

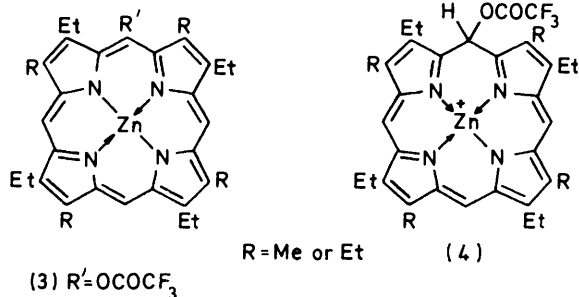
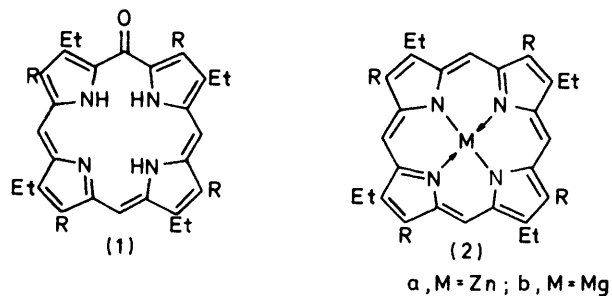
## Bile Pigment Studies. Part 4.<sup>1,2</sup> Some Novel Reactions of Metalloporphyrins with Thallium(III) and Cerium(IV) Salts. Ring Cleavage of *meso*-Tetraphenylporphyrin<sup>3</sup>

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Treatment of zinc(II) *meso*-tetraphenylporphyrin (5) with thallium(III) trifluoroacetate or nitrate, or cerium(IV) ammonium nitrate gives a mixture of the 5,15-dihydroxy-5,10,15,20-tetraphenylporphodimethenes (7), the 5-hydroxy-15-methoxy-derivatives (8), and the ring-opened bilinone (10) after acidic demetallation. An extra product when thallium(III) trifluoroacetate is employed is the trifluoroacetyl derivative (12) or (13). When thallium(III) nitrate or cerium(IV) ammonium nitrate are used, the  $\beta$ -nitro-*meso*-tetraphenylporphyrin (14) is also isolated. Nitration of zinc(II) octa-alkylporphyrins with these two salts is shown to be a general reaction which can be controlled to give mono- or di-nitration at the *meso*-positions. Mechanistic implications of the ring-cleavage and nitration reactions are discussed.

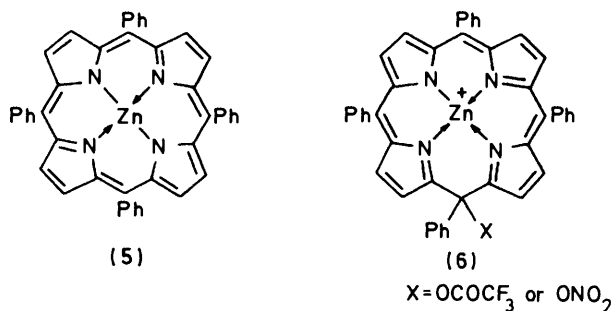
An earlier paper<sup>4</sup> described the efficient synthesis of oxophlorins (1) from zinc(II) or magnesium(II) complexes (2)



of octa-alkylporphyrins using thallium(III) trifluoroacetate (TTFA). Fully characterised intermediates in this transformation were the zinc(II) *meso*-trifluoroacetylporphyrin complexes (3), presumably obtained from the metallo-isoporphyrin cations (4) by loss of a proton. In the first part of this paper we report results from treatment of *meso*-tetraphenylporphyrin zinc(II) complex (5) with TTFA, or thallium(III) nitrate (TTN), or cerium(IV) ammonium nitrate (CAN); we reasoned that these reactions must give fundamentally different products since the corresponding metalloisoporphyrin

cation cannot lose a proton to enable it to reassume the porphyrin state. The latter part of this paper describes novel reactions of zinc(II) octa-alkylporphyrins (2a) with TTN.

Treatment of zinc(II) *meso*-tetraphenylporphyrin (5) in methylene chloride with slightly more than two electron equivalents of TTFA, TTN, or CAN in acetonitrile gave immediately a yellow-green solution. Spectrophotometry ( $\lambda_{\text{max}}$  780 and 860 nm) confirmed complete formation of the metalloisoporphyrin (6), presumably by abstraction of two electrons from (5) to give the  $\pi$ -dication, followed by attack by trifluoroacetate or nitrate (*cf.* ref. 5). After work-up (Experimental section), the products were chromatographed on alumina. Elution with methylene chloride gave first some unconsumed *meso*-tetraphenylporphyrin. In the case of the TTFA reaction, this was followed by a yellow-brown fraction which was shown by analytical t.l.c. to be a mixture of two major components. Preparative thick-layer chrom-



atography on Kieselgel G gave a fast-moving minor band and a less mobile major fraction. The latter was shown to be the 5,15-dihydroxyporphodimethenes (7) by

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<sup>1</sup> Part 3, F. Eivazi, M. F. Hudson, and K. M. Smith, *Tetrahedron*, 1977, **33**, 2959.

<sup>2</sup> Nomenclature follows I.U.P.A.C. suggestions: I.U.P.A.C. Commission on the Nomenclature of Tetrapyrroles, 6th Memorandum, 1976.

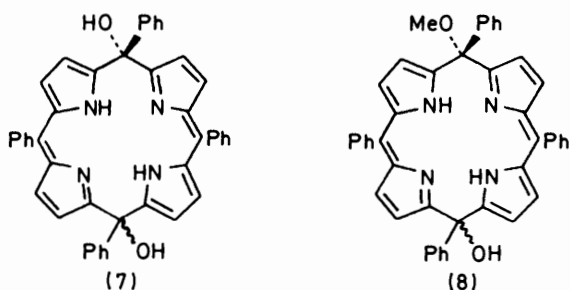
<sup>3</sup> Preliminary publication, B. Evans, K. M. Smith, and J. A. S. Cavaleiro, *Tetrahedron Letters*, 1976, 4863. This work was reported at the Middle Atlantic Region Meeting of the American Chemical Society, Newark, Delaware, April 1977, Abstract No. PH 34.

<sup>4</sup> G. H. Barnett, M. F. Hudson, S. W. McCombie, and K. M. Smith, *J.C.S. Perkin I*, 1973, 691.

<sup>5</sup> D. Dolphin, R. H. Felton, D. C. Borg, and J. Fajer, *J. Amer. Chem. Soc.*, 1970, **92**, 743.

elemental analysis, mass spectrometry, n.m.r. spectroscopy (which indicated a high degree of symmetry), and comparison with the data reported by Johnson and Winter<sup>6</sup> who had obtained the same compounds by treatment of *meso*-tetraphenylporphyrin with sulphuric-nitric acids. The more mobile band was identified as the monohydroxy-monomethoxy derivatives (8) by elemental analysis, mass spectrometry, and n.m.r. spectroscopy [which showed two types of AB quartet for the peripheral hydrogens compared with the single type in compound (7)]. The formation of product (8) also gave valuable information regarding mechanisms for the transformation of (5) into (7) (*vide infra*).

Further elution of the column for the TTFA reaction



gave a violet band and a less polar red-purple fraction. The electronic absorption spectrum of the violet substance (Figure 1) resembled that of a 19-acetylbilinone (9) isolated from our work with the *Chlorobium* chlorophylls,<sup>7</sup> and together with further evidence from mass spectrometry, i.r., and n.m.r. spectroscopy, enabled assignment of structure (10) to it. The 220 MHz n.m.r. spectrum (Figure 2) was particularly helpful, since it

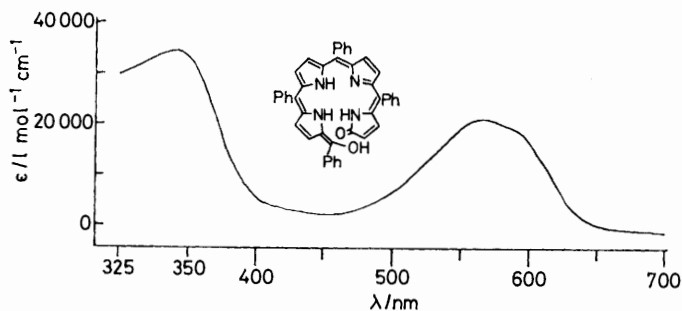


FIGURE 1 Electronic absorption spectrum (in  $\text{CHCl}_3$ ) of bilinone (10)

showed the molecule to be highly unsymmetrical with four different pairs of AB protons. In  $\text{CDCl}_3$  alone (Figure 2A) the spectrum also showed a singlet at  $\tau$  3.63 which like the NH peaks at  $\tau$  -2.45, -0.80, and 0.04 (not shown in Figure 2) was exchanged by  $\text{D}_2\text{O}$  treatment (Figure 2B). The fact that this peak was a singlet encouraged us to formulate the compound as the enol (10) rather than a keto [*e.g.* (11)] tautomer because the proton on carbon in the keto tautomer would be expected to

<sup>6</sup> A. W. Johnson and M. Winter, *Chem. and Ind.*, 1975, 351.

<sup>7</sup> G. W. Kenner, J. Rimmer, K. M. Smith, and J. F. Unsworth, *Phil. Trans. Roy. Soc., Ser. B*, 1976, **273**, 255.

couple with the adjacent  $\beta$ -proton, and no such coupling is apparent. On the other hand, a slight coupling is

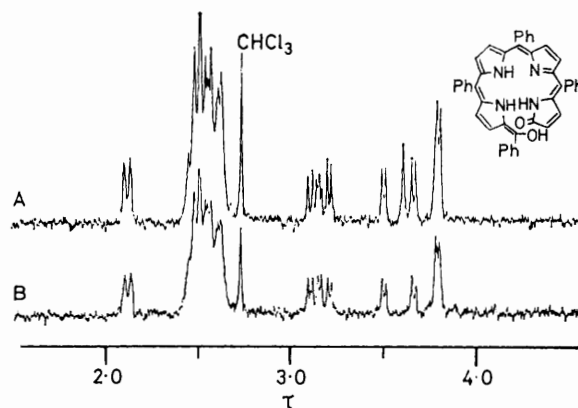
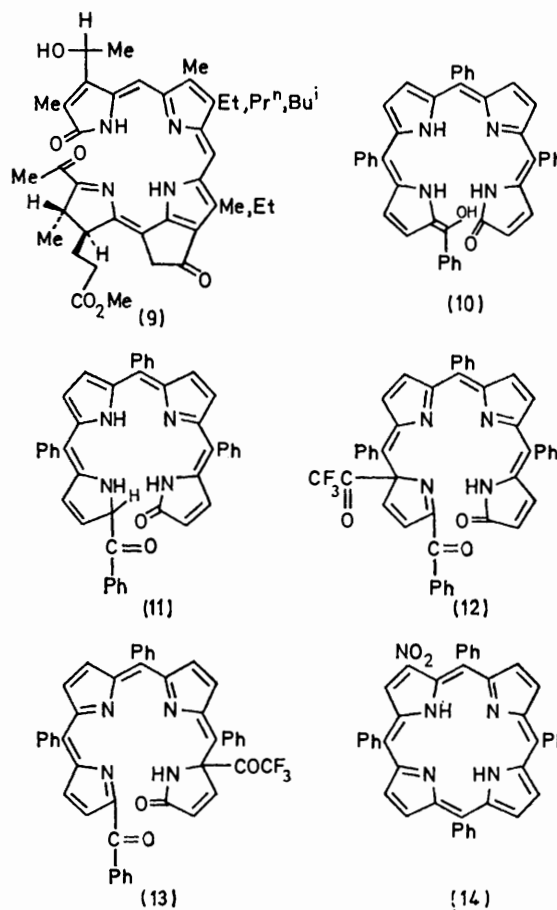


FIGURE 2 220 MHz N.m.r. spectrum of bilinone (10) ( $\tau$  2-4 region only); A, in  $\text{CDCl}_3$  alone; B, in  $\text{CDCl}_3$  after a  $\text{D}_2\text{O}$  shake

observed with the proton at  $\tau$  3.16, and this is removed by the  $\text{D}_2\text{O}$  shake (Figure 2B); this is presumably a  $\beta$ -H



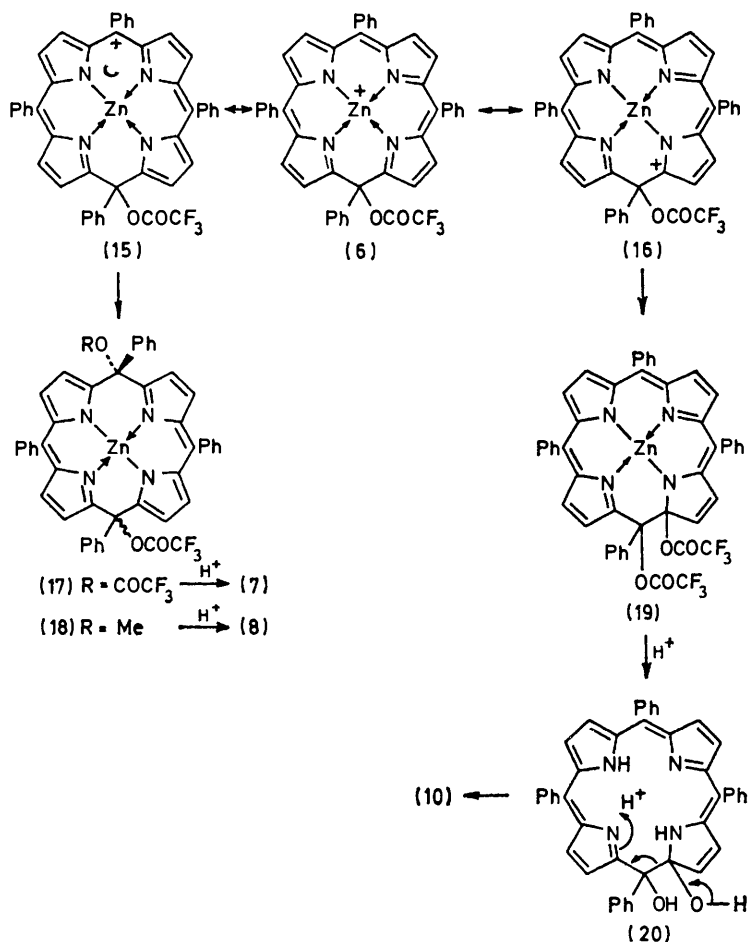
to NH coupling in the molecule because no other protons in Figure 2A show the same coupling.

The less polar red-purple compound was obtained in larger amounts if an excess of TTFA was used, and the

structures (12) or (13) are assigned to it on the basis of elemental analysis and spectroscopic data; the electronic absorption spectrum indicated that three rings of the pigment were conjugated, and it was similar to several other pigments we have recently described<sup>1,8,9</sup> which possessed such conjugated systems. At the present time it is not

with an authentic sample prepared by treatment of (5) with nitronium tetrafluoroborate, followed by an acidic work-up.

Scheme 1 shows plausible mechanisms for the formation of (7), (8), and (10); the isoporphyrin salt (6) can be assigned major resonance forms (15) and (16)



SCHEME 1

possible to differentiate between the two possible structures (12) or (13), but in support of structures with only one NH group, we were unable to prepare a zinc(II) complex of it under conditions which rapidly produced a zinc(II) complex of compound (10).

When TTN or CAN were used in place of TTFA compounds (7), (8), and (10) were likewise produced in similar yield. However, under these conditions another porphyrinic compound was obtained, and this ran chromatographically only slightly behind the *meso*-tetraphenylporphyrin usually recovered. Careful re-chromatography enabled purification, and the new product was shown to be mononitro-*meso*-tetraphenylporphyrin (14) using the usual spectroscopic methods. The structure (14) was finally confirmed by comparison of the material

\* Scheme 1 considers only the mechanisms in the TTFA reaction. In the TTN and CAN cases the OCOCF<sub>3</sub> functions are merely replaced with ONO<sub>2</sub>.

which would be expected to afford major contributions.\* Nucleophilic attack upon form (15) by trifluoroacetate or methanol would give (17) or (18) respectively, which after demetallation and cleavage of the COCF<sub>3</sub> groups would form (7) and (8) respectively. Attack upon the metalloisoporphyrin salt (16) by trifluoroacetate could produce (19) which would similarly be demetallated and cleaved by trifluoroacetic acid to give the species (20). Such compounds with substituents at the 'α-pyrrole' positions are known<sup>10</sup> to be unstable and would be expected to fragment, as shown, in a type of reverse-aldol reaction to give (10).

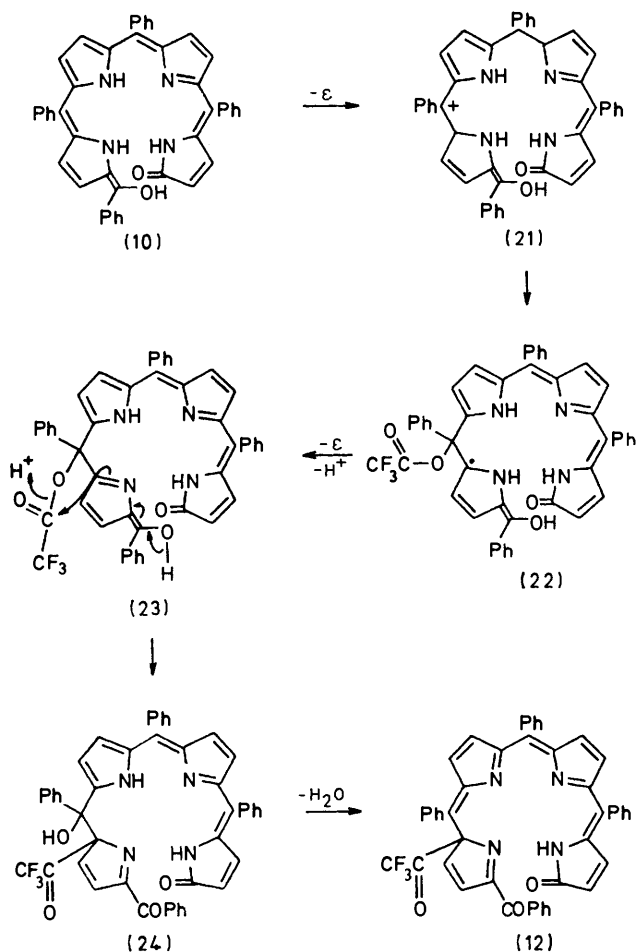
A pathway for the further transformation of (10) into

<sup>8</sup> F. Eivazi, M. F. Hudson, and K. M. Smith, *Tetrahedron Letters*, 1976, 3837.

<sup>9</sup> J. A. S. Cavaleiro and K. M. Smith, *J.C.S. Perkin I*, 1973, 2149.

<sup>10</sup> J.-H. Fuhrhop in 'Porphyrins and Metalloporphyrins,' ed. K. M. Smith, Elsevier, Amsterdam, 1975, p. 628.

(12) is given in Scheme 2. Oxidation of (10) with TTFA might be expected to give<sup>1,11</sup> the cation radical (21)



SCHEME 2

which could react with trifluoroacetate to give (22). Loss of a second electron and a proton would give (23) which might undergo acyl transfer<sup>1</sup> to afford (24). Dehydration would then give (12). A similar overall mechanism can be drawn to afford the alternative structure (13).

Production of mononitro-*meso*-tetraphenylporphyrin (14) in the TTN or CAN reactions is puzzling, though conditions have been devised (see Experimental section) to give acceptable yields of this compound. Nevertheless, this method is general for nitroporphyrin formation; for example, treatment of zinc(II) aetioporphyryn-I (2a; R = Me) in methylene chloride with TTN or CAN in dry tetrahydrofuran or acetonitrile after stirring for 2 h followed by an acidic work-up gives a 60% yield of

<sup>11</sup> F. Eivazi, W. M. Lewis, and K. M. Smith, *Tetrahedron Letters*, 1977, 3083.

<sup>12</sup> R. Bonnett and G. F. Stephenson, *J. Org. Chem.*, 1965, **30**, 2791.

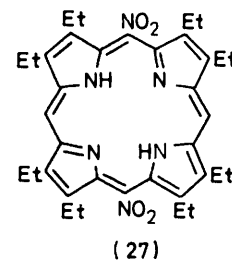
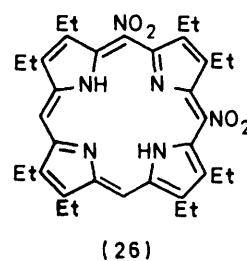
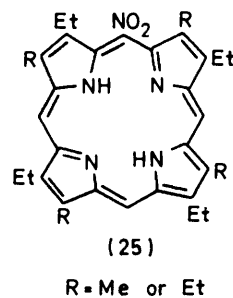
<sup>13</sup> G. H. Barnett and K. M. Smith, *J.C.S. Chem. Comm.*, 1974, 772.

<sup>14</sup> B. Evans and K. M. Smith, *Tetrahedron Letters*, 1977, 3079.

<sup>15</sup> E. C. Johnson and D. Dolphin, *Tetrahedron Letters*, 1976, 2197.

mononitroaetioporphyryn-I (25; R = Me). Likewise, a 43% yield of mononitro-octaethylporphyrin (25; R = Et) was obtained when zinc(II) octaethylporphyrin (2a; R = Et) was similarly treated. When (2a; R = Et) was treated in damp solvents with TTN or CAN then no mono-nitro products were isolated. Instead a statistical mixture of the 5,10-(26) (28% yield) and 5,15-(27) (13% yield) dinitroporphyrins was isolated, and these were separated by preparative thick-layer chromatography. Final proof of the identities of these products was obtained by comparison with authentic materials.<sup>12,13</sup> In all these reactions the cation-radical of the metalloporphyrin was initially obtained (spectrophotometric monitoring), but it is by no means certain that this species is the source of the nitro-products. It is possible that some of the nitrate liberated during the reduction of the thallium(III) or cerium(IV) species is itself reduced to nitrite or nitrogen dioxide which then reacts with the metalloporphyrin cation radical (e.g. refs. 13–15). Insertion of 'nitro' from 'nitrate' has been observed on several occasions<sup>16,17</sup> and most often during anodic oxidation in the presence of electrolytes possessing nitrate counterions.<sup>16</sup> On the other hand, nitration of aromatics can be readily accomplished<sup>17</sup> with titanium(IV) nitrate or with CAN.

Further work aimed at differentiating between the various possible mechanisms for the novel nitration reactions is in progress, as is a general investigation of the reactions of metalloisoporphyrin salts with various nucleophiles.



#### EXPERIMENTAL

M.p.s were measured on a hot-stage apparatus. Neutral alumina (Fluka, Brockmann Grade III) was used for column

<sup>16</sup> L. Ebersson and K. Nyberg, *Adv. Phys. Org. Chem.*, 1976, **36**; G. R. Davies and B. J. Woodhall, *J. Appl. Electrochem.*, 1971, **1**, 137.

<sup>17</sup> D. W. Amos, D. A. Baines, and G. W. Flewett, *Tetrahedron Letters*, 1973, 3191; B. Rindone and C. Scolastico, *J.C.S. Perkin I*, 1975, 1398.

chromatography, and Kieselgel G was used in all t.l.c. separations. Electronic absorption spectra were determined with a Unicam SP 800 spectrophotometer and n.m.r. spectra were measured with a Perkin-Elmer PE 34 (220 MHz) instrument (in  $\text{CDCl}_3$  solution with tetramethylsilane as internal standard). Mass spectra were determined with an A.E.I. MS12 or 902 spectrometer (at 50  $\mu\text{A}$  and 70 eV, direct insertion probe, source temperature ca. 200 °C).

**Reaction of Zinc(II) meso-Tetraphenylporphyrin (5) with TTFA.**—Chlorin-free  $^{18}$  zinc(II) meso-tetraphenylporphyrin (1.41 g) in methylene chloride (650 ml) was stirred during addition of TTFA (1.36 g) in acetonitrile (90 ml). After being stirred for a further 4 min the mixture was filtered by suction through a bed (ca. 100 g) of Kieselgel G (elution initially with methylene chloride and then 5% methanol in methylene chloride). The combined eluates were evaporated to dryness and the residue was taken up in trifluoroacetic acid (20 ml) and stirred during 3 min. Methylene chloride (250 ml) was then added and the mixture was poured into a separatory funnel containing water (500 ml). The organic phase was then washed with water, aqueous sodium hydrogen carbonate (which caused the colour of the solution to change from green to red), and finally water before drying ( $\text{Na}_2\text{SO}_4$ ) and evaporation to dryness. The residue was chromatographed on alumina (elution with methylene chloride) and five bands were clearly separated.

**Band 1** contained meso-tetraphenylporphyrin (735 mg, 57.5%); the yields of all other compounds are based on the amounts of (5) actually consumed in the reaction.

**Band 2** contained a green substance (21 mg), as yet unidentified.

**Band 3** was yellow-brown in colour, and after evaporation of the eluates the residue was shown by analytical t.l.c. to contain two major components. Preparative t.l.c. (silica gel, elution with methylene chloride–n-hexane, 2.5 : 1) gave a good separation; the most polar band was removed from the silica gel with methylene chloride–methanol (1 : 1), and after evaporation was crystallised from methylene chloride–n-hexane to give 5,15-dihydroxy-5,10,15,20-tetraphenylporphodimethene (7) (80 mg, 14%) as red-brown needles, m.p. 250–251 °C (decomp.) (Found: C, 80.6, 80.35; H, 5.15, 5.15; N, 8.4. Calc. for  $\text{C}_{44}\text{H}_{32}\text{N}_4\text{O}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ ; C, 80.3; H, 5.1; N, 8.5%),  $\lambda_{\text{max.}}(\text{CHCl}_3)$ , 326 ( $\epsilon$  19 200), 427 (48 500), and 491 nm (1 400);  $\lambda_{\text{max.}}(\text{CHCl}_3 + 0.5\% \text{ TFA})$  387 ( $\epsilon$  37 000), 461 (169 300), 516 (6 600), and 557 nm (6 900);  $\tau$  –3.5 (2NH, br), 2.22 (4 H, d,  $J$  8 Hz, 5,15-Ph *o*-H), 2.45–2.65 (16 H, m, Ph), 3.57 (4 H, d,  $J$  4 Hz) and 3.63 (4 H, d,  $J$  4 Hz) ( $\beta$ -H), and 6.30 (2 H, OH);  $\nu_{\text{max.}}(\text{KBr})$ , 3 430 (NH) and 3 280 (OH)  $\text{cm}^{-1}$ ;  $m/e$  648 (10%) and 614 (100). When an attempt was made to prepare the zinc complex of this compound (*cf.* ref. 6) using zinc(II) acetate in acetic acid, the corresponding metalloisoporphyrin was obtained; treatment of this with trifluoroacetic acid gave meso-tetraphenylporphyrin (74% yield). The less polar band from the preparative t.l.c. was similarly removed from the silica gel and crystallised from methylene chloride–n-hexane to give 5-hydroxy-15-methoxy-5,10,15,20-tetraphenylporphodimethene (8) (20 mg, 3.5%), m.p. >300 °C (Found: C, 80.6; H, 5.3; N, 8.5.  $\text{C}_{45}\text{H}_{34}\text{N}_4\text{O}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$  requires C, 80.45; H, 5.25; N, 8.35%),  $\lambda_{\text{max.}}(\text{CHCl}_3)$ , 325 ( $\epsilon$  19 000), 428 (49 000), and 490 nm (1 600);  $\tau$  –3.1 (2NH), 2.3–2.6 (14 H, m, Ph), 2.65–2.8 (6 H, m, Ph), 3.32 (2 H, d,  $J$  4 Hz), 3.42 (2 H, d,  $J$  4 Hz), and 3.52 (4 H, d,  $J$  4 Hz) ( $\beta$ -H), 6.69 (3 H, OMe), and 7.17 (1 H, OH);  $m/e$  662 (2%), 614 (100).

**Band 4** was red in colour, and evaporation of the eluates

followed by crystallisation from methylene chloride–n-hexane gave the 19-benzoyl(trifluoroacetyl)bilinone (12) or (13) (34 mg, 5%) as red prisms, m.p. 206–210 °C (Found: C, 72.7; H, 4.3; N, 7.1.  $\text{C}_{46}\text{H}_{29}\text{F}_3\text{N}_4\text{O}_3 \cdot \text{H}_2\text{O}$  requires C, 72.6; H, 4.1; N, 7.4%),  $\lambda_{\text{max.}}(\text{CHCl}_3)$  337 ( $\epsilon$  23 400), 396 (20 000), 547 (27 100), and 586 nm (29 900);  $\lambda_{\text{max.}}(\text{CHCl}_3 + 0.5\% \text{ TFA})$ , 353 ( $\epsilon$  23 800) and 573 nm (23 400);  $\tau$  1.68 (2 H, *o*-Ph), 2.2–2.8 (18 H, m, Ph), and 3.4–3.85 (8 H, m,  $\beta$ -H),  $\nu_{\text{max.}}(\text{KBr})$  1 700 ( $\text{COCF}_3$ ) and 1 610 ( $\text{C=O}$ )  $\text{cm}^{-1}$ ,  $m/e$  742 (100%), 673 (20), and 645 (5).

When this compound was treated with zinc(II) acetate in methanol there was no change in the electronic absorption spectrum of the solution even after it had been heated in a water-bath. When the reaction with zinc(II) meso-tetraphenylporphyrin was repeated, but using approximately twice as much TTFA as reported above, a 12% yield of the trifluoroacetyl compound was obtained.

**Band 5** was deep purple in colour, and evaporation of the eluates followed by crystallisation from methylene chloride–n-hexane gave the bilinone (10) (98 mg, 17%) as violet prisms, m.p. 136–139 °C (Found: C, 79.2, 79.45; H, 5.0, 5.2; N, 8.5.  $\text{C}_{44}\text{H}_{32}\text{N}_4\text{O}_2 \cdot \text{H}_2\text{O}$  requires C, 79.3; H, 5.1; N, 8.4%),  $\lambda_{\text{max.}}(\text{CHCl}_3)$  345 ( $\epsilon$  36 900), 565 (23 400), and 587 nm (21 600);  $\lambda_{\text{max.}}(\text{CHCl}_3 + 1\% \text{ TFA})$ , 375 ( $\epsilon$  27 500), 431 (16 800), and 585 nm (27 500);  $\tau$  (see Figure 2) –2.45, –0.80, 0.04 (3 NH, br), 2.12 (2 H, d,  $J$  10 Hz, *o*-Ph), 2.4–2.7 (18 H, m, Ph), 3.12 (1 H, d,  $J$  6 Hz), and 3.16 (1 H, t,  $J$  2 Hz), 3.23 (1 H, d,  $J$  5 Hz), 3.52 (1 H, d,  $J$  5 Hz), 3.68 (1 H, d,  $J$  5 Hz), and 3.82 (3 H, d,  $J$  5 Hz) ( $\beta$ -H), and 3.63 (1 H, OH). A  $\text{D}_2\text{O}$  shake caused disappearance of the NH and OH peaks, and the triplet at 3.16 became a doublet,  $J$  5 Hz;  $\nu_{\text{max.}}(\text{KBr})$  1 667  $\text{cm}^{-1}$  ( $\text{C=O}$ );  $m/e$  650 (80%), 648 (100), and 543 (60). Treatment of this compound with zinc(II) acetate in methanol followed by an aqueous work-up and crystallisation from methylene chloride–n-hexane gave the zinc(II) complex (96% yield), m.p. 209–211 °C (decomp.),  $\lambda_{\text{max.}}(\text{CHCl}_3)$  348 ( $\epsilon$  20 000), 458 (8 400), 540 nm (7 500), 582 (13 100), and 626 nm (17 000);  $\tau$  1.96 (2 H, d,  $J$  10 Hz, *o*-Ph), 2.4–2.9 (18 H, m, Ph), 3.0–4.0 (ca. 9 H, m,  $\beta$ -H and OH).

**Reaction of Zinc(II) meso-Tetraphenylporphyrin (5) with TTN.**—Treatment of zinc(II) meso-tetraphenylporphyrin (5) (350 mg) in methylene chloride (80 ml) with TTN (240 mg) in acetonitrile (18 ml) overnight with stirring, followed by a work-up as described above for the TTFA case, gave a residue which was chromatographed on alumina (elution with methylene chloride). First, meso-tetraphenylporphyrin (70 mg, 22%) was eluted; this was followed by a yellow-brown fraction which was evaporated and then carefully re-chromatographed on alumina (elution with toluene) to give, after crystallisation from methylene chloride–n-hexane, 2-nitro-5,10,15,20-tetraphenylporphyrin (14) (53 mg, 16%), m.p. >300 °C (Found: C, 79.9; H, 4.5; N, 10.8.  $\text{C}_{44}\text{H}_{29}\text{N}_5\text{O}_2$  requires C, 80.1; H, 4.4; N, 10.6%),  $\lambda_{\text{max.}}(\text{CHCl}_3)$  425 ( $\epsilon$  172 300), 534 (13 300), 559 (3 400), 600 (3 100), and 661 nm (6 900);  $\tau$  0.96 (1 H), 0.98 (1 H, d,  $J$  5 Hz), 1.06 (1 H, d,  $J$  5 Hz), 1.08 (1 H, d,  $J$  5 Hz), 1.11 (1 H, d,  $J$  5 Hz), and 1.28 (2 H, s) (7  $\beta$ -H), 1.7–1.85 (8 H, m, *o*-Ph), 2.2–2.3 (12 H, m, *m,p*-Ph), and 12.60 (2 NH);  $m/e$  659 (100%) and 613 (60).

Next, the porphodimethenes (7) and (8) were eluted in a combined yield (unseparated) of 12%. Finally, the solvent for elution was altered to chloroform (containing ca. 2%

<sup>18</sup> G. H. Barnett, M. F. Hudson, and K. M. Smith, *J.C.S. Perkin I*, 1975, 1401.

ethanol) and the purple bilinone (10) was obtained (45 mg, 13%) and shown to be identical with the material described above in the TTFA reaction.

*Reaction of Zinc(II) meso-Tetraphenylporphyrin (5) with CAN.*—In a similar reaction (except that the mixture was worked up after 5 min rather than being allowed to stand overnight), zinc(II) meso-tetraphenylporphyrin (5) (540 mg) in methylene chloride (100 ml) was stirred with cerium(IV) ammonium nitrate (886 mg) in acetonitrile (40 ml). Chromatography gave 2-nitro-5,10,15,20-tetraphenylporphyrin (14) (25 mg, 5%), porphodimethenes (7) and (8) (not separated) (10 mg, 2%), and the purple bilinone (10) (103 mg, 20%). If the reaction mixture was stirred overnight before being worked up then the major product was 2-nitro-5,10,15,20-tetraphenylporphyrin (14) [28%; 363 mg from 1.32 g of (5)].

*2-Nitro-5,10,15,20-tetraphenylporphyrin (14).*—A mixture of zinc(II) meso-tetraphenylporphyrin (370 mg) and nitronium tetrafluoroborate (68 mg) in acetonitrile (30 ml) and methylene chloride (100 ml) was stirred at room temperature overnight. The mixture was evaporated and the residue was stirred in trifluoroacetic acid (15 ml) for 5 min. Methylene chloride (300 ml) was then added and the solution was washed with water (300 ml), dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated to dryness. Chromatography of the residue on alumina (elution with toluene) gave a forerun containing meso-tetraphenylporphyrin (100 mg), followed by a yellow-brown band which was collected and evaporated to give a residue which was crystallised from methylene chloride-methanol to give purple prisms [80 mg; 32% based on consumed (5)], with m.p.  $>300^\circ\text{C}$ , and identical with the material described above.

*meso-Nitro-octaethylporphyrin (25; R = Et).*—(a) *Using nitronium tetrafluoroborate.* A solution of nitronium tetrafluoroborate (77 mg) in acetonitrile (25 ml) was added slowly to a stirred solution of octaethylporphyrin (200 mg) in chloroform (100 ml) under an atmosphere of nitrogen. After stirring overnight, aqueous sodium hydrogen carbonate (200 ml) was added and the organic phase was separated, washed with water, dried ( $\text{Na}_2\text{SO}_4$ ), and then evaporated to give a residue which was chromatographed on silica gel (MFC) (elution with toluene-hexane). Evaporation of the red-brown eluates gave a solid which was crystallised from methylene chloride-methanol as purple platelets (79 mg, 36%), m.p.  $243\text{--}245^\circ\text{C}$  (lit.,<sup>12</sup>  $250\text{--}252^\circ\text{C}$ ) (Found: C, 74.8; H, 7.9; N, 12.1. Calc. for  $\text{C}_{36}\text{H}_{45}\text{N}_5\text{O}_2$ : C, 74.6; H, 7.8; N, 12.1%).

(b) *Using TTN.* Zinc(II) octaethylporphyrin (2a; R = Et) (400 mg) was dissolved in very dry tetrahydrofuran (100 ml) and then flushed with nitrogen during 10 min. A solution of TTN (328 mg) in very dry acetonitrile (50 ml) was added during 5 min and the mixture was stirred for a further 2 h. Sulphur dioxide gas was bubbled through the mixture for 30 s before addition of concentrated hydrochloric acid (4 ml) in tetrahydrofuran (20 ml). The mixture was stirred for 5 min and then chloroform (350 ml) was added and the solution was washed with water (500 ml), aqueous sodium hydrogen carbonate (500 ml), and water (500 ml) once more. The organic phase was dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated to give a residue which was chromatographed on

alumina (elution with methylene chloride). Evaporation of the red-brown eluates and crystallisation of the residue gave purple prisms (168 mg, 43%), identical with the material described in (a).

(c) *Using CAN.* A 45% yield of (25; R = Et) was obtained from zinc(II) octaethylporphyrin in a similar reaction using CAN.

*meso-Nitroaetioporphyrin-I (25; R = Me).*—Zinc(II) aetioporphyrin-I (50 mg) was treated, as described in (b) above, with TTN (45 mg). The product was crystallised from methylene chloride-methanol to give the nitroporphyrin (28 mg, 58%) as a red-brown fluff, m.p.  $>300^\circ\text{C}$  (Found: C, 73.4; H, 7.2; N, 13.3. Calc. for  $\text{C}_{32}\text{H}_{37}\text{N}_5\text{O}_2$ : C, 73.4; H, 7.2; N, 13.4%).

*5,10-Dinitro-octaethylporphyrin (26) and 5,15-Dinitro-octaethylporphyrin (27).*—Zinc(II) octaethylporphyrin (2a; R = Et) was dissolved in tetrahydrofuran (100 ml) and flushed with nitrogen during 10 min. A solution of TTN (164 mg) in acetonitrile (50 ml) containing water (1 ml) was added and the mixture was stirred for 2 h. Sulphur dioxide gas was bubbled into the mixture for 30 s before addition of concentrated hydrochloric acid (2 ml) in tetrahydrofuran (10 ml). The mixture was stirred for 5 min after which chloroform (350 ml) was added to it; it was then washed with water (500 ml), aqueous sodium hydrogen carbonate (500 ml), and then water (500 ml) again. The dried ( $\text{Na}_2\text{SO}_4$ ) extracts were evaporated and the residue was chromatographed on silica plates [elution with light petroleum (b.p.  $60\text{--}80^\circ\text{C}$ )-toluene (2 : 1)]. The most polar component was extracted from the silica with methylene chloride and crystallised from methylene chloride-methanol as purple prisms of 5,10-dinitro-octaethylporphyrin (26) (58 mg, 28%), m.p.  $221\text{--}222^\circ\text{C}$  (lit.,<sup>12</sup>  $224\text{--}226^\circ\text{C}$ ) (Found: C, 69.1; H, 7.0; N, 13.6. Calc. for  $\text{C}_{36}\text{H}_{44}\text{N}_6\text{O}_4$ : C, 69.2; H, 7.1; N, 13.45%).

The zinc(II) complex was prepared as follows. Compound (26) (30 mg) in methylene chloride (25 ml) was treated with a solution of zinc(II) acetate (100 mg) in methanol (20 ml). Upon concentration the product crystallised as red prisms (32 mg, 98%), with m.p.  $>300^\circ\text{C}$  (Found: C, 63.0; H, 6.0; N, 12.25; Zn, 9.6.  $\text{C}_{36}\text{H}_{42}\text{N}_6\text{O}_4\text{Zn}$  requires C, 62.9; H, 6.15; N, 12.2; Zn, 9.5%),  $\lambda_{\text{max}}$  404.5 ( $\epsilon$  177 800), 537 (14 800), and 573.5 nm (17 100). The n.m.r. spectrum in  $\text{CDCl}_3$  was extremely concentration dependent and is the subject of a separate paper.<sup>19</sup>

The least-polar component was extracted from the silica with methylene chloride and was crystallised from methylene chloride-methanol, to give 5,15-dinitro-octaethylporphyrin (27) (27 mg, 13%), as purple plates, m.p.  $282\text{--}285^\circ\text{C}$  (lit.,<sup>12</sup>  $280\text{--}282^\circ\text{C}$ ) (Found: C, 69.4; H, 7.2; N, 13.3. Calc. for  $\text{C}_{36}\text{H}_{44}\text{N}_6\text{O}_4$ : C, 69.2; H, 7.1; N, 13.45%).

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<sup>19</sup> R. J. Abraham, B. Evans, and K. M. Smith, *Tetrahedron*, in the press.