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MESO-OXIDATION OF SOME METALLOPORPHYRINS[1]

G. H. BARNETT, B. EVANS and K. M. SMITH*
The Robert Robinson Laboratories, University of Liverpool, P.O. Box 147,
Liverpool L69 3BX

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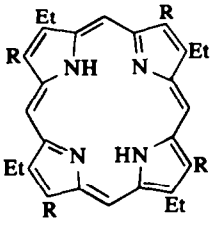
Abstract—Treatment of porphyrins with thallium(III) trifluoroacetate in the presence of trifluoroacetic acid results in uncontrolled oxidation at the macrocyclic *meso*-positions, presumably *via* radical processes. For example, a mixture of the thallium(III) $\alpha\gamma$-dioxoporphodimethene (**4a**; R = Et), the $\alpha\beta\gamma$-trioxo compound (**3**), and octaethylxanthoporphyrinogen (**6**) is obtained when octaethylporphyrin (**1**; R = Et) is oxidised in the presence of air. More controlled oxidation is achieved when the *meso*-trifluoroacetoxyporphyrin complexes (**8a, b**) or metallo-oxophlorins (**7a, b**) are treated with mild bases in air, the major products being metallo-$\alpha\gamma$-dioxoporphodimethenes (**4b, c**).

β-Hydroxy-α-oxophlorins (**16**) are isolated and characterised for the first time; aspects of the chemistry of this novel oxygenated porphyrin system are reported.

Thallium(III) complexes of porphyrins are readily obtained[1,2] by treatment of porphyrins [e.g. octaethylporphyrin (1; R = Et)] with thallium(III) salts. The products (**2a**) are inert towards attack[2,3] by excess thallium(III) trifluoroacetate (TTFA) owing to the high first and second oxidation potentials (1·00 and 1·31 V vs S.C.E.)[4] of thallium(III) porphyrins; interestingly, the thallium atom protects the macrocyclic nucleus from oxidation but allows efficient modification of labile side-chains.[5] In contrast, zinc(II) and magnesium(II) porphyrins (and others with low[4] oxidation potentials) do react at the nucleus with TTFA to furnish *meso*-trifluoroacetoxyporphyrins[6] and eventually oxophlorins.[6,7] Through a basically similar reaction, chlorins afford *meso*-trifluoroacetoxychlorins[8] and then 1,2-dihydro bile pigment analogues.[8,9]



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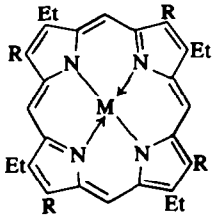
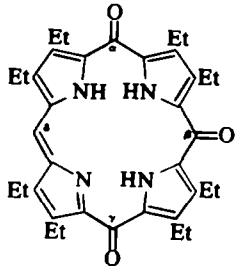


2

a: M = Tl – X
b: M = Mg
c: M = Zn

With excess of TTFA in the presence of trifluoroacetic acid, octaethylporphyrin (1; R = Et) reacted, almost certainly as its thallium(III) complex, affording a complex mixture of oxidation and chelation products which were separable by chromatography on alumina. The major product was thallium(III) octaethylporphyrin (**2a**; R = Et, X = OH) and this was the least polar component of the mixture. A red-brown band was next eluted and from this was isolated the novel $\alpha\beta\gamma$-trioxo-macrocycle (**3**); the metal-free compound was presumably isolated because the system is not sufficiently acidic to survive the work-up as a metal complex. The mass spectrum of this compound (**3**) was misleading in that it showed strong "M + 2" ions (cf. Ref. 10), but the structure was conclusively confirmed by elemental analysis and the NMR spectrum, which featured a one proton singlet at τ 3·04 (methine-H).



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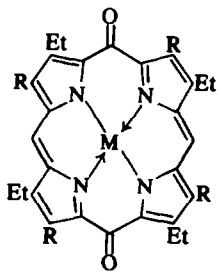
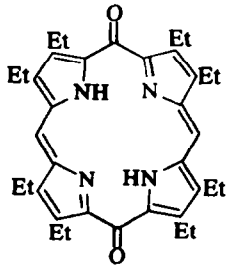


4

a: M = Tl–OH, H_2O
b: M = Mg
c: M = Zn

An orange-red band was next eluted and the substance isolated from this was shown to contain thallium by its NMR spectrum, which showed a two proton doublet (J_{Tl-H} 20 Hz) at τ 3·34, and by its mass spectrum, which indicated the presence of thallium in some ions. Mass spectrometry is less unequivocal for identification of thallium owing to the tendency of thallium(III) porphyrins to lose the metal atom in the source of the spectrometer.[11] The structure (**4a**; R = Et) was assigned to this substance on the above evidence, as well as the combustion analysis. Further confirmation was obtained by treatment of (**4a**; R = Et) with cold trifluoroacetic acid to give a high yield of the metal-free ligand (**5**). The physical constants showed this compound to be the same as that obtained[10] by ferric chloride oxidation of zinc(II) *meso*-amino-octaethylporphyrin, followed by hydrolysis and demetallation.



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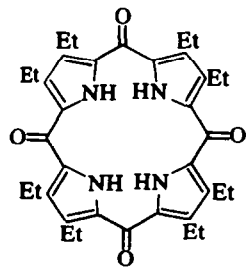

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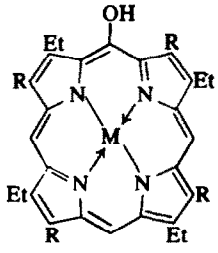
The final compound obtained from the column was not the least mobile component of the mixture, but it was eluted last because of its insolubility in methylene chloride; addition of a small amount of methanol to the eluting solvent facilitated the isolation of octaethylxanthoporphyrinogen (**6**) which was compared successfully with a sample of authentic material.[12,13]

In connection with attempts to prepare metallooxophlorins (**7**)† directly from metalloporphyrins [the oxophlorin synthesis[8] utilises acid treatment of metallo-*meso*-trifluoroacetoxyporphyrins (**8**) which cleaves the trifluoroacetoxyl group with concomitant demetallation], we attempted alkaline hydrolysis of the trifluoroacetoxy intermediates (**8**) because this should leave the central metal atom intact. In an earlier paper we reported[8] that the



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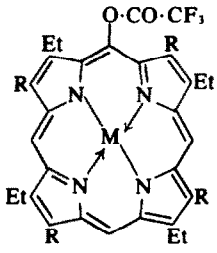
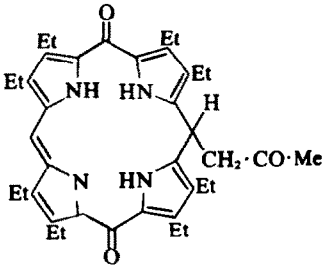


8

a: M = Zn
b: M = Mg
c: M = Tl–OCOCF$_3$

zinc(II) *meso*-trifluoroacetoxyporphyrin (**8a**; R = Et) was transformed into zinc(II) octaethyloxophlorin (**7a**; R = Et) by very brief treatment with dilute aqueous alkali, the reaction proceeding through the mono-anion. Similarly, treatment of the magnesium(II), zinc(II) and thallium(III) aetioporphyrin-I complexes [(**7b**, **7a**, **7c**; R = Me) respectively] with dilute alkali in complete absence of air gave rapidly the appropriate mono-anion (**9**; R = Me) (spectrophotometric analysis). The green anion in the thallium(III) case appeared to be fairly stable when exposed to air, though, over a period it decomposed to uncharacterised by-products. The zinc(II) oxophlorin anion reacted with methyl iodide (*cf.* Ref. 14) to give the zinc(II) *meso*-methoxyaetioporphyrin-I (**10**); when exposed to air, the anion (**9**) from (**7a**; R = Me) was slowly transformed into the zinc(II) $\alpha\gamma$-dioxoporphodimethene (**4c**; R = Me). However, the best yield of zinc(II) dioxoporphodimethene was obtained by shaking a solution of the zinc(II) oxophlorin (**7a**; R = Me) in tetrahydrofuran and methanol containing solid sodium carbonate.

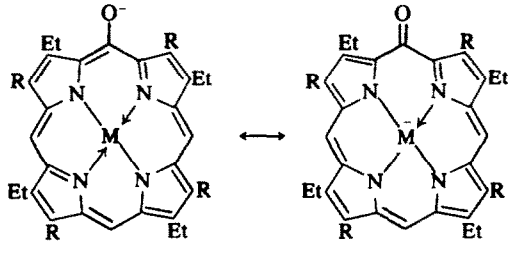
In spectroscopic experiments, the anion (**9**; R = Me) from the magnesium(II) *meso*-trifluoroacetoxyporphyrin (**7b**; R = Me) reacted very rapidly with oxygen to give the magnesium(II) $\alpha\gamma$-dioxoporphodimethene (**4b**; R = Me). Owing to further reactions of the product, the transformation gave only moderate yields of (**4b**; R = Me) on the preparative scale; for example, if the anion was prepared from (**7b**; R = Et) using sodium carbonate in damp acetone, the product (**11**) was obtained, presumably due to nucleophilic attack of the anion from acetone upon the pyrromethene system of the magnesium(II) $\alpha\gamma$-dioxoporphodimethene (**4b**; R = Et). Analogous reactions of dioxoporphodimethenes with alkyl lithium reagents afford products with alkyl substituents at the interpyrrolic carbon atom.[15]



11

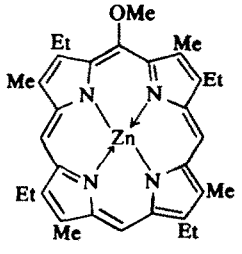
Since the rate of transformation of the anion (**9**) into $\alpha\gamma$-dioxoporphodimethene (**4**) appears to parallel the trend in oxidation potential of the corresponding metalloporphyrins (e.g.[4] $E^1_{1/2}$ MgOEP, 0·54; ZnOEP, 0·63; TlOEP(OH), 1·0 V) in any given solvent system, we presume that the rate determining step for this reaction is removal of one electron from the anion (**9**) to give the radical (**12**) (Scheme 1). This could react with triplet oxygen to give (**13**) which might abstract an electron [possibly from another molecule of the oxophlorin anion (**9**)] and a proton (from the medium) to give the hydroperoxide (**14**). Loss of water would lead directly to the metallo-$\alpha\gamma$-dioxoporphodimethene. Similar reactions of oxophlorin radicals with oxygen have been reported by Fuhrhop *et al.*[16a]

Significantly, oxophlorin complexes with metals such as zinc(II) and magnesium(II) react with oxygen at the methine position opposite to the oxophlorin O atom, whereas iron(III) oxophlorins[17,18] zinc(II) oxochlorins[8] and zinc(II) oxophlorins[16b] (photochemical reaction) react by addition of molecular oxygen across the oxo-group in the macrocycle. The appropriate oxidation potentials



9

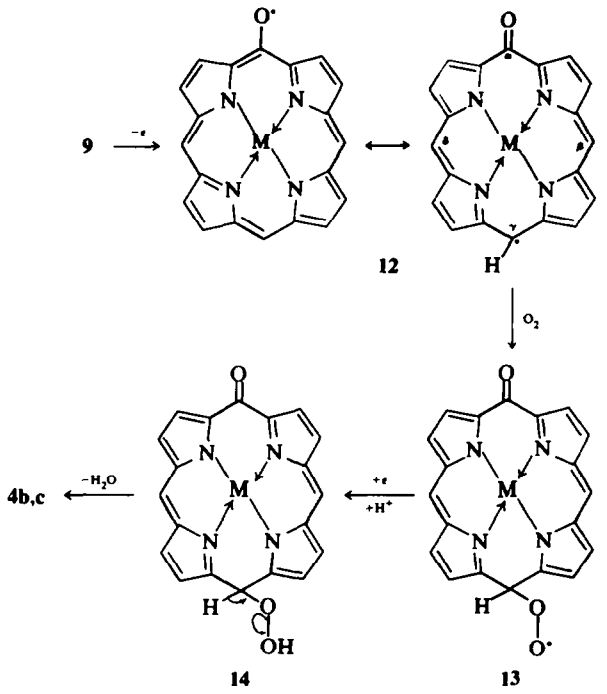
M = Mg; Zn, Tl–OH



10

†Owing to the lability of oxophlorins and some of their metal complexes, particularly towards oxidation, we have experienced some difficulty in the insertion of certain metal ions into the oxophlorin chromophore.

presumably dictate that these reactions with oxygen occur on a radical species of the macrocycle (*cf* Ref. 8), and one therefore needs to explain why, in the case of the iron(III) oxophlorin radical, for example, the free electron is

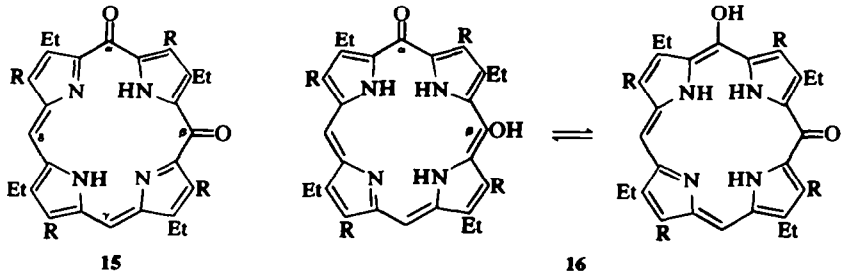


Scheme 1.

stabilised on a carbon atom adjacent to the oxophlorin CO group rather than on the other side of the macro-ring. One significant factor in this difference between iron(III) and other oxophlorins is the site from which the electron is removed. Abstraction of one electron from most metalloporphyrins gives π-cation radicals in which the electron has been removed from the organic ligand; however, in the case of iron porphyrins it is reported[19] that the electron is removed from the metal atom, giving an iron(IV) porphyrin. Hence, the apparent different reactivity towards molecular oxygen between iron(III) and other oxophlorins may be due to the fact that in the iron case the species actually produced is an iron(IV) oxophlorin; this might behave differently towards oxygen, perhaps by interaction with the oxygen at the metal followed by delivery of it to the area of the oxophlorin carbonyl. Iron(IV) porphyrins have recently been implicated[20] as intermediates in the functioning of catalase and peroxidase. Bonnett[21] has shown that the ability of iron(II) porphyrins to be converted into iron(III) oxophlorins is directly attributable to the ability of the metal to pass from iron(II) to iron(III); it is tempting to postulate that the further reaction of iron(III) oxophlorins to give ring-opened pigments is associated with the facility of the metal to go from its +3 to its +4 state. A combination of these factors, even neglecting its oxygen binding characteristics, makes iron a very special metal indeed.

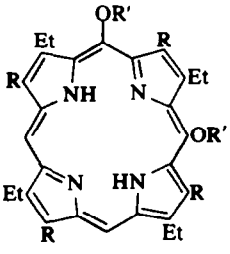
In the synthesis of oxophlorins[6,7] from zinc(II) and magnesium(II) porphyrins using TTFA we noted[7] the existence of small amounts of a pink by-product which was usually discarded. However, when larger excesses of TTFA were used the amounts of this by-product, especially in the aetioporphyrin-I case, were dramatically increased. We and others[16] have shown that a polar by-product from this synthesis is the $\alpha\gamma$-dioxoporphodimethene (e.g. **5**), and it seemed likely that the red-pink by-product might be the corresponding $\alpha\beta$-dioxo-isomer (**15**) because (i) the electronic absorption spectrum approximated to that expected for a compound with only three pyrrole rings in conjugation, and (ii) it was not obvious why all of the dioxoporphodimethene should have the $\alpha\gamma$-orientation of the CO groups. On the basis of the reasoning in Scheme 1, a resonance form of (**12**) with the radical located at the β or δ position is possible, though calculations might not favour this over the γ-radical.

The possibility that the red-pink by-product might be (**15**) was excluded by examination of the NMR spectrum which showed two non-equivalent methene protons, sharp singlets in the octaethyl case at τ 3·42 and 5·38, but somewhat broader in the aetio-I derivative. The mass spectrum suggested a molecular weight two mass units higher than expected on the basis of the formulation (**15**), but this was not strong evidence against it because the



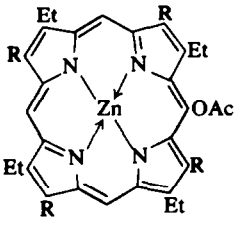
$\alpha\gamma$-isomer shows[10] strong "M+2" ions in its spectrum.

We assign the tautomeric β-hydroxy-α-oxophlorin structure (**16**) to the by-product on the following evidence: (i) Treatment with acetyl chloride in pyridine gave the $\alpha\beta$-di-acetoxyporphyrin (**17a**) which possessed a characteristic "phyllo" electronic absorption spectrum, and established that the unknown was at the porphyrin oxidation level and not at the di-dehydro-state required by structure (**15**). Use of benzoyl chloride in place of acetyl chloride gave the corresponding di-benzoyloxy derivative (**17b**). (ii) Treatment of zinc(II) *meso*-acetoxyporphyrins (**18**) with TTFA followed by an acidic work-up gave the



17

a: R′ = CO·CH₃
b: R′ = CO·Ph

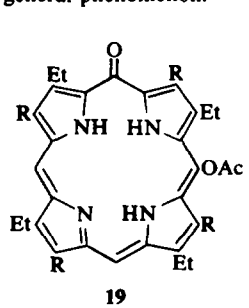


18

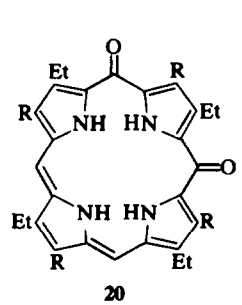
β-acetoxy-α-oxophlorin (**19**) which showed non-equivalent *meso*-protons in its NMR spectrum and could be converted into the bis-acetoxy-derivative (**17a**) by treatment with acetic anhydride in pyridine, or else hydrolysed to the hydroxy-oxophlorin (**16**). (iii) Treatment of zinc(II) octaethylporphyrin, or better, zinc(II) aetioporphyrin-I, with 2 equivalents of TTFA gave a good yield of the hydroxy-oxophlorin (**16**) after the usual acid work-up which accomplishes demetallation and hydrolysis of the *meso*-trifluoroacetoxy derivatives; the reaction presumably proceeds through the $\alpha\beta$-bis-trifluoroacetoxy zinc complex.

The β-hydroxy-α-oxophlorins (**16**) presumably exist in the hydroxy-oxo form rather than the $\alpha\beta$-dioxo-form (**20**) because of the steric constraints inherent with compounds (e.g. porphyrin dications[22]) having *four* inner hydrogen atoms. The molecule appears to prefer the tautomeric form (**16**) rather than lose aromaticity due to ring buckling inherent in structure (**20**).

It is not clear why these *meso*-substituted metalloporphyrins undergo further substitution at an adjacent rather than opposite *meso*-position. Preliminary experiments with metalloporphyrins with other *meso*-substituents indicate that the tendency towards α,β-di-substitution is a general phenomenon.



19



20

EXPERIMENTAL

M.ps 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 (in methylene chloride soln) were determined with a Unicam SP 800 spectrophotometer, and NMR spectra with a Varian HA-100 instrument (solns in $CDCl_3$; TMS as internal standard). Mass spectra were determined with an A.E.I. MS 12 spectrometer (at 50 μA and 70 eV).

Treatment of octaethylporphyrin with thallium(III) *trifluoroacetate and trifluoroacetic acid.* Octaethylporphyrin (500 mg) was dissolved in TFA (2 ml) and CH_2Cl_2 (10 ml) before treatment with a stock soln[23] of 0·88 M TTFA in TFA (3 ml). The soln was allowed to stand at room temp for 10 min before being poured into water (100 ml), diluted with CH_2Cl_2, extracted, separated, and the organic phase dried ($MgSO_4$). The filtered soln was evaporated to dryness and the residue was chromatographed on alumina (300 g). Elution with CH_2Cl_2, followed by evaporation of the eluates gave the following compounds:

(A) *Thallium*(III) *octaethylporphyrin hydroxide* (**2a**; R = Et), 322 mg, identical with a sample described earlier.[2]

(B) $\alpha\beta\gamma$-Tri-oxo-octaethylporphomethene (**3**), 32 mg, m.p. 228–230° from CH_2Cl_2/MeOH. (Found: C, 74·5; H, 7·6; N, 9·65. $C_{36}H_{44}N_4O_3$ requires: C, 74·45; H, 7·6; N, 9·65%); λ_{max} 336 (ϵ 35,600), 397 (18,000), and 540 nm (8000); *m/e* (%), 582 (80) and 580 (100); τ, −0·33 (2NH), 3·04 (methine-H), 7·0–7·6 (16H, m, CH_2CH_3), and 8·6–9·0 (24H, m, CH_2CH_3).

(C) *Thallium*(III) $\alpha\gamma$-*dioxo-octaethylporphodimethene hydroxide* (**4a**; R = Et), 27 mg, m.p. 259–263° from CH_2Cl_2/MeOH. (Found: C, 54·15; H, 5·5; N, 7·3. $C_{36}H_{45}N_4O_4Tl$ requires: C, 53·9; H, 5·65; N, 7·0%); λ_{max} 328 (ϵ 34,600), 444 (64,000), 542 infl (12,700), and 575 nm (32,300); *m/e* (%) 802(15), 800(6), 768–765 (5–2), 564(100); τ, 3·34 (2 methine-H, d, J = 20 Hz), 7·1–7·8 (16H, m, CH_2CH_3), and 8·7–9·0 (24H, m, CH_2CH_3).

(D) After addition of 5% MeOH to the elution solvent, *octaethylxanthoporphyrinogen* (**6**), 107 mg, m.p. 273–274° (lit.[12] 272–276°) from MeOH, was obtained, *m/e* 596 (100%).

The overall recovery of macrocyclic material from this reaction was approx 75%, and in subsequent experiments, the relative proportions of the products was shown to depend upon the duration of the reaction. When thallium(III) octaethylporphyrin hydroxide (322 mg, from above) was similarly treated with TTFA in TFA and CH_2Cl_2 during 5 min before work-up and chromatography as before, the product composition was: (**2a**; R = Et) 121 mg; (**3**) 84 mg; (**4a**; R = Et) 94 mg; and (**6**) 5 mg.

$\alpha\gamma$-*Di-oxo-octaethylporphodimethene* (**5**). Thallium(III) $\alpha\gamma$-di-oxo-octaethylporphodimethene (31 mg) was allowed to stand at room temp in TFA (5 ml) during 3 min. CH_2Cl_2 and $NaHCO_3$ aq were added and the organic phase was washed with H_2O, dried ($MgSO_4$), evaporated to dryness, and the residue was chromatographed on alumina (elution with CH_2Cl_2). Evaporation of the eluates and crystallisation from CH_2Cl_2/MeOH gave the porphodimethene as long brown needles (20·5 mg; 94%), m.p. 271–273° (lit.[10] 272–274°). (Found: C, 76·4; H, 8·0; N, 9·65. Calc. for $C_{36}H_{44}N_4O_2$: C, 76·6; H, 7·85; N, 9·9%); λ_{max} 315 (ϵ 33,000), 408 (70,000), and 492 nm (15,000); *m/e* (%), 566(30) and 564(100); τ, 3·32 (2 methine-H), 7·29 (8H, q) and 7·50 (8H, q) CH_2CH_3, 8·86 (12H, t) and 8·88 (12H, t) CH_2CH_3.

Aetio-oxophlorin-I. Aetioporphyrin-I (1 g) was dissolved in boiling chloroform (500 ml) and treated with a saturated soln of zinc acetate in MeOH (2 ml) before heating under reflux for a further 5 min. The soln was concentrated to *ca.* 100 ml, diluted with MeOH (100 ml) and the cooled solution was filtered to give zinc(II) aetioporphyrin-I (1·082 g; 95·5%). This was dissolved in dry THF (150 ml) and $CHCl_3$ (700 ml), treated with TTFA (1·18 g; 1·1 equiv) in THF (50 ml), and stirred for 1 min before treatment briefly with SO_2 gas, and addition of conc HCl (5 ml). The solution was stirred for 5 min before addition of CH_2Cl_2 and H_2O. The organic phase was washed with more water, dried (Na_2SO_4), and evaporated to dryness to give a residue which was chromatographed on alumina (elution with CH_2Cl_2). A forerun containing $\alpha\gamma$-di-oxo-aetioporphodimethene-I and β-hydroxy-aetio-oxophlorin-I (**16**; R = Me) (see later) was discarded; the subsequent deep blue eluates were evaporated and crystallisation from CH_2Cl_2/MeOH gave the required *oxophlorin* (756 mg; 78% from aetioporphyrin-I), m.p. >300°. (Found: C, 77·7; H, 7·9; N, 11·5. $C_{32}H_{38}N_4O$ requires: C, 77·7; H, 7·7; N, 11·3%); λ_{max} 402 (ϵ

90,000), 582 (7800), and 629 nm (14,100); in CH_2Cl_2 + 5% TFA, 409 (ε 187,000), 556 (8500), and 607 nm (8700); *m/e* 494 (100%); ν_{max} (KBr) C=O 1595 cm^{-1}; NMR in TFA, τ, −0·28 (2H, *meso*-H), 0·01 (1 *meso*-H), 5·8–6·4 (8H, m, CH_2CH_3), 6·52, 6·54, 6·55, and 6·66 ($4CH_3$), 8·27, 8·29, 8·39, and 8·44 (each 3H, t, CH_2CH_3).

Zinc(II) meso-*trifluoroacetoxyaetioporphyrin*-I (**8a**; R = Me)

(A) *From zinc*(II) *aetioporphyrin*-I *by treatment with TTFA.* Zinc(II) aetioporphyrin-I (300 mg) in THF (50 ml) and CH_2Cl_2 (100 ml) was treated with TTFA (330 mg; 1·1 equiv) in THF (20 ml). After stirring for 1 min the soln was treated with TLC grade Kieselgel G (*ca* 10 g) and the suspension was evaporated to dryness. CH_2Cl_2 (50 ml) was added and then likewise evaporated. More CH_2Cl_2 was added and the soln was filtered through a sintered glass funnel; concentration to low volume and addition of MeOH gave the required *zinc complex* (331 mg, from 3 crops; 91%), m.p. >300°. (Found: C, 60·8, 60·8; H, 5·6, 5·4; N, 8·5, 8·5; Zn, 9·7. $C_{34}H_{35}F_3N_4O_2Zn.H_2O$ requires: C, 60·8; H, 5·55; N, 8·3; Zn 9·7%); λ_{max} 402 (ε 352,700), 532 (16,800), and 572 nm (17,800); *m/e* (%) (^{64}Zn), 652 (100), 558 (30), and 326 (17); ν_{max} (KBr) C=O 1790 cm^{-1}; τ, 0·14 (2H, *meso*-H), 0·61 (1 *meso*-H), 5·8–6·6 (8H, m, CH_2CH_3), 6·32, 6·35, 6·36, 6·44 ($4CH_3$), 8·0–8·4 (12H, m, 4 CH_2CH_3) (spectrum concentration dependent.[24])

(B) *From* meso-*trifluoroacetoxyaetioporphyrin*-I. *meso*-Trifluoroacetoxyaetioporphyrin-I (50 mg) in $CHCl_3$ (30 ml) was treated with zinc acetate (100 mg) in MeOH (6 ml) and swirled for 5 min (spectrophotometry showed metal insertion to be complete). The mixture was poured into H_2O, extracted with CH_2Cl_2, washed three times with H_2O, and after drying of the organic phase (Na_2SO_4) and evaporation to dryness, the residue was crystallised from CH_2Cl_2/heptane to give the product (51 mg; 90%) identical with the sample described above.

meso-*Trifluoroacetoxyaetioporphyrin*-I. (*A*) *From aetio-oxophlorin*-I.-Aetio-oxophlorin-I (200 mg) in $CHCl_3$ (50 ml) was treated with trifluoroacetic anhydride (1·5 ml) added dropwise to the stirred solution. After 15 min the mixture was washed with H_2O, dried (Na_2SO_4), and evaporated to dryness. Crystallisation of the residue from CH_2Cl_2/hexane gave the required meso-*trifluoroacetoxyporphyrin* (218 mg; 90%), m.p. 280–286° dec., (Found: C, 67·15, 67·1, 67·25; H, 6·2, 6·3, 6·2; N, 9·3, 9·4. $C_{34}H_{37}F_3N_4O_2.H_2O$ requires: C, 67·1; H, 6·5; N, 9·2%); λ_{max} 400 (ε 154,000), 499 (14,500), 532 (7000), 571 (5700) and 624 nm (2700); in CH_2Cl_2 + 5% TFA, 409 (ε 238,000), 553 (16,000) and 597 nm (4500); *m/e* 590 (100%), 493 (70); ν_{max} (KBr) 1795 cm^{-1}; τ, −0·02 (2H, *meso*-H), 0·03 (1 *meso*-H), 5·8–6·2 (8H, m, CH_2CH_3), 6·43, 6·45, 6·48 and 6·58 ($4CH_3$), 8·0–8·4 (12H, m, CH_2CH_3).

Evaporation and chromatography of the mother liquors from the crystallisation (alumina, CH_2Cl_2) afforded a small quantity of the corresponding oxophlorin.

(B) *From zinc*(II) meso-*trifluoroacetoxyaetioporphyrin*-I. Zinc(II) *meso*-trifluoroacetoxyaetioporphyrin-I (200 mg) was stirred at room temp in dry TFA (20 ml) and CH_2Cl_2 (10 ml) during 50 min. The solvents were evaporated and the residue was dissolved in CH_2Cl_2, washed with H_2O, dried (Na_2SO_4), and evaporated to dryness. The residue was crystallised from CH_2Cl_2/MeOH to give the product (151 mg; 84%) identical with the material from (A). Chromatography of the mother liquors on alumina (Grade V) (elution with CH_2Cl_2), followed by crystallisation from CH_2Cl_2/MeOH gave aetio-oxophlorin-I (8 mg).

meso-*Acetoxyaetioporphyrin*-I. Aetio-oxophlorin-I (50 mg) was dissolved in pyridine (1 ml) by heating briefly at 75°. To this soln was added Ac_2O (0·2 ml) and after 10 min the mixture was diluted with toluene (250 ml) and evaporated. More toluene was added and the remaining pyridine was azeotroped off. The residue was chromatographed on alumina (elution with CH_2Cl_2) and the red eluates were evaporated to dryness and crystallised from CH_2Cl_2/MeOH to give the required meso-*acetoxyporphyrin* (51·5 mg; 95%), m. p. >300°. (Found: C, 76·1; H, 7·6; N, 10·5. $C_{34}H_{40}N_4O_2$ requires: C, 76·1; H, 7·6; N, 10·4%); λ_{max} 402 (ε 160,000), 500 (14,100), 533 (5200), 572 (5000) and 625 nm (1600); in CH_2Cl_2 + 5% TFA, 411 (ε 285,000), 554 (14,400) and 596 nm (3400); *m/e* (%), 536 (50), 494(100), 247 (7); ν_{max} (KBr) C=O 1760 cm^{-1}; τ, −0·09 (2H, *meso*-H), 0·08 (1 *meso*-H), 5·8–6·2 (8H, m, CH_2CH_3), 6·42, 6·43, 6·46, and 6·54 ($4CH_3$), 8·10 ($COCH_3$), 8·0–8·3 (12H, m, CH_2CH_3).

Zinc(II) *aetio-oxophlorin*-I (**7a**; R = Me). Aetio-oxophlorin-I (100 mg) in $CHCl_3$ (30 ml) was refluxed and then treated with zinc acetate (500 mg) in MeOH (20 ml). The *product* precipitated upon concentration of the soln and was recrystallised from THF/CH_2Cl_2/hexane to give 108 mg (96%) of red-brown prisms, m.p. >300°. (Found: C, 68·75; H, 6·4; N, 9·9; Zn, 11·65. $C_{32}H_{36}N_4OZn$ requires: C, 68·9; H, 6·5; N, 10·0; Zn, 11·7%); λ_{max} 412 (ε 172,000), 540 (8600), and 574 nm (4550); *m/e* (^{64}Zn) 556 (100%). This compound was not sufficiently soluble in $CDCl_3$ for its NMR spectrum to be measured.

Magnesium(II) meso-*trifluoroacetoxyaetioporphyrin*-I (**8b**; R = Me). (This compound was prepared for use in spectroscopic experiments, and owing to difficulties in separation from starting material (*cf* Ref. 6) while preserving the labile $OCOCF_3$ group, together with possible axial ligation at the metal, an analytically pure sample was not obtained.) Dipyridine magnesium(II) aetioporphyrin-I (prepared from aetioporphyrin-I by treatment with magnesium perchlorate in pyridine[cf6]) (132 mg) in $CHCl_3$ (50 ml) was treated with TTFA (114 mg) in THF (10 ml). After stirring for 2 min, TLC grade Kieselgel G (10 g) was added and the solvent was evaporated to dryness. CH_2Cl_2 was added, the suspension was filtered and the filtrate was washed with H_2O, dried (Na_2SO_4), and evaporated to dryness to give a residue which was crystallised from $CHCl_3$/heptane to give the porphyrin (56 mg), m.p. >300°. Analytical TLC showed the product to be contaminated with a small amount of magnesium(II) aetioporphyrin-I. *M/e* 612 (100%), 500 (100).

Thallium(III) meso-*trifluoroacetoxyaetioporphyrin*-I *trifluoroacetate* (**8c**; R=Me). *meso*-Trifluoroacetoxyaetioporphyrin-I (236 mg) in $CHCl_3$ (100 ml) was treated with TTFA (228 mg; 1·05 equiv) in CH_3CN (20 ml) and then swirled for 2 min. TLC grade Kieselgel G (10 g) was added and the suspension was evaporated to dryness. $CHCl_3$ was then added and the silicagel was removed by filtration through a sintered glass disc. The filtrate was evaporated to dryness and the residue was crystallised from CH_2Cl_2/heptane to give the *product* (231 mg; 64%), m.p. >300°. A satisfactory elemental analysis for this material could not be obtained, presumably owing to contamination with small amounts of product with hydroxide or chloride axial ligands (Found: C, 48·5; H, 4·5; N, 6·1. $C_{36}H_{33}F_6N_4O_4Tl$ requires: C, 47·7; H, 3·9; N, 6·2%); ν_{max} (KBr) 1795 cm^{-1}, compound was not sufficiently soluble in $CDCl_3$ for its NMR spectrum to be measured.

Magnesium(II) *αγ-dioxo-octaethylporphodimethene* (**4b**; R = Et). Dipyridine magnesium(II) octaethylporphyrin[6] (100 mg) in CH_2Cl_2 (40 ml) was treated with TTFA (84 mg; 1·1 equiv) in THF (15 ml), stirred for 10 min, and then evaporated to dryness. The solid was dissolved in THF (50 ml) and water (25 ml) and then titrated with 0·5% w/v aqueous sodium hydroxide until the absorption maxima at 520, 560 nm increased no further. The mixture was poured into water, extracted with CH_2Cl_2, and this was dried (Na_2SO_4) and evaporated to dryness. The residue was chromatographed on alumina (Grade V) (elution with CH_2Cl_2); evaporation of the orange eluates and crystallisation from ether/hexane gave the *product* (11 mg; 13%) (spectroscopic scale experiments indicated almost quantitative conversion of the magnesium(II) *meso*-trifluoroacetoxyporphyrin into magnesium(II) dioxoporphodimethene), m.p. >300°. (Found: C, 73·4; H, 7·3; N, 9·4; Mg, 4·6.* $C_{36}H_{42}MgN_4O_2$ requires: C, 73·65; H, 7·2; N, 9·5; Mg, 4·1%); λ_{max} (in ether), 327 (ε 36,100), 446 (68,300), 522 (12,750), and 560 nm (49,000); *m/e* 586 (100%) and 293 (10); ν_{max} (KBr) 1580 cm^{-1}, τ, 3·30 (2 methine-H), 7·1–7·8 (16H, m, CH_2CH_3), 8·8–9·1 (24H, m, CH_2CH_3).

αγ-Dioxo-β-(2-oxopropyl)-octaethylporpho-δ-methene (**11**). Magnesium octaethylporphyrin (150 mg) in CH_2Cl_2 (100 ml) was treated with TTFA (125 mg; 1·1 equiv) in THF (25 ml) with swirling for 2 min. The mixture was washed with water, dried (Na_2SO_4), evaporated to dryness, and then stirred during 30 min with a suspension of K_2CO_3 (1 g) in acetone (10 ml). Water and CH_2Cl_2 were added, the organic phase was dried (Na_2SO_4),

*High Mg figure is due to hygroscopic MgO.

evaporated, and the residue was chromatographed on alumina (elution with CH_2Cl_2). Evaporation of the red eluates, and recrystallisation from ether/hexane gave the *acetone adduct* (37 mg; 22%) as fine needles, m.p. 234–237°. (Found: C, 75·2; H, 7·95; N, 8·5. $C_{39}H_{50}N_4O_3$ requires: C, 75·2; H, 8·1; N, 9·0%). λ_{max} 304 (ϵ 36,000), 406 (17,000) and 533 nm (9600); *m/e* 622 (70%), 604 (13), 565 (100), 311 (15), m* 513 (622→565) and 586 (622→604); τ, −1·23 (2 NH, br), 3·02 (1 methine-H), 5·58 (1H, t J = 5 Hz, $CHCH_2CO$), 6·77 (2H, d J = 5 Hz, $CHCH_2CO$), 7·0–7·7 (16H, m, CH_2CH_3), 7·88 (3H, s, CH_2COCH_3) and 8·6–9·0 (24H, m, CH_2CH_3).

Zinc(II) meso-*acetoxyoctaethylporphyrin* (**18**; R = Et). Octaethyloxophlorin (150 mg) in pyridine (5 ml) at 75° was stirred with Ac_2O (1 ml) during 10 min. The mixture was evaporated to dryness and the residue was chromatographed on alumina (elution with CH_2Cl_2). The red eluates were treated with zinc acetate (200 mg) in MeOH (50 ml) and refluxed gently for 15 min. Concentration of the mixture to *ca.* 75 ml caused the required *zinc complex* to crystallise, yield 175 mg (93%), m.p. >300°C. (Found: C, 69·3; H, 7·1; N, 8·8; Zn, 10·1. $C_{36}H_{46}N_4O_2Zn$ requires: C, 69·6; H, 7·1; N, 8·5; Zn, 10·0%). λ_{max} 403 (ϵ 496,000), 532 (22,000) and 568 nm (21,000); *m/e* ^{64}Zn, 654 (100%), 612 (100); ν_{max} (KBr) C=O 1740 cm^{-1}; τ, 0·00 (2H, *meso*-H), 0·12 (1 *meso*-H), 5·8–6·2 (16H, m, CH_2CH_3), 7·10 (3H, s, $OCOCH_3$) and 8·0–8·3 (24H, m, CH_2CH_3).

Zinc(II) meso-*methoxyaetioporphyrin*-I (**10**). A suspension of K_2CO_3 (3 g) in dry MeOH (40 ml) was flushed with N_2 for 10 min before addition of a soln of zinc(II) aetio-oxophlorin-I (100 mg) in THF (50 ml); the soln immediately turned green (metallo-oxophlorin anion). MeI (20 ml) in THF (20 ml) was added and the soln was heated to 60° and kept under N_2 for 1 hr, after which time the soln had turned a red colour. It was poured into CH_2Cl_2 (200 ml), washed with H_2O (300 ml), dried (Na_2SO_4), evaporated to dryness, and the residue was chromatographed on alumina (150 g) (elution with CH_2Cl_2). The pink-red eluates were evaporated and the residue was crystallised from CH_2Cl_2/hexane to give red prisms of the *product* (57 mg; 56%), m.p. >300°. (Found: C, 69·4; H, 6·5; N, 10·0; Zn, 11·7. $C_{33}H_{38}N_4OZn$ requires: C, 69·3; H, 6·7; N, 9·8; Zn, 11·4%). λ_{max} 404 (ϵ 364,000), 533 (18,400) and 568 nm (11,200); *m/e* (^{64}Zn) 570 (100%), 555 (80), 540 (60); NMR in pyridine-d_5, τ, −0·24 (2H, *meso*-H), −0·16 (1 *meso*-H), 5·60 (3H, s, OMe), 5·8–6·1 (8H, m, CH_2CH_3), 6·35, 6·48, 6·50, 6·50 (4 CH_3), 8·0–8·4 (12H, t, CH_2CH_3).

Zinc(II) meso-*acetoxyaetioporphyrin*-I (**18**; R = Me). Aetio-oxophlorin-I (300 mg) in pyridine (15 ml) at 75° was treated with Ac_2O (3 ml) with stirring for 5 min. The soln was azeotroped to dryness with toluene before chromatography of the residue on alumina (200 g) (elution with CH_2Cl_2). The eluates were concentrated to 100 ml, zinc acetate (350 mg) in methanol (20 ml) was added, and the soln was further reduce in volume to *ca* 40 ml, whereupon the *product* crystallised as red prisms, (348 mg; 95%), m.p. >300°. (Found: C, 68·2; H, 6·55; N, 9·4; Zn, 10·9. $C_{34}H_{38}N_4O_2Zn$ requires: C, 68·05; H, 6·4; N, 9·3; Zn, 10·9%); λ_{max} 404 (ϵ 379,600), 530 (16,900) and 568 nm (14,800); *m/e* (%) (^{64}Zn) 598 (75), 556 (100), and 278 (15). The sample was not sufficiently soluble for its NMR spectrum to be determined. ν_{max} (KBr) C=O 1740 cm^{-1}.

Zinc(II) *αγ-dioxo-aetioporphodimethene* (**4c**; R = Me). Zinc(II) aetio-oxophlorin-I (250 mg) in THF (50 ml) was treated with a suspension of K_2CO_3 (3 g) in MeOH (20 ml) and the green soln was stirred in air for 1 hr. CH_2Cl_2 (200 ml) was added and the mixture was washed with water (200 ml), dried (Na_2SO_4), and then evaporated to dryness. The residue was chromatographed on alumina (CH_2Cl_2 + 0·5% MeOH as eluent). The orange eluates were evaporated to dryness and the residue was crystallised from CH_2Cl_2/MeOH to give the *zinc dioxoporphodimethene* (150 mg; 59%) as purple needles, m.p. >300°C. (Found: C, 66·9; H, 6·1; N, 9·6; Zn, 11·6. $C_{32}H_{34}N_4O_2Zn$ requires: C, 67·2; H, 6·0; N, 9·8; Zn, 11·4%). λ_{max} 434 (ϵ 51,000), 546 (10,500), and 581 nm (21,500); *m/e* (^{64}Zn), 570 (100%), 555 (40); the compound was not sufficeintly soluble in $CDCl_3$ for its NMR spectrum to be determined.

β-Hydroxy-octaethyl-α-oxophlorin (**16**; R = Et). Zinc(II) octaethylporphyrin[6] (150 mg) in THF (25 ml) and CH_2Cl_2 (150 ml) was treated with TTFA (168 mg; 1·1 equiv) in dry THF (25 ml) and left to stir for 10 min. A further portion of TTFA (152 mg; 1 equiv) in THF (25 ml) was then added, and after stirring for a further 10 min the soln was treated with SO_2 gas for 30 sec, and then conc HCl (2 ml) in THF (10 ml) was added. The reaction mixture was stirred for 5 min, CH_2Cl_2 (100 ml) was added and the mixture was washed with H_2O (3 × 300 ml), dried (Na_2SO_4), and then evaporated and chromatographed on alumina (150 g) (elution with CH_2Cl_2). Evaporation of the appropriate eluates and crystallisation from CH_2Cl_2/heptane gave red prisms of the *hydroxyoxophlorin* (59 mg; 42%), m.p. >300° (Found: C, 76·3; H, 7·9; N, 10·1. $C_{36}H_{46}N_4O_2$ requires: C, 76·3; H, 8·2; N, 10·0%). λ_{max} 347 (ϵ 21,450), 543 nm (6650); *m/e* 566 (100%), 550 (20); ν_{max} (KBr) 1605 cm^{-1}; τ, −1·7 (NH, br), 0·02, 1·32 (2NH), 3·42, 5·38 (2 methine-H), 7·0–8·3 (16H, m, CH_2CH_3) and 8·5–9·6 (24H, m, CH_2CH_3). Further elution of the column with CH_2Cl_2 afforded octaethyloxophlorin (11 mg) from CH_2Cl_2/MeOH.

β-Hydroxy-aetio-α-oxophlorin-I (**16**; R = Me). This compound was similarly prepared from zinc(II) aetioporphyrin-I (500 mg), and afforded the *hydroxyoxophlorin* (265 mg; 56%) as red prisms, m.p. >300°. (Found: C, 75·4; H, 7·4; N, 11·2. $C_{32}H_{38}N_4O_2$ requires: C, 75·25; H, 7·5; N, 11·0%). λ_{max} 345 (ϵ 21,000), 540 nm (6500); *m/e* 510 (100), 508 (5); ν_{max} 1605 cm^{-1}; τ, −1·65 (NH, vbr), 0·0, 1·25 (2NH, br), 3·46, 5·40 (2 methine-H), 7·0–8·5 (16H, m, CH_2CH_3), and 8·5–9·5 (24H, m, CH_2CH_3). Further elution of the column with CH_2Cl_2 afforded aetio-oxophlorin-I (40 mg), crystallised from CH_2Cl_2/MeOH.

β-Acetoxy-octaethyl-α-oxophlorin (**19**: R = Et). Zinc(II) *meso*-acetoxyoctaethylporphyrin (130 mg) in dry THF (25 ml) and $CHCl_3$ (200 ml) was treated with a solution of TTFA (118 mg) in THF (25 ml) and then stirred for 5 min. The mixture was flushed with SO_2 gas for 30 sec and conc. HCl (2 ml) in THF (15 ml) was added. After stirring for 5 min the mixture was washed with H_2O (3 × 300 ml), evaporated to dryness, and then chromatographed on alumina (150 g) (elution with $CHCl_3$). Evaporation of the blue eluates gave the required *acetoxyoxophlorin* (57 mg; 46%), m.p. 120–123°C. (Found: C, 75·1; H, 7·8; N, 9·4. $C_{38}H_{48}N_4O_3$ requires: C, 75·0; H, 7·95; N, 9·2%); λ_{max} 402 (ϵ 47,600), 574 (6600) and 627 nm (8200); *m/e* (%), 608 (25), 566 (50), and 550 (100); ν_{max} (KBr) C=O 1770 and 1570 cm^{-1}. Only broad resonances were observed in the NMR spectrum of this compound, presumably due to ready formation of radical species.

β-Acetoxy-aetio-α-oxophlorin-I (**19**; R = Me). This compound was similarly prepared from zinc(II) *meso*-acetoxyaetioporphyrin-I (160 mg) and afforded the *acetoxyoxophlorin* (96 mg; 65%) from ether, m.p. 155–158°C. (Found: C, 74·0; H, 7·5; N, 10·35. $C_{34}H_{40}N_4O_3$ requires: C, 73·9; H, 7·3; N, 10·1%). λ_{max} 400 (ϵ 55,500), 582 (7100), and 626 nm (9300); *m/e* 552 (3%), 510 (10%), and 494 (100); ν_{max} (KBr) C=O 1780 and 1605 cm^{-1}. A satisfactory NMR spectrum could not be obtained, presumably due to the ready formation of radical species.

Treatment of the acetoxyoxophlorin (5 mg) with CH_2Cl_2 and aqueous K_2CO_3 with vigorous shaking gave a good yield of the corresponding β-hydroxy-α-oxophlorin, identical with the material described above.

αβ-Diacetoxyaetioporphyrin-I (**17a**; R = Me)

(a) *From β-Acetoxyaetio-α-oxophlorin*-I. β-Acetoxy-aetio-α-oxophlorin-I (75 mg) in dry pyridine (10 ml) was stirred with Ac_2O (1 ml) during 10 min. The mixture was evaporated to dryness and chromatographed on alumina (elution with CH_2Cl_2). Evaporation of the red eluates and crystallisation of the residue from CH_2Cl_2/hexane afforded the *αβ-diacetoxyporphyrin* (30 mg; 37%) as red prisms, m.p. >300°C (Found: C, 73·1; H, 7·4; N, 9·7. $C_{36}H_{42}N_4O_4$ requires: C, 72·7; H, 7·1; N, 9·4%). λ_{max} 404 (ϵ 168,000), 501 (14,900), 532 (4400), 575 (5300) and 624 nm (760); *m/e* (%) 594 (15), 552 (25), 536 (25), 510 (100) and 494 (90); τ, 0·36 (2 *meso*-H), 6·0–6·4 (8H, m, CH_2CH_3), 6·5–6·8 (12H, m, CH_3), 7·24 (6H, s, $COCH_3$) and 8·2–8·4 (12H, m, CH_2CH_3); ν_{max} (KBr) C=O 1760 cm^{-1}.

(b) *From β-hydroxy-aetio-α-oxophlorin*-I. β-Hydroxy-aetio-α-oxophlorin-I (50 mg) in pyridine (10 ml) was treated with freshly distilled acetyl chloride (2 ml) for 10 min. The mixture was evaporated to dryness and the residue was chromatographed on alumina (50 g) (elution with CH_2Cl_2). Evaporation of the red

eluates and crystallisation of the residue from CH_2Cl_2/hexane gave the product (38 mg; 65%), identical with the material described in (a).

αβ-Dibenzoyloxyaetioporphyrin-I (**17b**; R = Me). β-Hydroxyaetio-α-oxophlorin-I (100 mg) in pyridine (10 ml) was heated at 70° with freshly distilled benzoyl chloride (5 ml) for 10 min. The mixture was evaporated to dryness, dissolved in CH_2Cl_2 (150 ml), washed with 10% aq. NaOAc (100 ml), dried (Na_2SO_4) and then evaporated to give a mobile oil. This was chromatographed on alumina, (elution with toluene), and the red eluates were evaporated. Crystallisation from CH_2Cl_2/hexane gave the *dibenzoyloxyporphyrin* (49 mg; 35%) as brick red microprisms, m.p. >320°C. (Found: C, 76·7; H, 6·6; N, 7·9. $C_{46}H_{46}N_4O_4$ requires: C, 76·85; H, 6·45; N, 7·8%). λ_{max} 405 (ε 200,000), 502 (18,800), 532 (3700), 575 (5300) and 625 nm (590); *m/e* (%), 718 (30), 613 (60), 597 (30), and 492 (100); τ, 0·14 (2 *meso*-H), 1·2–1·4 (4H, m, *o*-H), 2·2–2·4 (6H, m, *m*, *p*-H), 5·9–6·3 (8H, m, CH_2CH_3), 6·50, 6·53, 6·74, 6·74 (4 CH_3), 8·1–8·5 (12H, m, CH_2CH_3); ν_{max} (KBr) C=O 1760 cm^{-1}.

αβ-Diacetoxyoctaethylporphyrin (**17a**; R = Et). *meso*-Acetoxyoctaethyloxophlorin (140 mg) in pyridine (10 ml) was stirred with acetic anhydride (2 ml) for 5 min at 75°. The mixture was evaporated to dryness and the residue chromatographed on alumina (100 g) (elution with CH_2Cl_2). The red eluates were evaporated and the residue was crystallised from CH_2Cl_2/hexane to afford the *diacetoxyporphyrin* (97 mg; 66%) as red prisms, m.p. 199–201°. (Found: C, 73·8; H, 7·7; N, 8·8. $C_{40}H_{50}N_4O_4$ requires: C, 73·8; H, 7·7; N, 8·6%); λ_{max} 406 (ε 186,400), 503 (16,600), 534 (4600), 576 (5600), and 625 nm (1000); *m/e* (%), 650 (45), 608 (30), 592 (50), 566 (75), and 550 (100); τ, 0·14 (2 *meso*-H), 5·8–6·4 (16H, m, CH_2CH_3), 714 (6H, s, $COCH_3$) and 8·0–8·3 (24H, m, CH_2CH_3); ν_{max} (KBr) C=O 1760 cm^{-1}.

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