Some Reactions of *meso*-Formyloctaethylporphyrin

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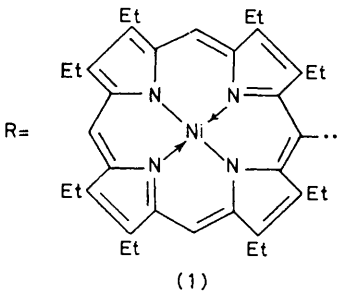
Grignard reactions on nickel *meso*-formyloctaethylporphyrin (1a) yield methyl and phenyl carbinols. The former is readily dehydrated to the *meso*-vinyl derivative, which by hydrogenation yields the *meso*-ethyl analogue, and by bromination and dehydrobromination affords the *meso*-ethynyl compound. The latter is readily oxidised to the 1,4-diporphyrinylbuta-1,3-diyne. Reaction of sulphuric acid with the *meso*-phenyl carbinol gives a *meso*-benzyl derivative in which one β-ethyl group has been dehydrogenated to give a β-vinyl substituent. Attempts to form a carbene from (1a) with triethyl phosphite gave the *meso*-propenyl compound and with boron trifluoride and zinc amalgam gave the *meso*-formyloxy derivative, which is transformed readily into the *meso*-methoxy compound. Mechanisms for these novel reactions are suggested.

Of the various *meso*-substituted octa-alkylporphyrins, the formyl compounds are fairly readily available and a number of reactions have been documented. *meso*-Formylporphyrins can be prepared by oxidation of *meso*-methylporphyrins [1], or better by removal of the metal from the nickel or copper complexes, which can be easily obtained by Vilsmeier formylation of the corresponding metal porphyrins.[2,3] Many of the standard reactions of aldehydes have been applied to the metal-free *meso*-formyl derivatives of porphyrin itself, pyrroporphyrin XV, aetioporphyrin I, and octaethylporphyrin (OEP), *e.g.* oxidation, reduction, and formation of oximes, semicarbazones, imines, and cyanhydrins as well as condensations with malonic esters and nitriles.[1-10] Some of these reactions have been demonstrated also for the metal complexes of *meso*-formyl-OEP but large differences in reactivities may be caused by the presence of the metal. Callot [11] has reported the reactions of nickel *meso*-formyl-OEP (1b) with a variety of Wittig reagents, *e.g.* the preparation of the *meso*-vinyl derivative (1b) (27%). More recently we have described [12] the reduction of (1a) to the primary carbinol (1c) and have shown that by the action of sulphuric acid it is converted into the dimer (1e). A similar sequence was observed with the copper(II) complex. This reaction was thought to involve electron transfer from the metal to the presumed carbocationic intermediate, giving rise to the radical which then dimerised.

In seeking to extend this observation, we have prepared the methyl carbinol (1d) and the phenyl carbinol (1f) by the appropriate Grignard reactions. The former compound was readily dehydrated, and direct reaction with toluene-*p*-sulphonic acid gave the *meso*-vinyl compound (1b) (50% overall), identical with the product described by Callot,[11] *i.e.* no dimerisation was observed in this case. Moreover, the vinyl compound was unchanged when a solution in dimethylformamide was heated with sulphuric acid, the conditions used for the dimerisation of the primary carbinol. Hydrogenation of the vinyl derivative gave the nickel *meso*-ethyl-OEP (1g), and bromination with pyridinium hydrobromide perbromide gave the *trans*-β-bromovinyl derivative (1h) as the major product (48%), together with the *cis*-isomer (1i) (14%). The unexpected formation of the vinyl substitution product rather than the 1,2-dibromide presumably results from steric inhibition. Dehydrobromination of (1h) and (1i) with sodium hydride in refluxing 1,2-dimethoxyethane gave a little of the *meso*-vinyl compound (1b) but mainly the purple ethynyl derivative (1j), which proved difficult to purify by chromatography because of oxidation to the green diacetylenic derivative (1k). These are the first *meso*-acetylenic porphyrin derivatives to be described. The diporphyrinyldiacetylene was also obtained, along with some of the *meso*-vinyl compound, from the monoethynyl compound by reaction of a solution in pyridine with copper(II) acetate. The formation of the *meso*-vinyl compound as well as the dimer suggests that a disproportionation reaction had accompanied the oxidative



(a) RCHO
(b) RCH:CH_2
(c) RCH_2OH
(d) RCH(OH)CH_3
(e) RCH_2·CH_2R
(f) RCH(OH)Ph
(g) RCH_2·CH_3
(h) RCH:CHBr (*trans*)
(i) RCH:CHBr (*cis*)
(j) RC:CH
(k) RC:C·C:CR
(l) RCH:CH·CH_3
(m) RO·CHO
(n) ROCH_3
(o) RCH:NOH
(p) RCN

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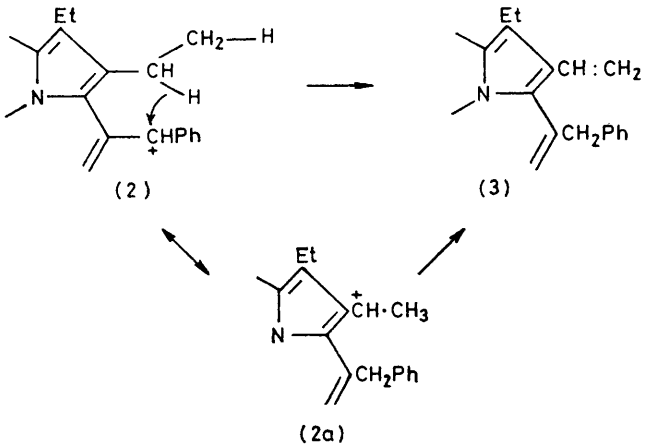
coupling. In the diporphyrinyldiacetylene (1k) there appeared to be considerable interaction between the two porphyrin rings, as the electronic spectrum of the diyne differed considerably from that of the monoyne. A marked bathochromic shift was observed as well as an intense band at 484 nm (ε 130 600) which is not present in any of the spectra of metalloporphyrins reported to date. The large porphyrin groups also exert a powerful steric effect on the butadiyne system and the diacetylene was unchanged after an attempted hydrogenation at



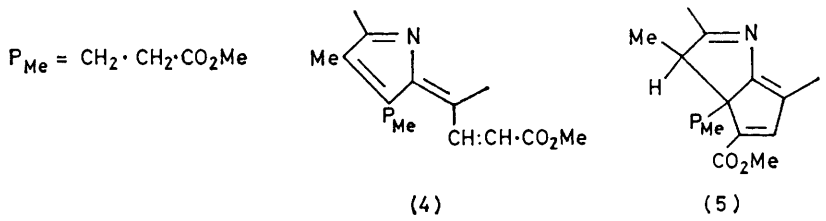
SCHEME 1

100 °C and 100 atm for 4 h in the presence of Raney nickel. The dimer was quite stable and the molecular ion was clearly observed at *m/e* 1226. Ions were observable for the loss of alkyl groups with the dimer still intact and also the ion M^{2+}.

Treatment of a solution of the phenyl carbinol (1f) in dimethylformamide with sulphuric acid gave a red nickel porphyrin (25%), the n.m.r. spectrum of which enabled the structure to be deduced. Integration showed that only seven of the original eight β-ethyl groups were present, along with a new β-vinyl substituent, revealed as an ABX system. Signals corresponding to another seven protons appeared in the region δ 6—7. These facts and elemental analysis supported the formulation of the compound as the nickel complex of *meso*-benzyl-β-vinylheptaethylporphyrin. The signals assignable to the benzyl protons showed a temperature dependence: on cooling from +45 to −50 °C, the signal varied from a singlet through a broad envelope to an AB quartet with J_{AB} 16 Hz. This behaviour is explained by restricted rotation about the *meso*-C-CH_2Ph bond, thus favouring a conformation where the benzyl protons are non-equivalent, one being adjacent to the 3-vinyl group and the other to the 7-ethyl group.

The reaction may be visualised as involving the benzylic cation (2) which then, in order to relieve strain, abstracts hydride from the neighbouring β-ethyl group to give the product (3), but it is more likely (as suggested by a referee) that an equilibrating mixture of cations (2) and (2a) is formed and as only (2a) can be deprotonated, the equilibrium is displaced, leading to the product (Scheme 1). Hydrogen transfer of a related type is involved in the porphyrin–purpurin transformation which was a key step in Woodward's chlorophyll synthesis [13] [(4) ⟶ (5); *cf.* ref. 7]. Thus the primary *meso*-carbinol and the secondary *meso*-methyl and phenyl (5) carbinols of NiOEP behave in completely different ways in the presence of sulphuric acid.

We have sought to establish conditions under which the single carbon substituent derived from the *meso*-formyl group might be incorporated into the porphyrin ring to yield a homoporphyrin. Callot [14] established that this could be achieved in an intramolecular manner when a carbanion was created on an α-carbon atom of the nickel porphyrin *N*-substituent. As the creation of a cationic centre on an α-*meso*-carbon atom led to reactions other than ring expansion, we have investigated the effect of creating a carbenoid centre in this position. The tosylhydrazone of nickel *meso*-formyl-OEP proved impossible to isolate, and the preparation of the unsubstituted hydrazone was likewise unreliable. Two other attempts to form such a carbene have led to unexpected results. Thus when the formyl compound (1a) was heated under reflux with triethyl phosphite for 3 h (*cf.* ref. 15) it gave a product (10%) which proved to be the *meso-trans*-propenyl derivative (1l). In the reaction of phthalic anhydride with triethyl phosphite,[15] the dimerisation of the proposed carbene intermediate was accompanied by the formation of the Arbuzov rearrangement product, diethyl ethylphosphonate [$(EtO)_2P(O)Et$]. In the present reaction, this last compound could be responsible for the formation of the product by a subsequent Wittig reaction (Scheme 2).



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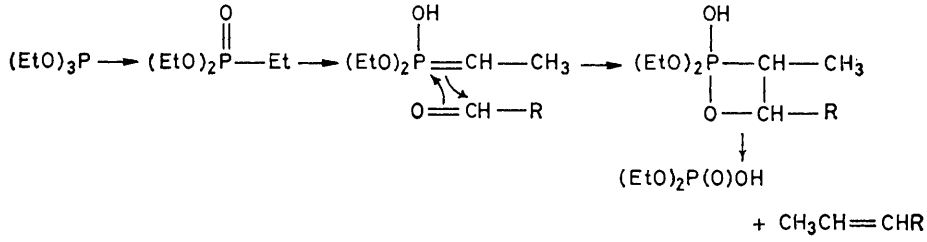
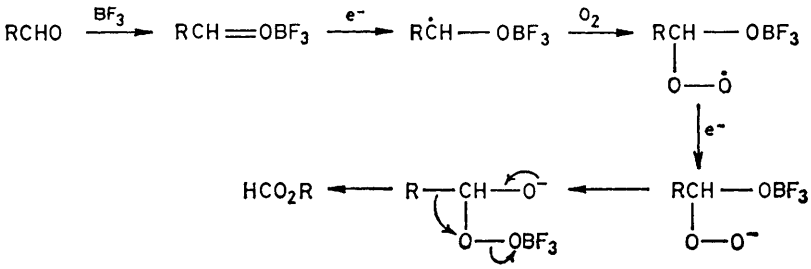
In another attempt to form the carbene, the aldehyde (1a) was treated with zinc amalgam and boron trifluoride–ether complex in tetrahydrofuran–1,2-dimethoxyethane for 3 days at room temperature (*cf.* ref. 16). In the presence of atmospheric oxygen, the major product was the *meso*-formyloxy derivative (1m), *i.e.* the product of a Baeyer–Villiger oxidation. Under nitrogen no appreciable reaction had occurred after an extended reaction time. A possible formulation of the mechanism is shown in Scheme 3. The product is the formate ester of the *meso*-hydroxyporphyrin, *i.e.* the enolic ester of



SCHEME 2



SCHEME 3

the oxophlorin which is a well known oxidation product of the porphyrin.[17] Hydrolysis of (1m) with methanolic potassium hydroxide followed by methylation with methyl iodide gave the *meso*-methoxy derivative (1n). A similar series of reactions was carried out with nickel aetioporphyrin I.

EXPERIMENTAL

N.m.r. spectra were measured for solutions in [^{2}H]-chloroform and u.v.–visible spectra for solutions in chloroform (except where otherwise stated) with instruments listed previously.[18] Mass spectra were determined with an A.E.I. MS30 instrument by direct insertion into the ion source.

Nickel meso-*Vinyl-OEP* (1b).—Nickel *meso*-formyl-OEP (100 mg) in dry tetrahydrofuran (50 ml) was heated under reflux for 12 h with a large excess of ethereal methylmagnesium iodide. The mixture was hydrolysed with saturated aqueous ammonium chloride and extracted with ether, and the organic layer was dried and evaporated, yielding a red solid. Normally this crude product was treated with toluene-*p*-sulphonic acid (10 mg) in dry benzene at room temperature for 6 h, which yielded nickel *meso*-vinyl-OEP (1b) (50 mg, 50%) after chromatography on alumina (30% $CHCl_3$–hexane as eluent) and crystallisation from CH_2Cl_2–MeOH. This product had spectral properties identical with those quoted for the compound prepared by the Wittig reaction.[11] On one occasion, the crude product from the Grignard reaction was chromatographed rapidly on an alumina column (elution with 50% CH_2Cl_2–hexane) and the purple product from the major band, nickel *meso*-(1-hydroxyethyl)-OEP (1d), was isolated; δ_H 1.04 [3 H, d, CH(OH)CH_3], 1.73 (24 H, t, peripheral ethyl CH_3), 3.76 (16 H, q, peripheral ethyl CH_2), 6.25 [1 H, m, CH(OH)CH_3], and 9.32 (s, 3 *meso*-H), $\lambda_{max.}$ 411, 544, and 587 nm. On keeping a solution of the product in $CDCl_3$, decomposition to the *meso*-vinyl derivative occurred rapidly (n.m.r.). A solution of the *meso*-vinyl derivative in dimethylformamide was heated under reflux for 16 h, but the starting material was recovered unchanged.

Nickel meso-*Ethyl-OEP* (1g).—The foregoing vinyl compound (50 mg) was dissolved in benzene, 10% palladium–charcoal (30 mg) was added, and the solution was stirred in hydrogen for 5 h at 50 °C. Removal of the catalyst and chromatography on alumina (50% benzene–hexane for elution) gave the *meso*-ethyl derivative together with a green impurity, presumably the chlorin ($\lambda_{max.}$ 630 nm). The mixture was treated with an excess of dichlorodicyanobenzoquinone (DDQ) in benzene, which re-oxidised the chlorin, and the deep red solution was chromatographed on alumina (25% benzene–hexane for elution). The product (28 mg, 56%) was crystallised from dichloromethane–methanol; it formed fine purple *needles*, m.p. 222–224°, δ_H 0.70 (3 H, t, *meso*-CH_2·CH_3), 1.81 (24 H, t, peripheral CH_2·CH_3), 3.82 (16 H, q, peripheral CH_2·CH_3), 4.53 (2 H, q, *meso*-CH_2·CH_3), and 9.33 (s, 3 *meso*-H); $\lambda_{max.}$ 303, 343, 411, 537, and 574 nm (ε 10 410, 12 470, 150 920, 8 780, and 11 130); *m/e* 618 (M^+, 100%) and 590 (M —

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C_2H_4, 30%) (Found: *m/e* 618.323 038. $C_{38}H_{48}N_4Ni$ requires *M*, 618.323 238).

cis- *and* trans-*Nickel* meso-β-*Bromovinyl-OEP* (1h *and* i).—Nickel *meso*-vinyl-OEP (260 mg) and pyridinium hydrobromide perbromide (130 mg) were heated under reflux for 12 h in 1,2-dichloromethane. The solution was washed with water, dried, and evaporated. The residue was chromatographed on an alumina column (elution with 25% $CHCl_3$–hexane). The product from the major red band was collected (210 mg). T.l.c. of this fraction showed the presence of a trace of unchanged nickel *meso*-vinyl-OEP. The major product was purified by preparative t.l.c. on silica plates (elution with 20% $CHCl_3$–hexane) and crystallized as red *needles* from CH_2Cl_2–methanol (140 mg, 48%) (Found: C, 66.0; H, 6.4; Br, 11.45; N, 8.0. $C_{38}H_{45}BrN_4Ni$ requires C, 65.55; H, 6.5; Br, 11.45; N, 8.0%), $\lambda_{max.}$ 568 (ε 16 200), 531 (10 400), 407 (171 000), and 347 nm (14 520), δ_H 1.63 and 1.73 (t, CH_3 of peripheral Et), 3.78 (q, CH_2 of peripheral Et), 5.45 (d, J_{trans} 14 Hz, CH:C*H*Br), 9.38 (d, *J* 14 Hz, C*H*:CHBr), and 9.43 (s, *meso*-H). The minor red component in the product was readily separated from the *trans*-nickel *meso*-β-bromovinyl-OEP by preparative t.l.c. and was crystallised from CH_2Cl_2–methanol, yielding bright violet *needles* (40 mg, 14%), m.p. 203—206° (Found: C, 65.45; H, 6.2; Br, 11.5; N, 8.0%. $C_{38}H_{45}BrN_4Ni$ requires C, 65.55; H, 6.5; Br, 11.45; N, 8.0%), $\lambda_{max.}$ 568 (ε 20 000), 531 (11 590), 407 (197 900), and 346 nm (16 650), δ_H 1.62, 1.69, and 1.76 (t, CH_3 of peripheral Et), 3.79 (q, CH_2 of peripheral Et groups), 6.83 (d, J_{cis} 7.5 Hz, CH:C*H*Br), 9.45 (s, *meso*-H), and 9.52 (d, *J* 7.5 Hz, C*H*:CHBr).

Nickel meso-*Ethynyl-OEP* (1j).—A mixture of the above bromovinyl compounds (150 mg) and sodium hydride (*ca.* 50 mg) in dry 1,2-dimethoxyethane (50 ml; distilled from $LiAlH_4$) containing dry dimethyl sulphoxide (0.1 ml) was heated under reflux with stirring for 12 h, during which the colour changed from red to purple. Evaporation, extraction of the residue with dichloromethane and water, separation of the organic layer, drying, and removal of solvent yielded a purple solid. Chromatography on alumina and elution with 30% $CHCl_3$–hexane did not completely separate the initial red band (shown by t.l.c. to be nickel *meso*-vinyl-OEP) from the closely following purple band of the major product. Further attempts at purification by column or thin-layer chromatography resulted in extensive decomposition with formation of a green compound (see below). A sample of *ca.* 80% purity was obtained for spectral analysis; $\lambda_{max.}$ 417, 549, and 592 nm (ε 15 : 1 : 1.3) δ_H 1.69 and 1.72 (24 H, t, CH_3 of peripheral Et), 3.74 (12 H, q, CH_2 of 6 peripheral Et), 4.12 (q, CH_2 of 3- and 7-Et), 4.42 (s, ethynyl H), and 9.39 (s, 3 *meso*-H), $\nu_{max.}$ 3 315 (≡CH) and 2 090 cm^{-1} (C≡C).

1,4-*Bis*-meso-(*nickel octaethylporphyrinyl*)-*buta*-1,3-*diyne* (1k).—The above nickel *meso*-ethynyl-OEP was dissolved in dry pyridine (30 ml) and stirred at 60 °C for 2 h with anhydrous copper(II) acetate. The colour of the solution rapidly became deep green. The pyridine solution was poured into 2N-HCl (600 ml) and the mixture was extracted with dichloromethane until the aqueous layer was colourless. The organic layer was dried and evaporated and the residue chromatographed on an alumina column (elution with 40% chloroform–hexane). The major green product was contaminated with nickel *meso*-vinyl-OEP, which could not be removed by column or thin-layer chromatography. Two precipitations by addition of methanol to a concentrated solution of the mixture in dichloromethane resulted in complete separation of the two components, the red nickel *meso*-vinyl-OEP remaining in the dichloromethane. Slow crystallisation from dichloromethane–methanol yielded the product as shiny very dark green *plates* (70 mg, 53% from bromovinyl derivatives), m.p. >300° (Found: C, 74.75; H, 7.15; N, 9.4. $C_{76}H_{86}N_8Ni$ requires C, 74.3; H, 7.05; N, 9.1%), $\lambda_{max.}$ 618 (ε 57 300), 484 (130 600), 457 (114 400), and 427 (112 800), $\lambda_{infl.}$ 574 (25 800), 531 (19 590), and 377 nm (35 800), $\nu_{max.}$ 2 120 cm^{-1} (C≡C), δ_H 1.71 and 1.86 (48 H, t, CH_3 of peripheral Et), 3.72, 3.77, and 4.20 (32 H, q, CH_2 of peripheral Et), 9.33 (s, 2, *meso*-H), and 9.38 (s, 4 *meso*-H), *m/e* 1 226 (*M*, 10%), 626 (20), 602 (100), 587 (20).

Nickel meso-α-*Hydroxybenzyl-OEP* (1f).—Nickel *meso*-formyl-OEP (1a) (230 mg) in tetrahydrofuran (100 ml) was heated under reflux for 12 h with phenylmagnesium bromide (*ca.* 20-fold excess) in ether. Although t.l.c. showed the presence of starting material, extended heating produced little further reaction. Work-up by treatment with saturated aqueous NH_4Cl and extraction with ether yielded a red–brown solution which was dried and evaporated. The residue was chromatographed on an alumina column (50% $CHCl_3$–hexane for elution). A green band of starting material was followed by the major red band, which was separated and the solution evaporated. Crystallisation of the residue from de-acidified CH_2Cl_2 and MeOH yielded the product as fine purple needles (120 mg, 46%). (Found: C, 73.9; H, 7.75; N, 7.85. $C_{43}H_{50}N_4NiO$ requires C, 74.05; H, 7.2; N, 8.05%), $\lambda_{max.}$ 307 (ε 10 900), 354 (14 400), 412 (160 400), 539 (8 500), and 579 nm (14 200), δ_H 1.36, 1.62, 1.72, and 1.74 (overlapping t, CH_3 of peripheral Et), 1.45 (s, OH, removed after D_2O exchange), 3.68—3.76 (overlapping q, CH_2 of peripheral Et), 6.5 and 6.9, (m, Ph), 7.55 [d, collapsed to s after D_2O exchange, C*H*(OH)Ph], 9.32 (s, 2 *meso*-H), and 9.39 (s, 1 *meso*-H), δ_C 71.64 [*C*H(OH)Ph], 126.00 and 127.61 (3 : 2, Ph) (all d in off-resonance), 144.98 (α-C, s in off-resonance), *m/e* 696 (100%), 680 (60), and 590 (55), $\lambda_{max.}$ 307 (ε 10 900), 354 (14 400), 412 (160 400), 539 (8 500), and 579 nm (14 200).

Nickel 5-*Benzyl*-3-*vinyl-OEP* (3).—The carbinol (1f) (100 mg) was heated at *ca.* 130 °C for 1 h in *NN*-dimethylformamide (10 ml) containing concentrated sulphuric acid (3 drops). The mixture was treated as usual and was chromatographed on an alumina column (elution with 50% $CHCl_3$–hexane changing to 100% $CHCl_3$). The initial red band, which was followed by a series of green, brown, and red bands, was subjected to t.l.c. on silica gel, with repeated elution by 10% $CHCl_3$–hexane. The major red component (3) was isolated and crystallised from CH_2Cl_2–MeOH as shining purple *plates* (20 mg), m.p. 246—248° (Found: C, 76.1; H, 7.1; N, 8.5. $C_{43}H_{48}N_4Ni$ requires C, 76.0; H, 7.1; N, 8.25%), *m/e* 678 (*M*, 77%) and 587 (*M* − C_6H_5·CH_2, 100%), *m** 530.9 and 508.2, δ_H 1.73 and 1.74 (21 H, overlapping t, peripheral CH_2·C*H*$_3$), 3.72 and 3.76 (14 H, overlapping q, peripheral C*H*$_2$·CH_3), 5.66 and 5.73 (both q, AB of ABX, J_{gem} 2, J_{cis} 11.5, J_{trans} 17 Hz, CH:C*H*$_2$), 6.09 (br s at 25 °C), 6.3 (br m), 6.77 (m, 3 signals of C_6H_5·CH_2), 7.65 (q, X of ABX), and 9.37, 9.38, and 9.43 (all s, 3 *meso*-H), $\lambda_{max.}$ 345 (ε 15 400), 411 (188 700), 534 (11 700), and 569 nm (16 500).

Nickel meso-*Propenyl-OEP* (1l).—Nickel *meso*-formyl-OEP (1a) (100 mg) was heated in triethyl phosphite (25 ml) under reflux for 3 h. The excess of solvent was removed under reduced pressure and the residue was chromatographed on alumina. The first purple-red band was eluted

with chloroform–light petroleum (1 : 1) and gave a purple solid which was crystallised from methylene chloride–methanol to give dark purple *needles* (10 mg, 10%), m.p. 275—277° (Found: C, 73.85; H, 7.6; N, 9.05. $C_{39}H_{48}N_4Ni$ requires C, 74.15; H, 7.65; N, 8.85%), *m/e* 630 (M^+), 601, and 590, $\lambda_{max.}$ 408 (ε 169 000), 530 (11 270), 566 nm (16 600), δ_H 1.70 (24 H, m, peripheral $CH_2{\cdot}CH_3$), 1.9 (d, CH_3 of side-chain), 3.8 (16 H, q, peripheral $CH_2{\cdot}CH_3$), 4.8 (1 H, m, $CH{:}CH{\cdot}CH_3$), 8.69 (1 H, d, *J* 16 Hz, $CH{:}CH{\cdot}CH_3$), and 9.40 (s, 3 *meso*-H).

Nickel meso-*Formyloxy-OEP* (1m).—Nickel *meso*-formyl-OEP (1a) (100 mg), boron trifluoride (2 ml), and amalgamated zinc (5 g) were stirred in dry tetrahydrofuran (15 ml) and 1,2-dimethoxyethane (15 ml) for 3 days. The solvent was removed under reduced pressure and the residue was extracted into benzene. Removal of the solvent *in vacuo* gave a red solid which was purified by preparative t.l.c. on silica (50% chloroform–light petroleum for elution). The major red band was removed and the product crystallised from dichloromethane–methanol to give the meso-*formate* as red needles (40 mg, 39%), m.p. 236—238° (Found: C, 69.4; H, 7.25; N, 8.75. $C_{37}H_{44}N_4NiO_2$ requires C, 69.9; H, 7.0; N, 8.8%), *m/e* 634 (M^+) and 606 ($M^+ - CO$), $\lambda_{max.}$ 559 (ε 19 360), 524 (11 500), and 402 nm (298 740), ν(KBr) 1 750 and 1 770 cm^{-1} (both sharp). δ_H 1.9 (overlapping t, 24 H of peripheral $CH_2{\cdot}CH_3$), 3.9 (unsym. q, 16 H of peripheral $CH_2{\cdot}CH_3$), 8.3 (s, O_2CH), 9.71 (s, 1 *meso*-H), and 9 76 (s, 2 *meso*-H).

Nickel meso-*Formyloxyetioporphyrin I*.—A similar reaction with nickel formyletioporphyrin I[3] (100 mg) gave the corresponding meso-*formate* as red needles (35 mg, 34%), m.p. 219—220° (Found: C, 68.05; H, 6.45; N, 9.4%; *m/e*, 578.218 985. $C_{33}H_{36}N_4NiO_2$ requires C, 68.4; H, 6.25; N, 9.65%; *M*, 578.219 153), *m/e* 578 (M^+) and 550 ($M^+ - CO$), $\lambda_{max.}$ 556 (31 510), 521 (17 810), and 400 nm (270 500), $\nu_{max.}$ 1 760 cm^{-1}, δ_H 1.73 (unsym. t, 12 H of peripheral $CH_2{\cdot}CH_3$), 3.35 (s, 12 H of peripheral CH_3), 3.8 (q, 8 H of peripheral $CH_2{\cdot}CH_3$), 8.4 (s, O_2CH), 9.5 (s, 1 *meso*-H), and 9 55 (s, 2 *meso*-H).

Nickel meso-*Methoxy-OEP* (1n).—Saturated methanolic potassium hydroxide (2 ml) was added to a solution of the corresponding *meso*-formyloxy-derivative (1m) (25 mg) in chloroform (25 ml). The mixture was stirred at room temperature for 15 min and after washing with water (3 ×) and drying (Na_2SO_4), the solution was evaporated to dryness *in vacuo*. The residue was dissolved in dry acetone (20 ml) and stirred with anhydrous K_2CO_3 for 5 min to give a green solution. Methyl iodide (2 ml) was added and the mixture stirred for a further 1 h at room temperature. The product was filtered and the solvent removed from the filtrate under reduced pressure. The residue was chromatographed on alumina (50% chloroform–light petroleum for elution) and the main band was separated. Removal of solvent gave the crude *product* which was crystallised from dichloromethane to yield purple needles (18 mg, 74%), m.p. 227—229° (Found: C, 71.7; H, 7.25; N, 9.45. $C_{37}H_{46}N_4NiO$ requires C, 71.5; H, 7.45; N, 9.0%), $\lambda_{max.}$ 405 (ε 208 970), 525 (14 140), and 560 nm (17 820), δ_H 1.8 (m, 24 H of peripheral $CH_2{\cdot}CH_3$), 3.8 (m, 19 H of peripheral $CH_2{\cdot}CH_3$ and OCH_3), 9.45 (s, 1 *meso*-H), and 9.48 (s, 2 *meso*-H).

Nickel meso-*Methoxyetioporphyrin I*.—A similar reaction with nickel *meso*-formyloxyetioporphyrin I (12 mg) gave the corresponding nickel meso-*methoxy-derivative* which formed purple needles (4 mg, 33%), m.p. 248—250° (from dichloromethane–methanol) (Found: C, 69.9; H, 6.8; N, 9.85%; *m/e* 564.239 935. $C_{33}H_{38}N_4NiO$ requires C, 70.1; H, 6.75; N, 9.9%; *M*, 564.239 888), $\lambda_{max.}$ 404 (199 360), 524 (12 250), and 559 nm (15 610), δ_H 1.82 (unsym. t, 12 H of peripheral $CH_2{\cdot}CH_3$), 3.47 (s, 9 H of 3 peripheral CH_3), 3.60 (s, 3 H of 1 peripheral CH_3), 3.91 (unsym q, 8 H of peripheral $CH_2{\cdot}CH_3$), 3.98 (3 H, s, OCH_3), 9.47 (s, 1 *meso*-H), and 9.51 (s, 2 *meso*-H).

Nickel meso-*Cyanoetioporphyrin I* (cf. *ref.* 3).—Nickel *meso*-formyletioporphyrin I[3] (120 mg) and hydroxylamine hydrochloride (70 mg) were dissolved in pyridine (80 ml) and heated on a water-bath for 1 h. The red solution was poured into water (150 ml) and the red-brown precipitate was filtered off, washed with water, and then extracted with CH_2Cl_2. The extract was dried and evaporated and the residue taken up in acetic anhydride (100 ml) and heated under reflux for 1 h. The mixture was poured into water (100 ml) and stirred for ½ h, then extracted with chloroform. The extract was dried and evaporated and the purple residue was chromatographed on an alumina column (75% chloroform–hexane for elution). The major purple band was isolated and the product crystallised from chloroform–methanol as purple *needles* (60 mg, 50%), m.p. >300°. A sample for analysis was obtained by t.l.c. on silica (20% $CHCl_3$–hexane for elution) followed by crystallization from chloroform–methanol (Found: C, 70.35; H, 6.4; N, 12.7. $C_{33}H_{35}N_5Ni$ requires C, 70.75; H, 6.3; N, 12.7%), $\lambda_{max.}$ 305 (ε 10 880), 406 (163 510), 550 (8 500), and 588 nm (20 510), $\nu_{max.}$ 2 215 cm^{-1} (CN), δ_H 1.68 and 1.74 (t, peripheral $CH_2{\cdot}CH_3$), 3 30 and 3 55 (s, 3 : 1, peripheral CH_3), 3.75 (q, peripheral $CH_2{\cdot}CH_3$), and 9.45 (s, 3 *meso*-H).

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