

Synthesis of Oxophlorins (Oxoporphyrins) from Magnesium and Zinc Porphyrin Chelates¹

By **Graham H. Barnett, Mervyn F. Hudson, Stuart W. McCombie, and Kevin M. Smith,*** The Robert Robinson Laboratories, University of Liverpool, P.O. Box 147, Liverpool L69 3BX

Treatment of magnesium or zinc porphyrins with thallium(III) trifluoroacetate, followed by an acidic work-up affords oxophlorins in high yield. The oxophlorin oxygen atom is shown to be trifluoroacetate-derived by the isolation of *meso*-trifluoroacetoxyporphyrins as stable intermediates; a radical mechanism is suggested for this transformation. Similar results are obtained when lead(IV) or mercury(II) trifluoroacetates are used as the oxidants, but the yields of oxophlorin are lower.

TREATMENT of porphyrins with thallium(III) trifluoroacetate (TTFa) in tetrahydrofuran and dichloromethane gives² the corresponding thallium(III) porphyrin chelates (1) after ligand exchange induced by chromatography on deactivated alumina. In the absence of

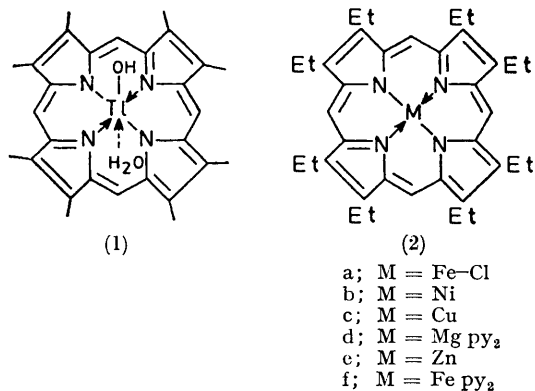
added trifluoroacetic acid, these thallium(III) chelates (1) appear to be inert to attack by excess of TTFa used in their generation, and, in view of current interest in the comparative chemistry of metalloporphyrins,

¹ Preliminary report, S. W. McCombie and K. M. Smith, *Tetrahedron Letters*, 1972, 2463.

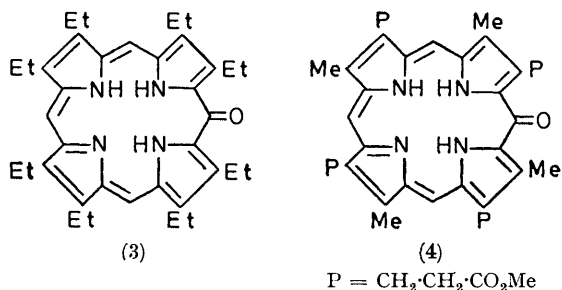
² K. M. Smith, *Chem. Comm.*, 1971, 540; R. J. Abraham, G. H. Barnett, E. S. Bretschneider, and K. M. Smith, *Tetrahedron*, 1973, in the press.

we now report our results on the reactions of common metalloporphyrins (2a–e) with TTFA, but in the absence of added trifluoroacetic acid.

Like the thallium(III) complex (1), the iron(III), nickel(II), and copper(II) chelates (2a–c) of octaethylporphyrin were inert to attack by TTFA in dichloromethane and tetrahydrofuran. However, the magnesium and zinc chelates (2d and e) reacted rapidly



with 1 equiv. of TTFA [or thallium(III) nitrate] to give green solutions (λ_{max} , 652–683 nm) lacking Soret absorption bands. The green species (λ_{max} , 657 nm) from zinc octaethylporphyrin (2e) and TTFA decayed rapidly to a red compound with a typical two-banded metalloporphyrin visible absorption spectrum. Demetallation with sulphur dioxide ($\text{Ti}^{\text{III}} \rightarrow \text{Ti}^{\text{I}}$) and acid, gave octaethyloxophlorin (3) in 79% yield from (2e). Likewise, a good yield of the oxophlorin (4) was obtained from zinc coproporphyrin-I tetramethyl ester. With dipyridinemagnesium octaethylporphyrin (2d) a 55% yield of oxophlorin (3) was obtained, and this



could easily be separated from a minor quantity of octaethylporphyrin, presumably produced by demetallation of the starting material with traces of trifluoroacetic acid liberated in the course of the reaction. The yield of oxophlorin based on consumed starting material is 73%, but this complication makes the method less attractive than that involving zinc porphyrin chelates.

* The compound was conveniently separated from thallium salts by percolation through a bed of t.l.c. grade silica (Kieselgel G).

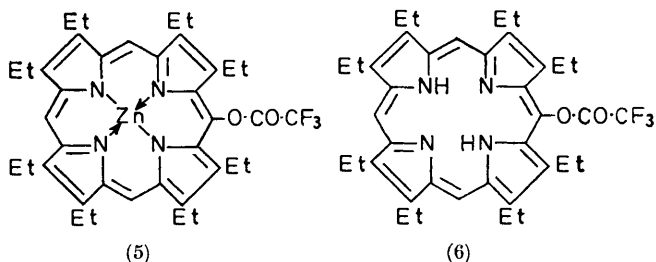
³ E.g. R. Lemberg, *Rev. Pure Appl. Chem.*, 1956, **6**, 1.

⁴ T. Kondo, D. C. Nicholson, A. H. Jackson, and G. W. Kenner, *Biochem. J.*, 1971, **121**, 601.

⁵ P. J. Crook, A. H. Jackson, and G. W. Kenner, *Annalen*, 1971, **743**, 26.

Iron complexes of oxophlorins have been postulated³ as intermediates in the catabolism of haemoproteins leading to bile pigments. Indirect evidence in support of this argument has been obtained recently⁴ from radiochemical labelling experiments. As a result of this suggested biological involvement, the metal-free oxophlorin ligand has been a synthetic target for several research groups. Biologically significant oxophlorins can only be synthesised isomerically pure by ring fabrication (e.g. refs. 5 and 6) but model compounds [e.g. (3)] can be prepared by the direct oxidation of porphyrins, or more usually iron porphyrins; reaction mixtures containing hydrogen peroxide are normally used with the latter substrate. The most efficient method⁷ of this general type is an application of the 'coupled oxidation' procedures,^{8,9} and makes use of the treatment of the pyridinium haemochrome (2f) with hydrogen peroxide in pyridine. The iron oxophlorin is isolated as its benzoyl derivative, which is then demetallated and debenzoylated, to give the oxophlorin (3) in an overall yield of 36% from (2f).⁷ The new method, from zinc porphyrins and TTFA, achieves more than twice this yield, and can be carried through from start to finish in less than 1 h.

We felt that determination of the origin of the oxophlorin oxygen atom would play a large part in establishing a mechanism for the transformation.¹ Repetition of the reaction with exclusion of oxygen did not decrease the oxophlorin yield, and neither did addition of methanol to the reaction mixture result in the production of *meso*-methoxyporphyrin, indicating that the new oxygen atom was probably not derived from aerial oxygen or water. The red metalloporphyrin obtained from the decay of the transient green species from zinc octaethylporphyrin (2e) and TTFA was therefore examined. Application of the usual spectroscopic techniques clearly established that this substance, isolated* crystalline in 74% yield, was zinc *meso*-trifluoroacetoxyoctaethylporphyrin (5). The ¹H n.m.r. spectrum indicated that *meso*-substitution had taken place, since



the *meso*-protons were observed as characteristic two- and one-proton singlets; a singlet in the ¹⁹F n.m.r.

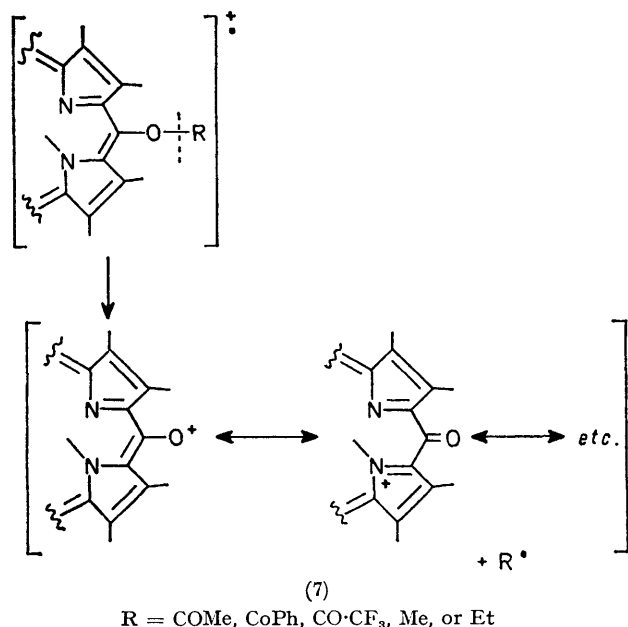
⁶ P. S. Clezy and A. J. Liepa, *Austral. J. Chem.*, 1970, **23**, 2477.

⁷ R. Bonnett and M. J. Dimsdale, *Tetrahedron Letters*, 1968, 731.

⁸ H. Fischer and H. Libowitzsky, *Z. physiol. Chem.*, 1938, **251**, 198; H. Libowitzsky, *ibid.*, 1941, **265**, 191; E. Stier, *ibid.*, 1942, **272**, 239.

⁹ R. Lemberg, B. Cortis-Jones, and M. Norrie, *Biochem. J.*, 1938, **32**, 171.

spectrum suggested the presence of a trifluoroacetyl function. This was confirmed by the i.r. spectrum, which showed a very sharp peak at 1795 cm^{-1} . The mass spectrum possessed a molecular ion [m/e (^{64}Zn) 708 (100%)] and a large fragment peak [m/e 611 (33%)] corresponding to loss of $\text{CO}\cdot\text{CF}_3$. Unlike porphyrins with normal bulky *meso*-substituents (which tend to undergo fragmentation at the porphyrin-substituent bond¹⁰), oxophlorin derivatives are characterised¹¹ by their tendency to follow fragmentation pathways which allow the oxophlorin oxygen atom to be retained by the macrocycle; this phenomenon is presumably a consequence of the extra charge stabilisation afforded by the ion (7).



When the zinc chelate (5) was treated with trifluoroacetic acid, the metal-free ligand (6) was obtained in good yield; the visible absorption spectrum of the latter was marginally of the 'aetio-' type¹² and the other spectroscopic properties were as expected by analogy with the zinc chelate and will not be further discussed. The identity of compound (6) was, however, confirmed by comparison with an authentic sample prepared from octaethyloxophlorin (3) with trifluoroacetic anhydride in pyridine. Brief treatment with aqueous alkali converted the *meso*-trifluoroacetoxy porphyrin (6) into oxophlorin (3), and also the zinc *meso*-trifluoroacetoxy porphyrin (5) into the corresponding zinc oxophlorin. The efficiency of these hydrolyses, and the relative ease of isolation and handling of the *meso*-trifluoroacetoxy porphyrins indicates that trifluoroacetoxy may be a

useful protecting or masking group for the carbonyl function of oxophlorins; *meso*-acetoxy-¹³ or *meso*-benzyloxy-⁷ derivatives have heretofore been employed, but low yields are usually encountered in the hydrolysis of these compounds to oxophlorins.

No attempt was made to isolate the *meso*-trifluoroacetoxy-intermediates from the oxophlorin synthesis involving magnesium octaethylporphyrin and TTFA, though visible absorption and i.r. spectroscopy confirmed their existence.

Preliminary experiments with other oxidants have shown that substitution of lead(IV) or mercury(II) trifluoroacetates for TTFA leads to the formation of the appropriate *meso*-trifluoroacetoxy porphyrins and oxophlorins after an acidic work-up. The yields of the latter were in each case less satisfactory than those from the TTFA reaction, and these oxidants offered no real advantages over the thallium salt. As mentioned earlier, treatment of zinc octaethylporphyrin with thallium(III) nitrate generated the transient green intermediate species, and on the basis of this observation, this alternative oxidant warranted further examination, though it was obvious that the same *meso*-substituted intermediates could not be obtained in this case. Acidic work-up of the thallium(III) nitrate reaction with zinc octaethylporphyrin gave rise to a very minor quantity of oxophlorin (3) (the origin of which was not further investigated) and demetallated starting material as the only recognisable products.

In an earlier paper¹⁴ we suggested that mechanisms involving radical processes would be likely for the *meso*-oxidation of porphyrins with TTFA, in contrast to those reactions of chlorins which underwent attack only at the *meso*-positions adjacent to the reduced ring, indicating electrophilic attack. The isolation of the *meso*-trifluoroacetoxy-intermediates (5) and (6) appeared to favour an ionic mechanism, though it was not obvious that the mechanisms of oxidation in the presence and absence of trifluoroacetic acid must be the same. Oxophlorins have been shown¹⁵ to be the keto tautomers of the phenolic analogues of porphyrins, and so it now seemed possible that the mechanism of oxophlorin formation from metalloporphyrins might be similar to that favoured¹⁶ for the conversion of benzenoid compounds into phenols with TTFA [*i.e.* electrophilic aromatic thallation to the arylthallium bis(trifluoroacetate) and collapse of this (by an unknown mechanism) to the aryl trifluoroacetate, followed by hydrolysis to the phenol]. Recent n.m.r. evidence¹⁷ which has demonstrated the intermediacy of the species (8) and (9) in the synthesis of phenols (10) from substituted benzenes with lead(IV) trifluoroacetate might also

¹⁰ E.g. D. R. Hoffman, *J. Org. Chem.*, 1965, **30**, 3512; B. V. Rozynov, A. F. Mironov, and R. P. Evstigneeva, *Khim. prirod. Soedinenii*, 1971, **7**, 197.

¹¹ K. M. Smith, Ph.D. Thesis, Liverpool, 1967.

¹² J. E. Falk, 'Porphyrins and Metalloporphyrins,' Elsevier, Amsterdam, 1964, p. 74.

¹³ A. H. Jackson, G. W. Kenner, G. McGillivray, and K. M. Smith, *J. Chem. Soc. (C)*, 1968, 294.

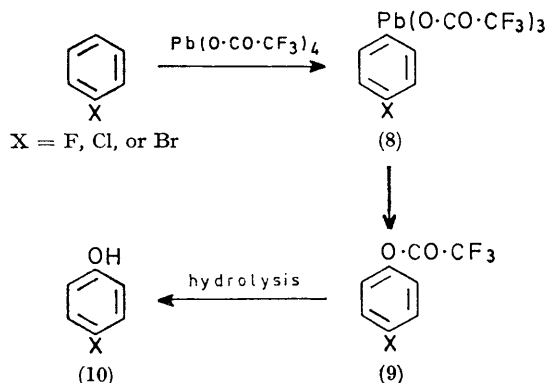
¹⁴ J. A. S. Cavaleiro and K. M. Smith, *Chem. Comm.*, 1971, 1384.

¹⁵ A. H. Jackson, G. W. Kenner, and K. M. Smith, *J. Amer. Chem. Soc.*, 1966, **88**, 4539; *J. Chem. Soc. (C)*, 1968, 302.

¹⁶ E. C. Taylor, H. W. Altland, R. H. Danforth, G. McGillivray, and A. McKillop, *J. Amer. Chem. Soc.*, 1970, **92**, 3520.

¹⁷ J. R. Campbell, J. R. Kalman, J. T. Pinhey, and S. Sternhell, *Tetrahedron Letters*, 1972, 1763.

appear to support the electrophilic substitution argument. However, we have found that electrophilic thallation of the porphyrin nucleus can be discounted,

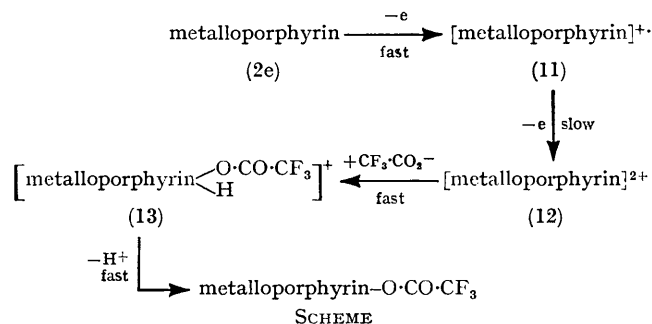


because the transient green species in the reactions show visible absorption and e.s.r. spectra similar to those from the π -cation radicals obtained¹⁸ from the appropriate metalloporphyrin and one equivalent of tris-(*p*-bromophenyl)ammoniumyl hexachloroantimonate.¹⁹ For example, the green species from dipyrindine-magnesium octaethylporphyrin (2d) showed a single e.s.r. line, width (peak-to-peak) 2.45 G at about g 2, whether generated with TTFA or the ammoniumyl salt; these values agree with the published data for the π -cation radicals of magnesium octaethylporphyrin obtained by electrolysis²⁰ or by chemical oxidation.²¹

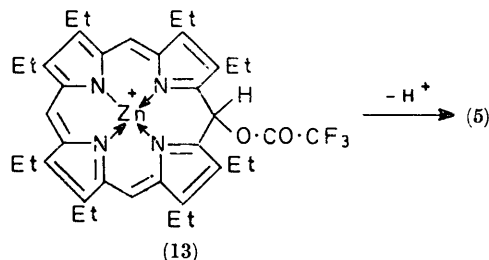
Since it is now established that the trifluoroacetoxylation step involves radical species, and that the first step is generation of the metalloporphyrin π -cation radical, there are three obvious mechanisms which can be suggested for the overall reaction: (1) combination of the π -cation radical with a trifluoroacetoxy radical [obtained by removal of one electron from a liberated trifluoroacetate anion or by disproportionation of an intermediate thallium(II) species], followed by loss of a proton; (2) removal of a second electron from the π -cation radical to give the π -dication, which is then attacked by trifluoroacetate anion and loses a proton; and (3) reaction of the metalloporphyrin π -cation radical with trifluoroacetate anion, followed by loss of a hydrogen atom.

The transformation of metalloporphyrin into metallo-*meso*-trifluoroacetoxy porphyrin clearly requires a two-electron change, and this is borne out by the stoichiometry of the reaction ($\text{Tl}^{\text{III}} \rightarrow \text{Tl}^{\text{I}}$). Mechanisms (1) and (2) differ only in the site from which the second electron is abstracted; mechanism (3) can be discounted since it is now well established²⁰ that metalloporphyrin π -cation radicals do not suffer attack by nucleophiles. In view of the expectation that trifluoroacetoxy

radicals would tend to undergo rapid decarboxylation, and since no trifluoromethyl-substituted products were isolated, mechanism (1) appears unlikely. However, mechanism (2) is supported by several observations in the literature. π -Cation radicals (11) of metalloporphyrins readily lose an electron to give²⁰ the π -dication (12), and these species are known²² to be very strong electrophiles. Thus, the general form of our favoured mechanism is as shown in the Scheme.



The fact that the π -dication (9) is not observed spectrophotometrically is presumably a consequence of the short lifetime of these species in the presence of nucleophiles, and the absence of any strong maxima in their visible absorption spectra.²⁰ It is interesting that metalloisoporphyrins similar to (13) have been isolated and characterised²² from the reaction of metalloporphyrin π -dications with nucleophiles; though not isolated in the present work, the same type of species [*e.g.* (13)] features prominently in our proposed mechanism (Scheme).



EXPERIMENTAL

M.p.s were measured on a hot-stage apparatus. Except where otherwise stated, neutral alumina (Brockmann grade III, Merck) was used for chromatographic separations. Electronic absorption spectra were determined with a Unicam SP 800 spectrophotometer, and n.m.r. spectra with a Varian HA-100 instrument (solutions in deuteriochloroform; tetramethylsilane as internal standard). Mass spectra were determined with an A.E.I. MS12 spectrometer (at 50 μA and 70 eV).

Dipyridinemagnesium Octaethylporphyrin (2d).—Octaethylporphyrin (500 mg) and commercial magnesium perchlorate (1.5 g) were suspended in pyridine (75 ml) and heated under reflux (oil-bath; 130°) during 30 min. After cooling, the mixture was diluted with ether (1 l) and

¹⁸ G. H. Barnett, S. W. McCombie, and K. M. Smith, unpublished results.

¹⁹ F. A. Bell, A. Ledwith, and D. C. Sherrington, *J. Chem. Soc. (C)*, 1969, 2719.

²⁰ J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *J. Amer. Chem. Soc.*, 1970, **92**, 3451.

²¹ J.-H. Fuhrhop and D. Mauzerall, *J. Amer. Chem. Soc.*, 1969, **91**, 4174.

²² D. Dolphin, R. H. Felton, D. C. Borg, and J. Fajer, *J. Amer. Chem. Soc.*, 1970, **92**, 743.

washed with water (3×500 ml) and finally with saturated brine (500 ml). The ether layer was dried (Na_2SO_4), diluted with n-hexane (200 ml), and then evaporated *in vacuo* to low volume. The product was filtered off, washed with n-hexane, and then dried *in vacuo* at room temperature. The filtrate was evaporated to dryness and the residue was crystallised from dichloromethane-n-hexane to give a second crop; total yield 680 mg (>95%) of glistening purple prisms.

Zinc Octaethylporphyrin (2e).—Octaethylporphyrin (400 mg) was dissolved in hot chloroform (200 ml) before addition of a solution of zinc acetate (500 mg) in methanol (100 ml) containing acetic acid (1 ml). The solution was then boiled gently, with periodic addition of small amounts of methanol, until most of the chloroform had been removed. After cooling, the product was filtered off, washed with methanol and ether, and then dried *in vacuo* at 100° , giving 410 mg (92%) of fluffy red needles.

Zinc Coproporphyrin-I Tetramethyl Ester.—Coproporphyrin-I tetramethyl ester²³ (100 mg) was dissolved in dichloromethane (50 ml) and a solution of zinc acetate (250 mg) in methanol (20 ml) and acetic acid (1 ml) was added. The mixture was heated under reflux during 10 min before evaporation of the dichloromethane. The product was filtered off, washed with a little methanol, and then dried *in vacuo* at 100° , giving 106 mg (>95%) of fluffy red needles, m.p. $302\text{--}303^\circ$ (lit.,²⁴ 299° corr.).

1,2,3,4,5,6,7,8-Octaethyl- α -hydroxyporphin † ('Octaethyl-oxophlorin') (3).—(a) From zinc octaethylporphyrin (2e) and TTFA. Zinc octaethylporphyrin (415 mg) in tetrahydrofuran (30 ml) and dichloromethane (100 ml) was treated with a solution of dry TTFA (480 mg, 1.25 equiv.) in tetrahydrofuran (20 ml) and then stirred during 1 min. Water (0.25 ml) in tetrahydrofuran (10 ml) was added, and after stirring for a further 10 min the solution was treated briefly with sulphur dioxide gas. Concentrated hydrochloric acid (2 ml) was added and the solution was stirred during 5 min before being poured into water (250 ml) and extracted with dichloromethane (250 ml). The organic phase was washed with water (2×500 ml), dried (Na_2SO_4), and evaporated to dryness; the residue was chromatographed on alumina (200 g) with dichloromethane as eluant. A small forerun containing pink material was discarded and the deep blue eluates were evaporated to dryness. Crystallisation of the residue from dichloromethane-methanol gave deep blue needles (302 mg, 79%), m.p. $254\text{--}256^\circ$ (when placed on a heated block at about 230° and then heated rapidly to the m.p.) (lit.,⁷ 255°) (Found: C, 78.5; H, 8.3; N, 10.2. Calc. for $\text{C}_{36}\text{H}_{46}\text{N}_4\text{O}$: C, 78.5; H, 8.4; N, 10.2%).

(b) From dipyrindinemagnesium octaethylporphyrin (2d). Dipyrindinemagnesium octaethylporphyrin (395 mg) was dissolved in tetrahydrofuran (30 ml) and dichloromethane (30 ml) and stirred during the rapid addition of TTFA (330 mg, 1.1 equiv.) in tetrahydrofuran (10 ml). After stirring for a further 15 min the solution was worked-up as in (a). Chromatography on alumina in dichloromethane gave octaethylporphyrin (54 mg), which was crystallised from dichloromethane-methanol, and then octaethyl-oxophlorin (168 mg, 55%), which was crystallised from the same solvent mixture. The latter product was identical with the octaethyl-oxophlorin obtained in (a).

† In earlier publications, e.g. ref. 13, it has been most convenient to name oxophlorins (in Experimental sections) systematically as derivatives of the tautomeric hydroxyporphyrin form.

(c) From zinc octaethylporphyrin (2e) and lead(IV) trifluoroacetate. Freshly prepared lead(IV) trifluoroacetate (194 mg, 1.5 equiv.) was stirred in dichloromethane (40 ml) and tetrahydrofuran (10 ml) and zinc octaethylporphyrin (50 mg) was added; stirring was then continued for a further 3.5 h. Concentrated hydrochloric acid (0.7 ml) was added and stirring was continued for 15 min before dichloromethane (100 ml) and dilute aqueous sodium hydrogen carbonate (2%; 100 ml) were added. The organic phase was separated, dried (Na_2SO_4), and evaporated to dryness to give a blue residue which was chromatographed on alumina (100 g), with dichloromethane as eluant. The first fraction, containing a little porphyrin together with brown by-products, was discarded, and the blue eluates were evaporated to dryness. The product was crystallised from dichloromethane-methanol giving 17.2 mg (37%) of the required oxophlorin, which was identical with the material described in (a).

(d) From zinc octaethylporphyrin (2e) and mercury(II) trifluoroacetate. To a stirred solution of zinc octaethylporphyrin (50 mg) in tetrahydrofuran (15 ml) and dichloromethane (10 ml) was added mercury(II) trifluoroacetate (90 mg, 2.5 equiv.). Stirring was continued for a further 1.5 h before dichloromethane (320 ml) was added, and the resultant solution was stirred at room temperature during 72 h. The solution was concentrated to low volume (ca. 20 ml) and then treated with concentrated hydrochloric acid (0.5 ml). After stirring during 15 min, dichloromethane (100 ml) was added and the solution was washed with water (2×100 ml), dried (Na_2SO_4), and evaporated to dryness. The residue was chromatographed on alumina (100 g), with dichloromethane as eluant. Evaporation of the eluates afforded octaethylporphyrin (13 mg), which was crystallised from dichloromethane-methanol, and then octaethyl-oxophlorin (9 mg, 19%), crystallised from the same solvent mixture. The oxophlorin was identical with the material synthesised as described in (a). Repetition of this reaction with zinc aetioporphyrin gave yields of the appropriate oxophlorin between 25 and 37%.

α -Hydroxy-2,4,6,8-tetrakis-(2-methoxycarbonyl)ethyl-1,3,5,7-tetramethylporphin ('Copro-oxophlorin-I Tetramethyl Ester') (4).—Zinc coproporphyrin-I tetramethyl ester (62 mg) in dichloromethane (25 ml) was stirred during the addition of TTFA (55 mg, 1.25 equiv.) in tetrahydrofuran (6 ml). Stirring was continued for a further 1 min before water (0.5 ml) in tetrahydrofuran (10 ml) was added. After 10 min, the solution was treated briefly with sulphur dioxide gas and was then stirred with concentrated hydrochloric acid (1 ml) during 2 min. Dichloromethane (100 ml) was added and the mixture was washed with dilute aqueous sodium hydrogen carbonate and then water. The organic phase was dried (Na_2SO_4) and evaporated to dryness, and the residue was chromatographed on alumina (100 g; Brockmann grade V) with dichloromethane as eluant. The dark blue eluates were evaporated to dryness and the residue was crystallised from dichloromethane-n-hexane to give the oxophlorin (35 mg, 60%), m.p. 239° (lit.,⁸ 258°) (Found: C, 66.2; H, 6.5; N, 7.8. Calc. for $\text{C}_{40}\text{H}_{46}\text{N}_4\text{O}_9$: C, 66.1; H, 6.4; N, 7.7%), τ ($\text{CF}_3\text{CO}_2\text{H}$) — 0.2 (2H, s) and 0.13 (1H, s) (*meso*-H), 5.6—5.9 (8H, m) and 6.6—7.0 (8H, m) ($\text{CH}_2\text{CH}_2\text{CO}$), 6.0 (3H, s) and 6.2 (9H, s)

²³ K. M. Smith, *J.C.S. Perkin I*, 1972, 1471.

²⁴ H. Fischer and H. Orth, 'Die Chemie des Pyrrols,' Akademische Verlag, Leipzig, vol. III, 1937, p. 486.

(OMe), and 6.48, 6.52, 6.54, and 6.77 (each 3H, s, β -Me), *m/e* 726(100%).

Zinc 1,2,3,4,5,6,7,8-Octaethyl- α -trifluoroacetoxyphorphin ('*Zinc meso-Trifluoroacetoxyoctaethylporphyrin*') (5).—Zinc octaethylporphyrin (150 mg) was dissolved in dichloromethane (60 ml) and tetrahydrofuran (30 ml) and then treated with TTFA (135 mg) in tetrahydrofuran (9 ml) and stirred during 5 min before addition of silica (10 g; Merck Kieselgel G). After a further 10 min the mixture was filtered through a bed of silica, which was washed with dichloromethane, and the combined filtrates were evaporated to dryness. The residue was crystallised from dichloromethane-n-hexane and afforded the *zinc chelate* (131 mg, 74%), with m.p. $>300^\circ$ (Found: C, 64.0; H, 6.1; N, 7.9; Zn, 9.2. $C_{38}H_{43}F_3N_4O_2Zn$ requires C, 64.3; H, 6.1; N, 7.9; Zn, 9.2%), λ_{max} (CH_2Cl_2) 404 (ϵ 329,000), 533 (16,000), and 571 nm (15,900), τ (ca. 0.08M) 0.17 (2H, s) and 0.72 (1H, s) (*meso*-H), 5.8–6.6 (16H, m, $CH_2\cdot CH_3$), 8.0–8.5 (24H, m, $CH_2\cdot CH_3$), ^{19}F δ 8.67 p.p.m. (s) downfield from $CF_3\cdot CCl_3$, ν_{max} (KBr) 1795 cm^{-1} (C=O), *m/e* (^{64}Zn) 708 (M^+ , 100%) and 611 ($M^+ - CO\cdot CF_3$, 33).

1,2,3,4,5,6,7,8-Octaethyl- α -trifluoroacetoxyphorphin ('*meso-Trifluoroacetoxyoctaethylporphyrin*') (6).—(a) *From zinc meso-trifluoroacetoxyoctaethylporphyrin*. The zinc chelate (50 mg) was kept in trifluoroacetic acid under nitrogen for 15 min, then poured into water and extracted with dichloromethane (3×50 ml). The organic phase was dried (Na_2SO_4) and evaporated to dryness and the red residue was crystallised from dichloromethane-methanol, to give the *meso-trifluoroacetoxyphorphyrin* (31 mg, 68%) \dagger m.p. 208–210° (Found: C, 70.65; H, 7.2; N, 8.5. $C_{38}H_{45}F_3N_4O_2$ requires C, 70.6; H, 7.0; N, 8.7%). λ_{max} (CH_2Cl_2) 399 (ϵ 156,000), 500 (14,300), 533 (7400), and 625 nm (2600), λ_{max} ($CH_2Cl_2 + 5\% CF_3\cdot CO_2H$) 411 (ϵ 323,000), 555 (15,700), and 599 nm (5200), τ 0.4 (2H, s) and 0.16 (1H, s) (*meso*-H), 5.8–6.4 (16H, m, $CH_2\cdot CH_3$), 8.17 (24H, t, $CH_2\cdot CH_3$), and 13.56br (2H, s, NH), ^{19}F δ 8.56 p.p.m. (s) downfield from $CF_3\cdot CCl_3$, ν_{max} (KBr) 1795 cm^{-1} (C=O), *m/e* 646 (M^+ , 100%) and 549 ($M^+ - CO\cdot CF_3$, 75).

(b) *From octaethylxophlorin* (3). Octaethylxophlorin (100 mg) in pyridine (10 ml) was treated with trifluoroacetic anhydride (1 ml) and after occasional swirling during

5 min the mixture was evaporated to dryness *in vacuo*. The residue was dissolved in dichloromethane (50 ml); the solution was washed with water (50 ml), dried (Na_2SO_4), and evaporated to dryness. The red residue crystallised from dichloromethane-methanol as purple prisms (81 mg, 76%), \dagger identical with the material described in (a).

Zinc 1,2,3,4,5,6,7,8-Octaethyl- α -hydroxyphorphin ('*Zinc Octaethylxophlorin*').—(a) *From octaethylxophlorin*. Octaethylxophlorin (75 mg) dissolved in dichloromethane (15 ml) was treated with a solution of zinc acetate (190 mg) in methanol (8 ml). The mixture was stirred during 5 min and then the dichloromethane was removed by evaporation. The *zinc chelate* was filtered off and washed well with methanol before recrystallisation from dichloromethane-methanol, which afforded 83 mg (99%) of product, m.p. $>300^\circ$ (Found: C, 70.4; H, 7.2; N, 9.3; Zn, 10.7. $C_{38}H_{44}N_4OZn$ requires C, 70.4; H, 7.2; N, 9.1; Zn, 10.65%), λ_{max} (CH_2Cl_2) 406 (ϵ 221,000), 534 (12,700), and 568 nm (6600), ν_{max} (CH_2Cl_2) 3630 cm^{-1} (OH), *m/e* (^{64}Zn) 612 (100%). The product was not soluble enough in $CDCl_3$ for n.m.r. data to be obtained.

(b) *From zinc meso-trifluoroacetoxyoctaethylporphyrin* (5). Zinc *meso*-trifluoroacetoxyoctaethylporphyrin (5 mg) was dissolved in tetrahydrofuran (10 ml) and treated with aqueous 0.5N-potassium hydroxide (0.5 ml) during 1 min. The green solution of the zinc oxophlorin anion¹⁵ was quickly poured into water (100 ml) and dichloromethane (100 ml) was added. The organic phase was separated, dried (Na_2SO_4), and evaporated to dryness to give the zinc oxophlorin (5 mg), which was crystallised from dichloromethane-methanol, and was identical with the product from (a). In particular, the i.r. spectrum showed no significant peak in the region 1700–1800 cm^{-1} , but a characteristic peak at 3630 cm^{-1} (OH).

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\dagger The mother liquors from these crystallisations contained octaethylxophlorin, which made up the mass balance for the reactions.