387; 1973, 3192; *Tetrahedron*, 1973, **29**, 899.

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[4] R. Grigg, G. Shelton, A. Sweeney, and A. W. Johnson, *J.C.S. Perkin I*, **1972**, 1789.