Reaction of Copper(II) Octaethylporphin with Ethoxycarbonylcarbene

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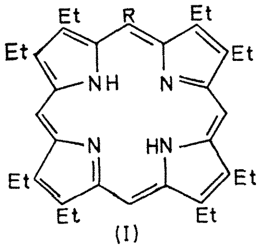
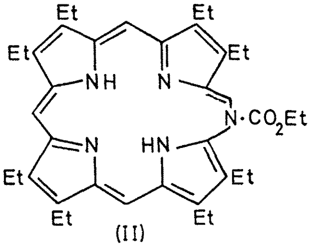
Summary. Reaction of copper(II) octaethylporphin with ethyl diazoacetate in presence of copper(I) iodide gives two isomeric chlorins (III) containing fused cyclopropane rings as well as *meso*-ethoxycarbonylmethyloctaethylporphin (I; R = $CH_2{\cdot}CO_2Et$).

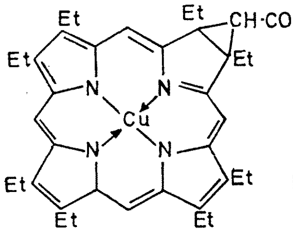
THE reaction of ethoxycarbonylnitrene with octaethylporphin (I; R = H) was described by Grigg,[1] who showed that the main product was (II), formed by insertion of the reagent into the macrocycle. In contrast, we have found that octaethylporphin fails to react with the corresponding carbene, but when the copper derivative[2] of the porphin was heated with ethyl diazoacetate in presence of copper(I) iodide in refluxing benzene for 30 min., two major products (each *ca*. 30% yield based on converted porphin) were isolated as well as a new red copper porphin and another copper chlorin in lower yields. The two main copper chlorins, m.p. 213—215° and 237—239°, respectively, formed black crystals with a violet reflex, and are formulated as isomers of (III) [ν_{max} 1710 and 1640 cm.$^{-1}$; 1720 and 1645 cm.$^{-1}$ ($CHCl_3$), respectively; *M* (mass spectrum) 681·324 for each; $C_{40}H_{50}CuN_4O_2$ requires 681·323].

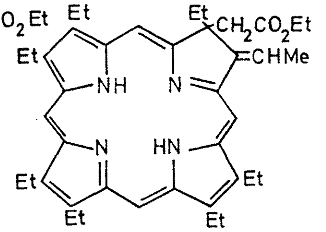
The formation of (III) involves the copper-catalysed decomposition (*cf*. ref. 3) of ethyl diazoacetate to ethoxycarbonylcarbene, which then adds to one of the cross-conjugated double bonds of the porphin. Demetallation of each of the copper chlorins with sulphuric acid gave an equilibrium mixture of the isomeric chlorins, m.p. 198—200°

and 220—223° respectively, which was separated by chromatography. The structures of the chlorins which differed only in the configurations of the ester groups, were deduced partly from n.m.r. spectra (singlets at τ 0·27 and 0·85 for each of two pairs of *meso*-protons, indicating a plane of symmetry in the molecule), by the typical metal chlorin visible spectra, and by mass spectrometry. The free chlorins could be re-converted into the isomeric copper derivatives without inversion, the isomer, m.p. 198—200° giving the copper complex, m.p. 237—239°. The same chlorin, m.p. 198—200° gave the isomer, m.p. 220—223° when heated at 270—290° for 10 min., but when a cyclohexane solution was irradiated with visible light (2 × 100 w bulbs at 5 cm.) for 4½ hr., another black crystalline produtc was obtained (*ca.* 50%) which resulted from fission of the cyclopropane ring (*cf.* 4). The structure of the new product (IV) was deduced from the mass spectral fragmentation pattern which showed prominent peaks for M — Et, M — CO_2Et, and M — $CH_2{\cdot}CO_2Et$ (M = 620).


(I)


(II)


(III)


(IV)

The red copper porphin has been identified as the copper complex of the *meso*-ethoxycarbonylmethylporphin (I; R = $CH_2{\cdot}CO_2Et$) and it was converted into the metal-free compound with sulphuric acid. The visible spectrum of the corresponding nickel complex was nearly superimposable on that of another nickel *meso*-ethoxycarbonylmethyl-octa-alkylporphin.[5] A product (I; R = $NH{\cdot}CO_2Et$) analogous to (I; R = $CH_2{\cdot}CO_2Et$) was isolated when (II), was heated to *ca.* 160°, and was obtained from the copper porphin directly by reaction with ethoxycarbonylnitrene.[1] Finally, the copper chlorin obtained in small yield appears, from its spectra and mass spectrum, to be a *meso*-ethoxycarbonylmethyl derivative of (III) but it was isolated only in very small quantity and it has not been possible to achieve a complete purification.

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[2] H. H. Inhoffen, J. H. Fuhrhop, H. Voigt, and H. Brockmann, jun., *Annalen*, 1966, **695**, 133.
[3] W. R. Moser, *J. Amer. Chem. Soc.*, 1969, **91**, 1135, 1141.
[4] R. M. Roberts and R. G. Landolt, *J. Amer. Chem. Soc.*, 1965, **87**, 2281 have described the ready photolytic cleavage of acetylcyclopropanes.
[5] R. Grigg, A. W. Johnson, K. Richardson, and K. W. Shelton, *J. Chem. Soc.* (*C*), 1969, 655.