Polyformylation of Copper(II) Complexes of Octa-alkylporphyrins [1]

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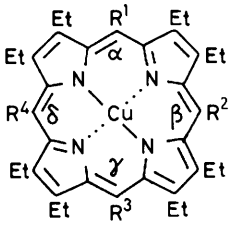
Vilsmeier formylation of copper(II) octaethylporphyrin (1) affords the copper(II) complexes of α-formyloctaethylporphyrin, α,γ- and α,β-diformyloctaethylporphyrins, α,β,γ-triformyloctaethylporphyrin, and α,β,γ,δ-tetraformyloctaethylporphyrin [(13), (2), (3), (14), and (15), respectively]. Similar results are obtained when copper(II) etioporphyrin-I (5) is formylated. It therefore appears that there exists no difference in regioselectivity in the diformylation reactions between the copper(II) octaethyl- and copper(II) etioporphyrin-I series. Earlier work which indicated that in the octaethylporphyrin series there is a preference for formation only of the copper(II) α,γ-diformylporphyrin (2) is suggested to be a result of preferential crystallization of the least-soluble α,γ-compound from an almost equal mixture of the two isomers.

We recently showed [2,3] that a variety of complicated substituents can be attached to the *meso*-positions of porphyrins, and such compounds are potential models for haemoglobins and cytochromes once iron is inserted into the porphyrin macrocycle. The complex *meso*-substituents were fashioned from porphyrins which had initially been formylated by way of the Vilsmeier procedure, and the resulting formylporphyrins were reduced and acetylated to give acetoxymethylporphyrins which smoothly underwent reactions with oxygen-, nitrogen-, and carbon-nucleophiles.[3] As part of a plan designed to accomplish the synthesis of porphyrins bearing a single substituent ' strapped ' across the α and γ *meso*-positions,[4] we required the corresponding α,γ-diformylporphyrin; use of an α,β-diformylporphyrin would defeat the objective of preparing the strapped porphyrin since the appended substituent would not pass over the centre of the porphyrin core, and would therefore not interact with a chelated metal ion.

Our attention was drawn to a publication by Watanabe *et al.*[5] which showed that diformylation of copper(II) octaethylporphyrin (1) using the Vilsmeier procedure gave only the α,γ-diformyl copper(II) porphyrin (2), with none of the isomer (3) being observed. Though these conclusions were contrary to those of Grigg, Johnson, and their co-workers who obtained [6] both the α,β- and α,γ-



(1) R^{1-4} = H
(2) R^1 = R^3 = CHO; R^2 = R^4 = H
(3) R^1 = R^2 = CHO; R^3 = R^4 = H
(13) R^1 = CHO; R^2 = R^3 = R^4 = H
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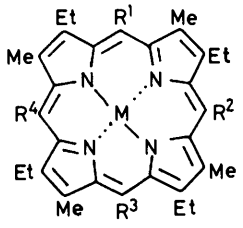
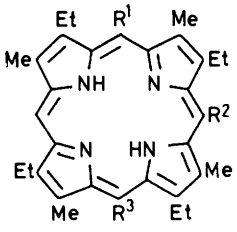
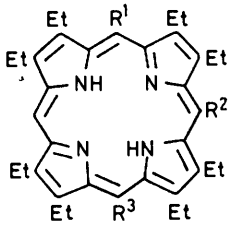
(15) R^{1-4} = CHO



(4) M = Co; R^{1-4} = H
(5) M = Cu; R^{1-4} = H
(6) M = Cu; R^1 = R^3 = CHO; R^2 = R^4 = H
(7) M = Cu; R^1 = R^2 = CHO; R^3 = R^4 = H
(8) M = Cu; R^1 = R^2 = R^3 = CHO; R^4 = H
(9) M = Cu; R^{1-4} = CHO



(10) R^1 = R^3 = CHO; R^2 = H
(11) R^1 = R^2 = CHO; R^3 = H
(12) R^{1-3} = CHO



(16) R^1 = CHO; R^2 = R^3 = H
(17) R^1 = R^3 = CHO; R^2 = H
(18) R^1 = R^2 = CHO; R^3 = H
(19) R^{1-3} = CHO

isomers by Vilsmeier formylation of cobalt(II) etioporphyrin-I (4), we could readily accept that the copper(II) and cobalt(II) substrates might behave differently in this poorly understood area of porphyrin polysubstitution. Furthermore, Ponomarev *et al.* had recently confirmed both Grigg *et al.*'s conclusions regarding polyformylation of cobalt(II) etioporphyrin-I,[7] and Watanabe *et al.*'s results with copper(II) octaethylporphyrin,[8] though in the latter case the Russian workers preferred an alternative explanation for the unique formation of only the α,γ-diformyl copper(II) complex.

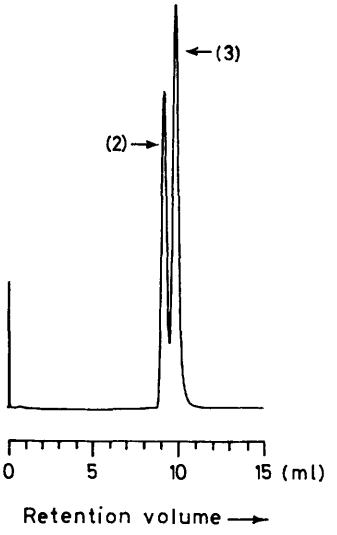


FIGURE 1 High-pressure liquid chromatogram of the copper(II) diformyloctaethylporphyrins (2) and (3). Solvent: 0.2% MeOH in CH_2Cl_2, 2 ml/min, with *ca.* 2 000 lb in^{-2} back-pressure

There seems to be no discernible theory which can explain the literature results on polysubstitution of porphyrins and metalloporphyrins.[9] Nitration of α-nitroporphin gives[10] α,β-dinitroporphin, but the α,γ-disubstitution product is obtained[5] when zinc(II) octaethylporphyrin is nitrated using $Zn(NO_3)_2 \cdot 6H_2O$ in acetic anhydride. However, nitration of metal-free octaethylporphyrin gives[11] a mixture of α,β- and α,γ-dinitro-octaethylporphyrins, whereas chlorination affords[12] only the α,γ-dichloro-derivative. To this situation the formation of only one Vilsmeier diformylation product from copper(II) octaethylporphyrin (1), but both possible products from cobalt(II) etioporphyrin-I (4), merely added more confusion.

On the basis of the literature results, we anticipated that Vilsmeier diformylation of copper(II) etioporphyrin-I (5) would yield only the copper(II) α,γ-disubstitution product (6), but this result was not obtained, as was subsequently demonstrated by Ponomarev *et al.*[7] Thus, prolonged Vilsmeier formylation ($POCl_3$–DMF) of copper(II) etioporphyrin-I gave a mixture of products which were separated by preparative thick-layer chromatography on silica gel. Four major bands were isolated, and in increasing order of polarity, these yielded copper(II) α,γ diformyletioporphyrin-I (6) (13%), copper(II) α,β-diformyletioporphyrin-I (7) (16%), copper(II) α,β,γ-triformyletioporphyrin-I (8) (16%), and copper(II) α,β,γ,δ-tetraformyletioporphyrin-I (9) (<1%); the last of these compounds was identified only by mass spectrometry, but the others were fully characterized and then demetallated to give the corresponding metal-free porphyrins (10)—(12), which were characterized by comparison with data available in the literature.

The above results suggested that the reason for the formation of both di-formylated products in the cobalt(II) etioporphyrin-I example[6,7] but only the α,γ-disubstitution product in the copper(II) octaethylporphyrin case,[5,8] must be associated with the nature of the porphyrin rather than the chelating metal ion. Indeed, some discussion of steric and electronic factors in the etio- and octaethyl-porphyrin series had been published.[5,8]

Copper(II) octaethylporphyrin (1) was, therefore, subjected to Vilsmeier formylation. Prolonged treatment of compound (1) with an excess of the $POCl_3$–DMF reagent at 80 °C in 1,2-dichloroethane for 3 h gave a mixture of formylated products. This was subjected to initial separation using column chromatography (silica gel) and afforded copper(II) α-formyloctaethylporphyrin (13) (20%), copper(II) diformylporphyrin (23%), copper(II), α,β,γ-triformyloctaethylporphyrin (14) (9%), and copper(II) α,β,γ,δ-tetraformyloctaethylporphyrin (15) (<1%). Again, the last of these was identified only by mass spectrometry because of the limited amounts available. The formation of monoformylporphyrin (13) in the octaethylporphyrin series but *not* in the etioporphyrin-I series is in accord with the conclusions of Ponomarev *et al.*[7,8] that the former, for steric reasons, is less reactive towards electrophilic substitution than the latter series. When the copper(II) diformylporphyrin was subjected to high-pressure liquid chromatography (normal phase) *before any attempt at crystallization*, two diformylated products were clearly indicated (Figure 1), in approximately equal amounts. These could only be the copper(II) α,γ- and α,β-isomers [(2) and (3), respectively], and they were separated by careful preparative thick-layer chromatography or by carrying out multiple high-pressure liquid chromatography injections. The α,β-isomer (3) was shown to be the most polar of the two isomers and was identified by co-injection with an authentic sample obtained[13] by Vilsmeier formylation of copper(II) *trans*-octaethylporphyrin followed by re-oxidation to the porphyrin oxidation level. The copper(II) complexes (2) and (3) were obtained in 10 and 11% yields, respectively. When the Vilsmeier formylation reaction was carried out under conditions identical with those described by Watanabe *et al.*,[5] the yields were 28% of (13), 18% of (2), and 18% of (3).

The copper(II) complexes (13), (2), (3), and (14) were demetallated using 1 : 1 H_2SO_4–CF_3CO_2H, and were further characterized as the metal-free compounds (16)—(19), respectively. In particular, n.m.r. spectroscopy at 360 MHz of the metal-free diformyl compounds

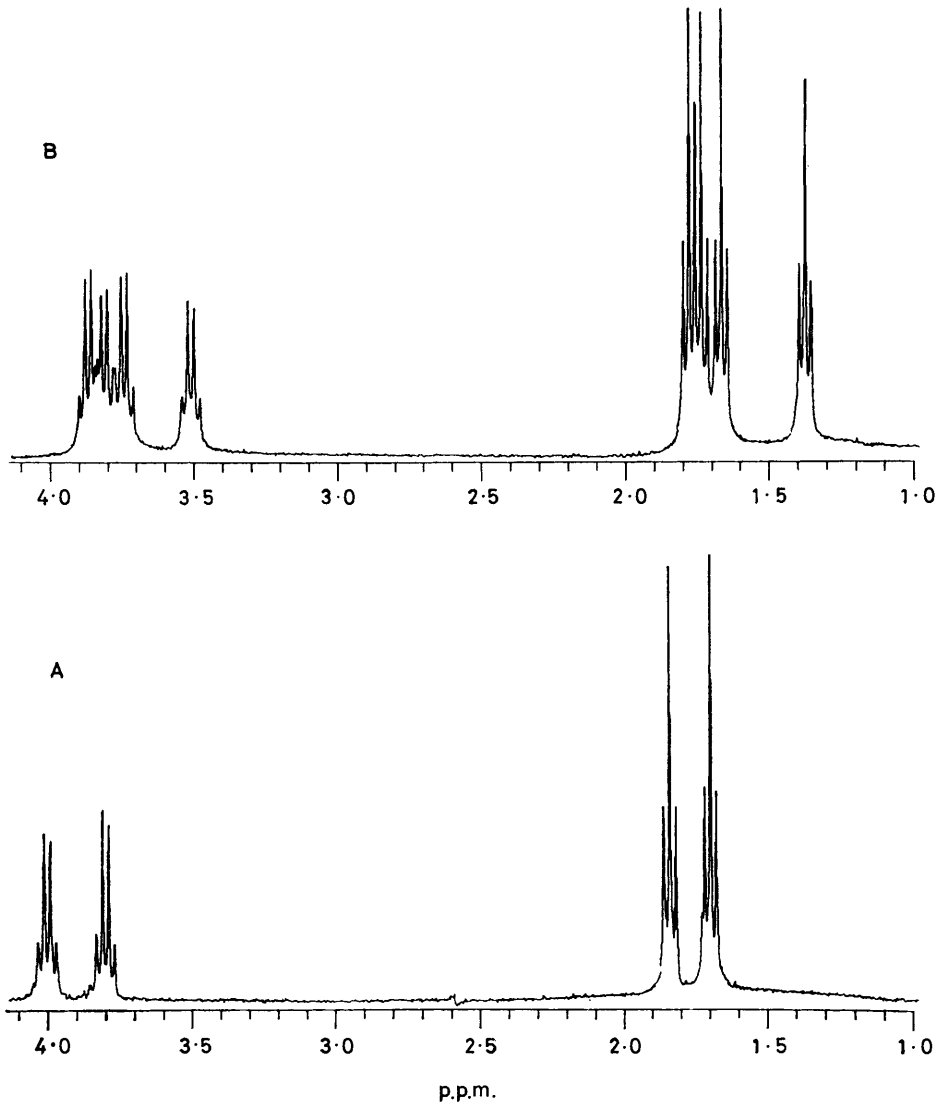


FIGURE 2 360 MHz proton n.m.r. spectra, in $CDCl_3$, of the methylene and methyl protons in *A* α,γ-diformyloctaethylporphyrin (17), and *B*, α,β-diformyloctaethylporphyrin (18)

(17) and (18) was very diagnostic.[14] The α,β-compound (Figure 2) showed four different types of methylene/methyl proton, and the α,γ-isomer showed only two, as expected on the basis of its symmetry.[5] Both isomers showed only one type of formyl and one type of *meso*-proton.

There are several reasons why previous workers might only have observed the α,γ-diformylated products (2) and (17). We had earlier suggested [1] that either (*a*) the α,β-compound (3) deformylates faster than (2) in 100% H_2SO_4 (used by previous workers) but not in 1 : 1 H_2SO_4–CF_3CO_2H (used in the present work), to give the monoformylporphyrin (16), or (*b*) the earlier workers had been misled in their identification, by n.m.r. spectroscopy, of the α,γ-isomer (17) owing to signal averaging by aggregation effects,[15] or (*c*) the preferential crystallization of copper(II) complex (2) or metal-free porphyrin (17) from the corresponding α,β-isomers caused the incorrect interpretation of the regioselectivity of the substitution reaction. We have found that there is very little deformylation of any of the isomers in either pure H_2SO_4 or 1 : 1 H_2SO_4–CF_3CO_2H, thus eliminating possibility (*a*). Further, the chemical shifts reported for the α,γ-isomer (17) are very similar to those we have observed ourselves, and there is no characteristic upfield shift which would be expected [15] by a face-to-face aggregation. Moreover, admixture of compounds (17) and (18) affords a spectrum in which both compounds can be clearly identified, and not a spectrum which has been averaged by donor-acceptor interactions. On the other hand, we have found that the α,β-isomers (3) and (18) are dramatically more soluble than the α,γ-isomers (2) and (17) in solvents such as methylene chloride and chloroform. It is our conclusion, therefore, that the earlier workers preferentially fractionated their isomeric products during the crystallization procedure; as a

result, we deduce that there is no dramatic difference in regioselectivity between the *meso*-positions during diformylation of copper(II) octaethylporphyrin, and, therefore, that the reactivity in this series parallels that in the etioporphyrin-I system. A minor statistical difference is apparent, however, in that one would expect twice as much of the α,β-compound as of the α,γ-isomer; such a product ratio was observed by Ponomarev *et al.*[7] for the formylation of the nickel(II) and copper(II) complexes of etioporphyrin-I.

EXPERIMENTAL

M.p.s were measured on a microscopic hot-stage apparatus, and are uncorrected. T.l.c. monitoring of all reactions was performed with Merck silica gel 60 F254 precoated sheets (0.2 mm), and preparative t.l.c. separations were carried out on 20 × 20 cm glass plates coated with Merck GF 254 silica gel (1.5 mm). Column chromatography was carried out using Merck silica gel. High-pressure liquid chromatography was performed on a Waters Associates ALC/GPC-201 instrument with Perkin-Elmer LC 55B variable wavelength detector set at 405 nm. One Merck LiChrosorb Si 60 (25 cm × 4.6 mm l.d.) column was used, and the solvent was 0.2% methanol in methylene chloride. Electronic absorption spectra were measured with a Cary-17 spectrophotometer (solutions in methylene chloride), and ^{1}H n.m.r. spectra were determined in deuteriochloroform solution with tetramethylsilane as internal calibrant, on a Nicolet NT-360 (360 MHz) system. Mass spectra (direct insertion probe, 70 eV, 50 μA, source temperature *ca.* 200 °C) were measured using a Finnegan 3200 mass spectrometer.

All reactions were run in the absence of light (aluminium foil) and under nitrogen atmosphere. Octaethylporphyrin [16] and etioporphyrin-I [17] were prepared according to literature procedures, and copper(II) was inserted using copper(II) acetate in methanol.[18]

Polyformylation of Copper(II) *Octaethylporphyrin* (1).—To dimethylformamide (50 ml) was added, with stirring at 0 °C, phosphorus oxychloride (60 ml). Dry 1,2-dichloroethane (100 ml) was then added and the mixture was warmed to 50 °C before addition of copper(II) octaethylporphyrin (1) (510 mg) in 1,2-dichloroethane (250 ml), dropwise. The solution was then heated under reflux for 10 h before cooling and neutralization with saturated aqueous sodium acetate (400 ml). *Caution!* This reaction can become vigorous and material can be lost due to frothing. The mixture was then stirred for 3 h at 80 °C before cooling and extraction with methylene chloride (3 × 200 ml). The organic phase was washed with water (200 ml), saturated aqueous sodium hydrogen carbonate (2 × 200 ml), and then water (2 × 200 ml) again, before being dried (Na_2SO_4) and evaporated to dryness. The red solid residue was chromatographed (elution with toluene); the first fraction, after recrystallization from methylene chloride–methanol, yielded copper(II) α-formyloctaethylporphyrin (13) (106 mg, 20%), identical in all respects with an authentic sample.[19] A second fraction (128 mg) proved to be (*vide infra*), on the basis of high-pressure liquid chromatographic (Figure 1) and t.l.c. analyses, an approximately 1 : 1 mixture of the copper(II) α,γ- and α,β-diformyloctaethylporphyrins (2) and (3), respectively. Fraction 3 was crystallized from methylene chloride–methanol to give *copper*(II) α,β,γ-*triformyloctaethylporphyrin* (14) (52 mg, 9%), m.p. 162 °C (Found: C, 68.6; H, 6.25; Cu, 9.05; N, 8.35. $C_{39}H_{44}CuN_4O_3$ requires C, 68.85; H, 6.52; Cu, 9.35; N, 8.24%), *m/e* (%), ^{63}Cu ions, 679 (100), 665 (7), 651 (81), 637 (7), 623 (25), 607 (7), 595 (13), and 579 (8); $\lambda_{max.}$ 432 (ε 99 000), 568sh (5 300), 600sh (7 600), and 652 nm (9 600). A very minor fourth fraction was obtained, and the material from this was shown, by mass spectrometry [*m/e* (%), ^{63}Cu ions, 707 (100), 691 (14), 679 (63), 664 (8), 651 (23), 637 (7), 623 (26), and 595 (71)] to be *copper*(II) α,β,γ,δ-*tetraformyloctaethylporphyrin* (15).

The material from fraction 2 was separated by preparative thick-layer chromatography (elution with toluene) and the two clearly resolved bands were extracted from the silica gel using 10% methanol in methylene chloride. After recrystallization from methylene chloride–methanol, the less-polar green band * was identified as *copper*(II) α,γ-*diformyloctaethylporphyrin* (2) (55 mg, 10%), m.p. >300 °C (Found: C, 69.8; H, 6.7; Cu, 9.55; N, 8.55. Cal. for $C_{38}H_{44}CuN_4O_2$: C, 69.96; H, 6.80; Cu, 9.74; N, 8.59%), *m/e* (%), ^{63}Cu ions, 651 (100), 636 (5), 622 (35), 607 (4), 595 (4), and 325.5 (4); $\lambda_{max.}$ 406 (ε 115 000), 537 (5 100), 576 (7 200), and 640 nm (6 100). The more-polar green band was identified as *copper*(II) α,β-*diformyloctaethylporphyrin* (3) (61 mg, 11%), m.p. 239 °C (Found: C, 70.0; H, 6.5; Cu, 9.2; N, 8.85. $C_{38}H_{44}CuN_4O_2$ requires C, 69.96; H, 6.80; Cu, 9.74; N, 8.59%), *m/e* (%), ^{63}Cu ions, 651 (100), 636 (5), 622 (30), 595 (5), and 325.5 (20), $\lambda_{max.}$ 408 (ε 125 000), 424sh (82 000), 541 (6 500), 577 (9 200), and 644 nm (7 100).

When the above reaction was carried out [5] with phosphorus oxychloride (63.5 g), and dimethylformamide (28 g) in 1,2-dichloroethane (50 ml), and copper(II) octaethylporphyrin (280 mg) in 1,2-dichloroethane (200 ml) at 50 °C for 3 h, the products obtained were copper(II) α-formyloctaethylporphyrin (13) (83 mg, 28%), and a 1 : 1 mixture (108 mg) of copper(II) α,γ- and α,β-diformyloctaethylporphyrins [(2) and (3), respectively].

Demetallation of Copper(II) *Porphyrins*.—The general procedure employed involved dissolving the copper(II) porphyrin (*ca.* 50 mg) in a 1 : 1 mixture (20 ml) of concentrated sulphuric and trifluoroacetic acids. After 1 h at 25 °C the mixture was treated carefully with water (100 ml) and methylene chloride (100 ml). The aqueous phase was back-extracted until colourless with fresh methylene chloride and then the combined organic phases were washed with water (3 × 250 ml), dilute aqueous sodium hydrogen carbonate (2 × 250 ml), and finally water (100 ml) again, before being dried (Na_2SO_4) and evaporated to dryness. The resulting metal-free porphyrins were then either chromatographed or else crystallized directly. In this way the following porphyrins were obtained from the corresponding copper(II) complexes; yields in all cases were >85%.

α,γ-*Diformyloctaethylporphyrin* (17).—This had m.p. 275 °C (lit.,[5] 259 °C); on the basis of the n.m.r. spectrum reported,[5] we deduce that the lower literature melting point is due to contamination with a small amount of the α,β-isomer (18); [1] *m/e* (%), 590 (100), 575 (23), 561 (58), 546 (11), 534 (83), and 519 (32); $\lambda_{max.}$ 415 (ε 125 000), 514 (7 000), 546 (8 100), 586 (9 300), and 663 nm (4 000); δ(5 mg/ml), −1.50 (2 H, s, NH), 1.69, 1.83 (each 12 H, t,

* This band turned red as the silica gel plate dried out. The material isolated from this chromatographic band was found to be considerably less soluble in chloroform and methylene chloride than that from the more-polar band.

CH_2CH_3), 3.70, 4.00 (each 8 H, q, CH_2CH_3), 10.07 (2 H, s, β,δ-*meso*-H), and 12.73 (2 H, s, CHO).

α,β-*Diformyloctaethylporphyrin* (18).—This had m.p. 191 °C (Found: C, 77.1; H, 7.8; N, 9.3. $C_{38}H_{46}N_4O_2$ requires C, 77.25; H, 7.85; N, 9.48%), *m/e* (%), 590 (100), 561 (44), 546 (10), 532 (64), and 519 (21); $\lambda_{max.}$ 416 (ε 120 000), 517 (6 000), 542 (6 000), 590 (7 200), and 667 nm (3 600); δ(5 mg/ml), −1.50 (2 H, s, NH), 1.37, 1.66, 1.73, and 1.78 (each 6 H, t, CH_2CH_3), 3.50, 3.74, 3.81, and 3.86 (each 4 H, q, CH_2CH_3), 9.61 (2 H, s, γ,δ-*meso*-H), and 12.35 (2 H, s, CHO).

α,β,γ-*Triformyloctaethylporphyrin* (19).—This had m.p. >300 °C (Found: 75.45; H, 7.5; N, 8.9. $C_{38}H_{46}N_4O_3$ requires C, 75.70; H, 7.49; N, 9.05%), *m/e* (%), 618 (100), 604 (4), 590 (65), 576 (5), 562 (20), 534 (10), and 518 (4); $\lambda_{max.}$ 425 (ε 98 000), 556 (5 000), 624 (7 000), and 671 (5 400); δ(5 mg/ml), −1.32 (2 H, s, NH), 1.34, 1.56, 1.74 (12 H, 6 H, 6 H, each t, CH_2CH_3), 3.42, 3.50, 3.61 (8 H, 4 H, 4 H, each q, CH_2CH_3), 9.28 (1 H, s, *meso*-H), and 12.10 and 12.15 (1 H, 2 H, each s, CHO).

α-Formyloctaethylporphyrin (16),[19] α,γ- and α,β-diformyletioporphyrins-I [(10) and (11), respectively],[7] and α,β,γ-triformyletioporphyrin-I (12),[7] were identified by comparison with physical and spectroscopic data in the literature.

Polyformylation of Copper(II) *Etioporphyrin-I* (5).—Copper etioporphyrin-I (5) was subjected to Vilsmeier formylation as described above, except that the reaction was run for 18 h instead of 10 h. Work-up and preparative thick layer chromatography (elution with toluene) afforded four major bands, which, in increasing order of polarity, gave the following copper(II) porphyrins: band 1 gave *copper*(II) α,γ-*diformyletioporphyrin-I* (6) (13%), m.p. >300 °C (Found: C, 68.3; H, 6.2; N, 9.35. $C_{34}H_{36}CuN_4O_2$ requires C, 68.49; H, 6.09; N, 9.40%), *m/e* (%), ^{63}Cu ions, 595 (100), 567 (68), 539 (73), 524 (10), 509 (10), and 297.5 (4); $\lambda_{max.}$ 407 (ε 110 000), 534 (5 000), 572 (7 100), and 630 nm (6 000). Band 2 afforded *copper*(II) α,β-*diformyletioporphyrin-I* (7), (16%), m.p. >320 °C (Found: C, 68.3; H, 6.2; N, 9.5. $C_{34}H_{36}CuN_4O_2$ requires C, 68.49; H, 6.09; N, 9.40%), *m/e* (%), ^{63}Cu, 595 (100), 567 (20), 539 (100), 524 (45), 509 (20), and 297.5 (2); $\lambda_{max.}$ 406 (ε 122 000), 424 sh (90 000), 540 (6 400), 574 (9 000), and 644 nm (6 900). From band 3, *copper*(II) α,β,γ-*triformyletioporphyrin-I* (8) (16%), was obtained, m.p. 275 °C (Found: C, 67.2; H, 5.7; N, 9.1. $C_{35}H_{36}CuN_4O_3$ requires C, 67.34; H, 5.81; N, 8.98%), *m/e* (%), ^{63}Cu ions, 623 (100), 595 (25), 567 (15), 539 (12), 524 (7), and 311.5 (8); $\lambda_{max.}$ 431 (ε 97 000), 565sh (5 300), 621sh (7 700), and 652 nm (8 700). Band 4 afforded *copper*(II) α,β,γ,δ-*tetraformyletioporphyrin-I* (9), (<1%), *m/e* (%), ^{63}Cu ions, 651 (82), 635 (8), 623 (61), 595 (47), 567 (100), and 325.5 nm (2), $\lambda_{max.}$ 435, 576sh, 606sh, and 647 nm.

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