Quinone-capped Porphyrins: Synthesis and some Chemical Properties

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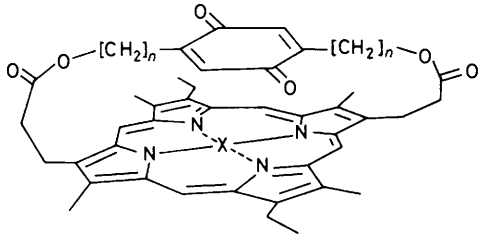
The 2,5-bis(hydroxyethyl) and 2,5-bis(hydroxypropyl) derivatives of hydroquinone bis(methoxymethyl) ether have been synthesised and used to 'cap' mesoporphyrin-II. Deprotection, oxidation, and metallation gave the title compounds. Several anomalous reactivities were observed in the capped series which may be attributed to the proximity of quinone and porphyrin moieties.

PORPHYRINS which are capped (or bridged) across one or both faces have been much used as synthetic models of biologically important haems. Most work has centred around oxygen carriers [1-5] but more recently several cytochromes and oxidases have also been modelled.[6-8] In each case the focus of attention has been control of the reactivity and properties of the central metal ion or of two proximate metal ions;[8-10] the role of the cap has been passive, protective, or at most, co-ordinative. Prompted by interests in photosynthesis and electron-transfer chemistry we have synthesised quinone-capped porphyrins (1) and (2), and the metallated derivatives (3) and (4), in which the cap is designed to participate directly in the chemistry and photochemistry of the molecule.

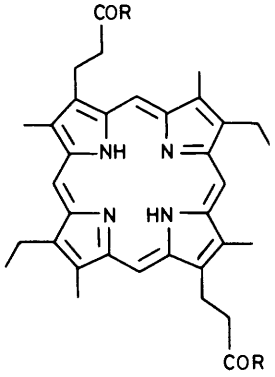


(1) $n = 2$, X = H_2
(2) $n = 3$, X = H_2
(3) $n = 2$, X = Mg
(4) $n = 3$, X = Mg

There have been numerous laboratory approaches to photosynthetic and electron-transfer systems including those based on chlorophylls,[11-14] or on porphyrins.[15-17] The approach exemplified by molecules such as (3) and (4) appeared attractive to us because relative oxidation/reduction potentials, chromophore separation and orientation, absorption characteristics, and co-ordination properties can all, in principle, be controlled by rational synthesis. Here we describe the synthesis of the quinone-capped metalloporphyrins (3) and (4), and some chemical consequences of bringing the porphyrin and aromatic groups together in one molecule. The following paper discusses the n.m.r. spectroscopic properties, conformation, and co-ordination chemistry of these compounds. Some of this work has appeared in preliminary form.[18]

RESULTS

Our synthetic strategy was based on the capping of mesoporphyrin-II (5) which was available to us [as the ester (6)] through the generosity of Professor A. R. Battersby. Ideally we wanted to use 2,5-bis-alkylated quinones with suitable amino- or hydroxy-substitution such as compounds (8) and (9). However, these compounds were very difficult to handle; they are likely to undergo intramolecular nucleophilic attack so we sought protected hydroquinones with the intention of deprotecting and oxidising the capped products.



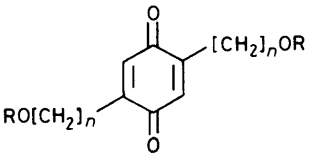
(5) R = OH
(6) R = OEt
(7) R = Cl

1,4-Dimethoxybenzene (12) was chloromethylated to give exclusively the 2,5-bisalkylated product (13). (Friedel-Crafts reactions normally yield both 2,5- and 2,6-bisalkylated products [19]). Compound (13) was transformed, *via* the corresponding nitrile (14) and acid (15) to the diethyl ester (16). Reduction gave the diol (17) needed for the capping reaction. In model oxidative deprotection studies with the acetate (18), ceric ammonium nitrate [20] and argentic oxide [21] each gave quantitative yields of the quinone acetate (10); added porphyrins were recovered unchanged from the reaction mixture in reasonably good yield, apparently indicating the suitability of this approach to the capped series. The amine (19) [obtained by reduction of the benzyl nitrile (14)] was intended to provide an amide-linked capped porphyrin but solubility problems precluded any useful synthetic reactions and that approach was abandoned.

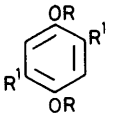
In the capping step mesoporphyrin-II bis(acid chloride) (7) (from 5) was treated with the diol (17) in dichloromethane at high dilution (1.0 mg porphyrin/ml solvent) by addition of the two solutions dropwise, simultaneously, during 8 h to stirred dichloromethane. The capped product (30) was isolated in 8% yield by chromatography. We were, however, unable to deprotect (30) oxidatively to give the desired quinone (1): ceric ammonium nitrate gave meso-nitrated porphyrins, presumably *via* the radical-cation. Argentic oxide, amongst other reactions, inserted silver into the por-

phyrin. Boron tribromide and trimethylsilyl iodide also failed to deprotect without damage.

We decided, therefore, to change the protecting group before capping, and chose methoxymethyl ether (MME = OCH_2OMe) as this is normally very easy to hydrolyse. We also decided to synthesise the quinone cap with hydroxypropyl rather than hydroxyethyl side-chains in the hope



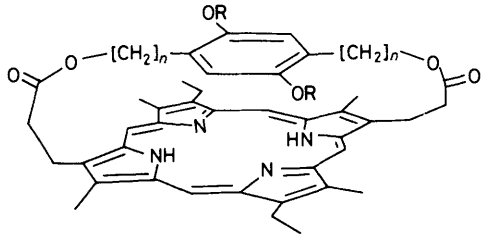
(8) $n = 2$, R = H
(9) $n = 3$, R = H
(10) $n = 2$, R = $COCH_3$
(11) $n = 3$, R = $COCH_3$



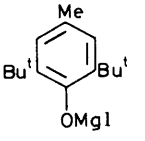
(12) R = Me, R^1 = H
(13) R = Me, R^1 = CH_2Cl
(14) R = Me, R^1 = CH_2CN
(15) R = Me, R^1 = CH_2CO_2H
(16) R = Me, R^1 = CH_2CO_2Et
(17) R = Me, R^1 = CH_2CH_2OH
(18) R = Me, R^1 = CH_2CH_2OAc
(19) R = Me, R^1 = $CH_2CH_2NH_3^+Cl^-$
(20) R = H, R^1 = CH_2CH_2OAc
(21) R = CH_2OMe, R^1 = CH_2CH_2OAc
(22) R = CH_2OMe, R^1 = CH_2CH_2OH
(23) R = Me, R^1 = $CH_2CH(CO_2Et)_2$
(24) R = Me, R^1 = $CH_2CH_2CO_2Et$
(25) R = Me, R^1 = $CH_2CH_2CH_2OH$
(26) R = Me, R^1 = $CH_2CH_2CH_2OAc$
(27) R = H, R^1 = $CH_2CH_2CH_2OAc$
(28) R = CH_2OMe, R^1 = $CH_2CH_2CH_2OAc$
(29) R = CH_2OMe, R^1 = $CH_2CH_2CH_2OH$

that higher yields of, presumably, less-strained capped porphyrin would be obtained. Reaction of the bis-chloromethyl compound (13) with diethyl malonate gave the tetraester (23) which was de-ethoxycarbonylated [22] in wet refluxing dimethyl sulphoxide (DMSO) to yield the diester (24). Reduction and acetylation gave the desired bis-(hydroxypropyl) compound (25) and its diacetate (26). As expected, the capping reaction with (25) proceeded in 20% yield to give compound (31). No attempt was made to deprotect this since our actual targets were the MME-protected compounds (32) and (33).

Rather than simply demethylate the acetate (18), it proved faster and cleaner to deprotect it in a two-step oxidation-reduction sequence *via* the quinone (10) using ceric ammonium nitrate followed by sodium dithionite. The resulting hydroquinone (20) was readily transformed into the MME diacetate (21) and MME diol (22). In the same way, (26) was oxidatively deprotected to (11), reduced to (27), and converted into compounds (28) and (29).



(30) $n = 2$, R = Me
(31) $n = 3$, R = Me
(32) $n = 2$, R = CH_2OMe
(33) $n = 3$, R = CH_2OMe
(34) $n = 2$, R = H
(35) $n = 3$, R = H



(36)

The capping reactions of the MME diols (22) and (29) with (6) were carried out as before but with catalytic triethylamine present and with the addition spread over 24 h. Compound (6) was stable during this period. The capped products (32) and (33) were isolated in 7 and 15% yields respectively after repeated chromatography over silica gel. Uncyclised products containing both porphyrin and cap components were sometimes isolated and characterised but, in general, uncyclised material was hydrolysed: the regenerated mesoporphyrin (5) was recovered for use in further reactions.

To our surprise even the deprotection of the capped MME ethers proved troublesome: aqueous acidic hydrolysis conditions led only to the porphyrin dications! Presumably the proximity of dication inhibited acetal protonation. Deprotection was eventually achieved in 90% yield with boron trichloride at −40 °C, giving the hydroquinones (34) and (35). Lead dioxide oxidation [23] led remarkably rapidly to the desired quinone-capped porphyrins (1) and (2) in 90% yield. The latter were stable, easily handled compounds. The capped hydroquinones, however, appeared to decompose to an additional compound at room temperature, but the ' decomposed ' mixture still gave 90% yield of quinone on oxidation. The ' decomposition ' product appears to be the semiquinone radical anion. This idea is supported by preliminary electrochemical data which indicate that in the absence of central metal ion, E_0 for quinone reduction is more negative (*i.e.* more difficult) than in simple quinones. The unusually rapid PbO oxidation is also explained by this electrochemical result.

In preliminary experiments, magnesium perchlorate in refluxing pyridine cleanly metallated the hydroquinone methyl ether capped porphyrins (30) and (31) at least three times faster than in the corresponding reaction with simple porphyrins. Similar reactions of compounds (1) and (2) gave intractable mixtures, but with Eschenmoser's magnesium phenoxide [24] reagent (36) metallation was complete in a few minutes and 75% yields were obtained after chromatography.

Such rapid metallation seems to be a general feature of capped porphyrins independently of whether the cap is functionalised with a co-ordinating group.[25] The source of this reactivity is not at all clear: it may reflect the higher oxidation potential of the free-base porphyrin, the greater accessibility of the central N–H protons in a non-planar structure, or lesser aromatic character of the severely distorted macrocycle.

Preliminary electrochemical results indicate that in compound (2) quinone reduction is more difficult than in simple quinones, but in compound (4) quinone reduction is easier than normal. U.v.–visible absorption spectra of the capped porphyrins show only small differences from normal porphyrins, and indicate little interaction between the chromophores. The nanosecond photochemistry of (2) and (4) shows more substantial but still undramatic deviations from the norm. The question of the lack of substantial chromophore interaction is taken up in the following paper in connection with the conformation and co-ordination

chemistry of this series of compounds. Some details of the n.m.r. spectra of capped porphyrins are also given in the following paper.

EXPERIMENTAL

N.m.r. spectra of quinones and hydroquinones were obtained at 60 MHz (Varian EM 360) in deuteriochloroform. Chemical shifts are in δ units (p.p.m. from $SiMe_4$). Mass spectra were generally acquired on A.E.I. MS 30 or MS 902 spectrometers, but high-resolution results for molecular weight greater than 700 were obtained on an MS 50 instrument. I.r. spectra were recorded for Nujol mulls, and u.v.–visible spectra in dichloromethane solution.

M.p.s were recorded on a Kofler hot-stage apparatus and are uncorrected. All capped porphyrins had m.p. >300 °C. T.l.c. was carried out with silica-gel plates, the solvent generally being chloroform–methanol (97 : 3). The capped porphyrins were purified by preparative thick-layer chromatography over silica gel (2 mm thickness, E. Merck precoated analytical plates). Magnesium porphyrins were purified over a column of neutral alumina UGl. Dichloromethane was distilled from calcium hydride and stored over molecular sieves 5A.

2,5-*Bischloromethyl*-1,4-*bismethoxybenzene* (13).—Reaction of 1,4-dimethoxybenzene (10.3 g) in dioxan with concentrated hydrochloric acid, hydrogen chloride gas, and formalin yielded, after recrystallisation from acetone, the product (13) (15 g, 86%), m.p. 160 °C (lit., 162 °C).[19]

2,5-*Bis*(*ethoxycarbonylmethyl*)-1,4-*bismethoxybenzene* (16). This compound was prepared from (13) *via* the biscyanide (14) and bis-acid (15) as described by Wood and Gibson, m.p. 115 °C (lit.,[19] 115 °C).

2,5-*Bis*(*aminoethyl*)-1,4-*bismethoxybenzene Dihydrochloride* (19).—This compound was prepared from the biscyanide (14) by diborane reduction; it had m.p. 330 °C (decomp.) (lit.,[19] 335 °C).

2,5-*Bis*(2,2′-*diethoxycarbonylethyl*)-1,4-*bismethoxybenzene* (23).—This compound was prepared from diethyl malonate (16 ml), sodium ethoxide (2.3 g in 100 ml of absolute ethanol), and the chloromethyl compound (13) (12.0 g) in the usual way. The tetra ester (23) was obtained in 75% yield after recrystallisation from ethanol, m.p. 101 °C (lit.,[26] 104 °C); δ 1.2 (6 H, t, $CO_2CH_2CH_3$), 3.15 (4 H, d, benzylic CH_2), 3.75 (6 H, s, OMe) partially overlapping with a triplet, 2 H, $CH(CO_2Et)_2$, 4.15 (4 H, q, *J* 7, $CO_2CH_2CH_3$), and 6.65 (2 H, s, Ar).

2,5-*Bis*(3-*ethoxycarbonylpropyl*)-1,4-*dimethoxybenzene* (24). —A solution of the tetraethyl ester (23) (19 g, 0.04 mol), in dimethyl sulphoxide (250 ml) was refluxed with sodium chloride (8 g) and H_2O (8 ml), for 4 h. The reaction mixture was concentrated to 100 ml under reduced pressure and diluted with ice-cold water. The product was extracted into ether (3 × 100 ml), and the extract washed with water and dried (Na_2SO_4). On concentration, a gum was obtained, (10.5 g, 79%), which crystallised slowly from ethanol to yield the *diester* (24), m.p. 90 °C (Found: M^+, 338.1756, $C_{18}H_{26}O_6$ requires *M*, 338.1765), δ 1.24 (6 H, t, *J* 7, CO_2Et) 2.71 (8 H, m, $ArCH_2CH_2CO_2R$), 3.82 (6 H, s, OMe), 4.09 (4 H, q, CO_2Et), and 6.69 (2 H, s, Ar).

2,5-*Bis*(*hydroxyethyl*)-1,4-*bismethoxybenzene* (17). The diethyl ester (16) (6 g) in tetrahydrofuran (100 ml; freshly distilled from CaH_2) was added to a well stirred slurry of lithium aluminium hydride (3 g) in tetrahydrofuran (50 ml). After aqueous acid work-up and extraction of the aqueous layer with additional tetrahydrofuran (4 × 50 ml), the organic solvent was removed to give a white solid. Recrystallisation of the latter from hot water yielded the *diol* (17) (3.2 g, 75%), m.p. 135 °C (Found: M^+, 226.1205. $C_{12}H_{18}O_4$ requires *M*, 226.1205), δ 2.9 (4 H, t, benzylic CH_2), 3.8 (6 H, s, OMe) overlapped by 3.8 (4 H, t, CH_2OH), 6.7 (2 H, s, Ar). Acetylation of compound (17) gave 2,5-bis(2-acetoxyethyl)-1,4-dimethoxybenzene (18), m.p. 70 °C (lit.,[27] 74 °C).

2,5-*Bis*(3-*hydroxypropyl*)-1,4-*dimethoxybenzene* (25).—The diethyl ester (24) in a similar reduction gave the corresponding *diol* (25) (82%) as needles, m.p. 78 °C after recrystallisation from hot water (Found: M^+, 254.1516. $C_{14}H_{22}O_4$ requires *M*, 254.1517), δ 1.76 (4 H, quint, *J* 6, $CH_2CH_2CH_2$), 2.67 (4 H, t, $ArCH_2$), 3.51 (4 H, t, CH_2OH), 3.76 (6 H, s, OMe), and 6.67 (2 H, s, Ar). Acetylation of the latter compound with acetyl chloride–pyridine gave 2,5-*bis*(3-*acetoxypropyl*)-1,4-*dimethoxybenzene* (26), m.p. 68 °C (Found: *M*, 254.1516. $C_{18}H_{26}O_6$ requires *M*, 254.1517), δ 1.82 (4 H, quint, *J* 6, $CH_2CH_2CH_2$), 2.1 (6 H, s, OAc), 2.67 (4 H, t, $ArCH_2$), 3.79 (6 H, s, OMe), 4.1 (4 H, t, CH_2OAc), and 6.7 (2 H, s, Ar).

2,5-*Bis*(3-*acetoxyethyl*)-1,4-*benzoquinone* (10).—The hydroquinone dimethyl ether (18) (5.5 g) was dissolved in acetonitrile (50 ml) and an aqueous solution of ceric ammonium nitrate (32 g in 50 ml of H_2O) was added dropwise with stirring during 10 min. A transient blue colour was observed during the addition and the addition of oxidant was stopped when the solution failed to produce a blue colour. After being stirred for a further 30 min at room temperature, the reaction mixture was extracted into chloroform and the extract washed with water and dried; on concentration the extract yielded the quinone (10) (4 g, 80%). It recrystallised from hot light petroleum as transparent yellow needles, m.p. 81—83 °C (lit.,[26] 87 °C).

2,5-*Bis*(3-*acetoxypropyl*)-1,4-*benzoquinone* (11).—The diacetate (26) (3 g) dissolved in acetonitrile (40 ml) was oxidised to the quinone with ceric ammonium nitrate by a similar procedure. The quinone (11) (2.5 g, 80%), appeared pure by n.m.r. spectroscopy but could not be induced to crystallise (lit.,[26] m.p. 57 °C).

2,5-*Bis*(2-*acetoxyethyl*)-1,4-*hydroquinone* (20).—The benzoquinone (10 (5.5 g) was suspended in ether (100 ml) and saturated aqueous sodium dithionite was added with shaking. The yellow colour of the solution was discharged, *via* a transient orange-red colouration, to give a colourless solution. The clear organic layer was separated and dried ($MgSO_4$). Evaporation yielded a white solid (4.5 g, 81%) which on crystallisation from hot water gave white needles of the *hydroquinone* (20), m.p. 178 °C (Found: M^+, 282.1106. $C_{14}H_{18}O_6$ requires *M*, 282.1102), δ 2.1 (6 H, s, OAc), 2.61 (4 H, t, *J* 6, $ArCH_2$), 4.15 (4 H, t, CH_2OAc), and 6.61 (2 H, s, Ar).

2,5-*Bis*(3-*acetoxypropyl*)-1,4-*hydroquinone* (27).—The quinone (11) was reduced with dithionite in an analogous way to that described above to yield the hydroquinone (27), m.p. 235—238 °C (Found: M^+, 310.1407. $C_{16}H_{22}O_6$ requires *M*, 310.1414), δ 1.95 (4 H, quint, $CH_2CH_2CH_2$), 2.12 (6 H, s, OAc), 2.67 (4 H, t, $ArCH_2$), 4.1 (4 H, t, CH_2OAc), and 6.58 (2 H, s, Ar).

2,5-*Bis*(2-*hydroxyethyl*)-1,4-*bis*(*methoxymethoxy*)*benzene* (22).—The hydroquinone (20) 5.5 g was suspended in dichloromethane (75 ml) and triethylamine (30 ml) was added to give a clear solution. Chloromethyl methyl ether (12.8 ml) was then added carefully and the reaction mixture was refluxed for 4 h. The excess of reagent was evaporated off

under reduced pressure and the residue was dissolved in ether. Concentration of the dried ethereal layer gave a gum which could be crystallised from ether–pentane to yield the bis-methoxy methyl diacetate (21) (5.2 g, 74%), m.p. 172 °C. This diacetate (4 g) was dissolved in tetrahydrofuran and refluxed with aqueous sodium hydroxide (2N; 50 ml), for 5 h. The excess of tetrahydrofuran was distilled off and the aqueous residue extracted into ether (3 × 50 ml). The organic layer on concentration produced a gum (3 g) which could be crystallised from ether–pentane to give the *diol* (22) (2.5 g, 88%), m.p. 76 °C (Found: M^+ 286.1403. $C_{14}H_{22}O_6$ requires M, 286.1417), δ 2.63 (4 H, t, J 6, ArCH_2), 3.27 (6 H, s, OMe), 3.61 (4 H, t, CH_2OCH_2OMe), 4.91 (4 H, s, OCH_2O), and 6.73 (2 H, s, Ar).

2,5-*Bis*(3-*hydroxypropyl*)-1,4-*bis*(*methoxymethoxy*)*benzene* (29).—This compound was prepared from the hydroquinone diacetate (27) by an analogous procedure *via* the bis-(methoxymethoxy) ether diacetate (28) to give the desired diol (29), m.p. 38 °C (Found: M^+, 314.1729. $C_{16}H_{26}O_6$ requires 314.1727).

General Procedure for Capping Reactions.—Mesoporphyrin-II-biscarboxylic acid (5) (0.5 g, 0.8 mmol) [prepared by hydrolysis of compound (6)], was suspended in dichloromethane (50 ml) and treated with oxalyl chloride (0.5 ml) and dimethylformamide (0.01 ml; freshly passed over silica). The mixture was stirred in the dark for 30 min by which time it had become a clear red solution. Solvent and excess of reagent were rapidly removed on a rotary evaporator to yield the bis(acid chloride) (7) as a red gum which was used immediately in the capping reaction. Thus, the chloride dissolved in dry dichloromethane (250 ml) was slowly added with stirring to a solution of triethylamine (0.5 ml) in dichloromethane (50 ml) in a three-necked flask. A solution of the relevant diol (0.88 mmol) in dichloromethane (250 ml) was added simultaneously to the flask and the rates of addition of the two solutions were maintained equal. The addition was completed during a period of 5 h after which the solution was stirred for a further 15 h. It was then refluxed for 30 min and concentrated to 200 ml. After washing with water and drying ($MgSO_4$), the solution was concentrated to yield a dark gum. The capped porphyrin was isolated by preparative t.l.c. over silica-gel plates. The plates were run in dichloromethane–methanol (97 : 3) after the tank had been saturated for a minimum of 6 h. The capped porphyrin was the fastest moving band and was, therefore, always easily recognised. Slower moving bands were generally isolated together and hydrolysed to regenerate the bisacid (5).

3,13-[2,5-*Dimethoxyphenylenebis*(*ethyleneoxycarbonylethylene*)]*etioporphyrin-I* (30).—The capping reaction between mesoporphyrin-II-bis(acid chloride) (6) (550 mg) and the bis(methoxyether)diol (17) was carried out as described to yield the capped porphyrin (30) (60 mg, 8%) (Found: M^+ 756.3887. $C_{46}H_{52}N_4O_6$ requires M, 756.3887), $\lambda_{max.}$ 403 (ε 5.43), 498 (4.39), 532 (4.30), 564 (4.18), and 620 nm (3.98).

3,13-[2,5-*Dimethoxyphenylenebis*(*trimethyleneoxycarbonylethylene*)]*etioporphyrin-I* (31).—Similarly the bis(acid chloride) (6) (280 mg) and the diol (25) yielded the capped porphyrin (31) (78 mg, 20%) (Found: M^+, 784.4205. $C_{48}H_{56}N_4O_6$ requires M, 784.4200).

3,13-[2,5-*Bismethoxymethylphenylenebis*(*trimethyleneoxycarbonylethylene*)]*etioporphyrin I* (33).—Analogous reaction of the diol (29) gave the capped *product* (33) (75 mg, 15%) (Found: M^+, 844.4394. $C_{50}H_{60}N_4O_8$ requires M, 844.4408), $\lambda_{max.}$ 405 (ε 5.67), 4.97 (4.59), 530 (4.52), 568 (4.43), and 620 nm (4.24).

3,13-[2,5-*Bismethoxymethylphenylenebis*(*ethyleneoxycarbonylethylene*)]*etioporphyrin I* (32).—Similarly the diol (22) gave the capped porphyrin (32) (35 mg, 7%) which was used without further purification or characterisation.

3,13-[2,5-*Dihydro*-2,5-*dioxophenylenebis*(*trimethyleneoxycarbonylethylene*)]*etioporphyrin I* (2).—The cyclic diester (33) 20 mg, was dissolved in dichloromethane (10 ml) and the solution was cooled to −40 °C in a solid CO_2–acetone bath. This was then treated with boron trichloride (0.3 ml), in the dark under a nitrogen atmosphere. The solution was stirred for 7 h during which period it was slowly allowed to attain room temperature. The reaction mixture was then poured onto ice–water to decompose excess of reagent and was worked up in dichloromethane. The organic layer was washed successively with aqueous saturated sodium carbonate (to remove boron salts), water, and aqueous sodium chloride. It was then dried ($MgSO_4$) and the solvent evaporated to yield the unstable hydroquinone capped porphyrin (35) (15 mg, 80%) as a red powder which was used immediately: it was dissolved in benzene–dichloromethane (1 : 1) and treated with lead dioxide (30 mg). The mixture was stirred at room temperature in the absence of light for 5 min. T.l.c. at this point showed a single spot, faster moving than the starting compound. The lead dioxide was filtered off and washed with dichloromethane. The filtrate on concentration gave a pink solid which was purified by preparative chromatography on silica gel plates, developed with dichloromethane–methanol (97 : 3). The quinone capped porphyrin (2) (13 mg, 90% from hydroquinone) was recrystallised from dichloromethane–methanol (Found: C, 71.35; H, 6.65; N, 7.3. $C_{46}H_{50}N_4O_6 \cdot H_2O$ requires C, 71.47; H, 6.78; N, 7.25), $\lambda_{max.}$ 253 (ε 3.62), 400 (5.58), 496 (4.52), 538 (4.38), 565 (4.29), and 620 nm (4.09); M^+, 754.

3,13-[2,5-*Dihydro*-2,5-*dioxophenylenebis*(*ethyleneoxycarbonylethylene*)]*etioporphyrin-I* (1).—Similarly the methoxymethoxyporphyrin (32) (18 mg) was de-protected to give the hydroquinone capped porphyrin (34) and oxidised to the quinone capped porphyrin (1) [12 mg, 70% from compound (32)] which was recrystallised from dichloromethane–methanol (Found: C, 69.85; H, 6.35; N, 7.65. $C_{44}H_{46}N_4O_6 \cdot 2H_2O$ requires C, 69.30; H, 6.49; N, 7.34), $\lambda_{max.}$ 256 (ε 2.2), 400 (5.18), 498 (4.09), 534 (3.98), 566 (3.87), and 620 nm (3.61); M^+, 726.

Metallation Procedure: Preparation of the Reagent (36).—Freshly sublimed 4-hydroxy-2,6-di-t-butyltoluene (BHT) (780 mg) was dissolved in dry dichloromethane (15 ml; freshly distilled over calcium hydride under a nitrogen atmosphere). Into this solution was injected an ethereal solution of fresh ethylmagnesium iodide (from 96 mg of magnesium, 0.8 ml of ethyl iodide in 15 ml of dry ether); the mixture was stirred in the dark for 10 min. During this period, a vigorous reaction occurred and the solution became clear. The temperature was kept at 10 °C. The reagent was used within 30 min since prolonged exposure to air led to decomposition, to produce a deep yellow colour.

Magnesium(II) 3,13-[2,5-*Dihydro*-2,5-*dioxophenylenebis*-(*trimethyleneoxycarbonylethylene*)]*etioporphyrinate-I* (4).—The porphyrin (2) (20 mg) in dry dichloromethane (10 ml) was treated with the BHT reagent (36) in the absence of light at 10 °C. The reaction was followed by u.v.–visible spectroscopy and was essentially complete in 10 min. The reaction mixture was diluted with saturated aqueous sodium hydrogen phosphate to decompose the excess of reagent and

the product extracted into tetrahydrofuran (2 × 100 ml). The extract was washed successively with aqueous sodium hydrogen phosphate, water, and aqueous sodium chloride, dried ($MgSO_4$), and concentrated to yield a reddish brown mass. This was passed through a column of neutral alumina with, successively, light petroleum, increasing amounts of dichloromethane in light petroleum, and finally pure dichloromethane as eluants. The initial yellow band that separated out was eluted completely with dichloromethane. 2% Methanol in dichloromethane eluted a bluish pink band of the *porphyrin* (4) (15 mg, 75%) (Found: C, 68.7; H, 6.4; N, 6.9. $C_{46}H_{48}N_4O_6Mg \cdot 1.5H_2O$ requires C, 68.74; H, 6.35; N, 6.97%), $\lambda_{max.}$ 260 (ε 4.23), 332 (4.22), 405 (5.27), 540 (4.08), 576 nm (4.01); M^+, 776.

Magnesium(II) 3,13-[2,5-*Dihydro*-2,5-*dioxophenylenebis*-(*ethyleneoxycarbonylethylene*)]*etioporphyrinate-I* (3).— Similarly the quinone capped porphyrin (1) (20 mg) gave the magnesium quinone capped porphyrin (3) (15 mg, 75%) (Found: M^+, 748.3127. $C_{44}H_{44}MgN_4O_6$ requires 748.3111), $\lambda_{max.}$ 252 (ε 4.93), 332 (4.28), 400 (5.84), 540 (4.26), 578 nm (4.10).

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