*Tetrahedron* Vol. 38, No. 5, pp. 685 to 692, 1982
Printed in Great Britain.

0040-4020/82/050685-08$03.00/0
Pergamon Press Ltd.

# EFFICIENT PERIPHERAL FUNCTIONALIZATION OF PORPHYRINS

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(*Received in the UK 25 August* 1981)

**Abstract**—Details are given for the mild and efficient synthesis of β-substituted "capped"-porphyrins and *meso*-tetraphenylporphrins from the corresponding porphyrins. The nitro derivatives are cleanly reduced to β-aminoporphyrins, which are susceptible to hydrolysis but otherwise may be further derivatized on nitrogen by standard procedures. Treatment of β-nitroporphyrins with thiolate ions in DMF gave β-alkylthioporphyrins, β-arylthioporphyrins or the corresponding denitrated porphyrin, depending on the thiol.

We required mild methods for efficient, direct functionalization of the outer periphery of a porphyrin. A functional group on the β-pyrrolic position of a *meso*-tetrasubstituted porphyrin could then be elaborated into a substituent bearing a ligand *L*, which would serve as the apical base, schematically as **1**, in compounds designed to mimic the haemoproteins, haemoglobin and myoglobin and cytochromes.

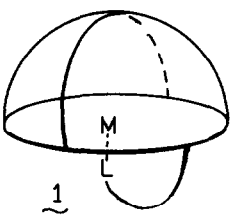


Diagram 1.

At the outset of this work mild methods for functionalization of a *meso*-tetrasubstituted porphyrin at a β-pyrrolic position were restricted to Shine's communication[1] that zinc *meso*-tetraphenylporphyrin π-cation radical perchlorate [$ZnTPP^{+\cdot}$, $ClO_4^-$] yielded a β-pyridinium salt in modest yield on treatment with pyridine. Several reports of nucleophilic substitution at the more reactive *meso*-position of porphyrin π-cation radicals[2,3] and dications[4,5] have appeared. Extrapolation of the nitration method of Smith,[6] and modification of reaction procedures to avoid generation of π-cation radicals in a separate step has enabled us to develop extremely good methods for substitution at the β-pyrrolic position of porphyrins.

In our initial communication[7] we reported the efficient nitration of zinc "$C_2$-capped"-porphyrin[8] **3** and subsequent conversions to β-amino-"capped"-porphyrin derivatives. We now report these studies in full and in addition we report a method for the preparation of β-porphyrin sulphides, the first example of nucleophilic displacement of nitro groups on a porphyrin nucleus, and also a new method for denitration of nitroporphyrins; all of which proceed under extremely mild conditions.

## RESULTS AND DISCUSSION

### *Nitroporphyrins*

Attempts to nitrate the "$C_2$-capped"-porphyrin **2** by conventional electrophilic procedures with concentrated nitric acid in acetic or sulphuric acid or with nitronium fluoroborate led to mixtures of products resulting from pernitration and from hydrolysis of the capping ester groups.

By contrast, nucleophilic nitration with nitrite ion of the porphyrin π-cation radical, generated *in situ*, proceeds extremely well. Thus treatment of zinc "$C_2$-capped"-porphyrin[8] **3** with iodine and silver nitrite in dichloromethane/acetonitrile at room temperature for 35 min gave a quantitative yield of zinc β-mononitro-"$C_2$-capped"-porphyrin, $M^+$ 1143/1145, showing the typical zinc isotope pattern. In contrast to other nitrations of porphyrin π-cation radicals, no ring opened products resulting from attack at *meso* or at α-pyrrolic positions[9,10] were formed and no dinitration was observed.

The product was an equimolar mixture of **4** and **5**, isomers[11] with respect to the capping structure as a result of the $C_{2v}$ symmetry of the starting porphyrin **3**. The presence and ratio of isomers is clearly defined by the NMR signals from the capping protons, which appear, with equal weight, as four singlets at δ 5.03, 5.78, 5.43 and 5.57, two for each isomer.

The isomers were separated by hplc into the (±)2-nitro compound **4** and the (±)7-nitro compound **5** in high overall yield. The structures were assigned on the basis of the proton magnetic resonances of the capping benzene ring. The chromatographically less-polar isomer, with one-proton singlets at δ 5.43 and 5.57, was assigned as the (±)7-nitro compound **5** since in this structure the nitro group has an edge-on orientation to the pyromellitate ring and the capping benzenoid protons are a similar distance from the nitro group. In the other isomer **4** the nitro group is end-on with respect to the capping benzene ring with one proton being substantially closer to the nitro group than the other. The larger difference in these proton resonances of the chromatographically more-polar isomer, one-proton singlets at δ 5.03 and 5.78,

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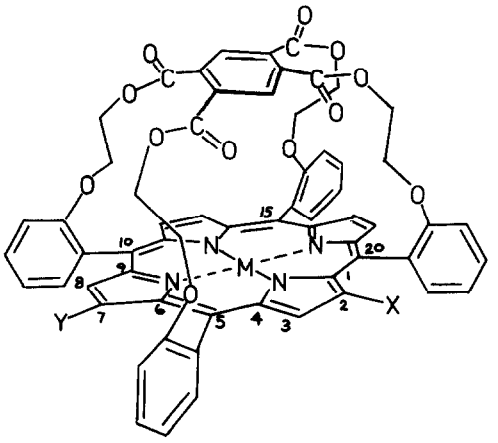


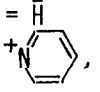
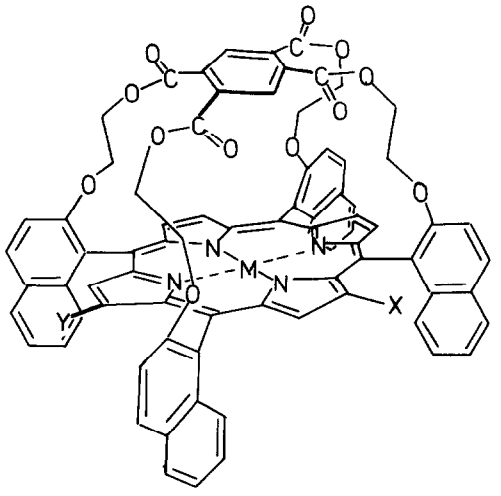
2 M = 2H, X = Y = H
3 M = Zn, X = Y = H
4 M = Zn, X = $NO_2$, Y = H
5 M = Zn, X = H, Y = $NO_2$
6 M = 2H, X = $NO_2$, Y = H
34 M = Zn, X = H, Y =  , $ClO_4$

Diagram 2. Efficient peripheral functionalization of porphyins.



8 M = Zn, X = Y = H
9 M = Zn, X = $NO_2$, Y = H
10 M = Zn, X = H, Y = $NO_2$
11 M = 2H, X = $NO_2$, Y = H
12 M = 2H, X = H, Y = $NO_2$
22 M = 2H, X = $NH_2$, Y = H
23 M = 2H, X = H, Y = $NH_2$
28 M = 2H, X = $NHCOCMe_3$, Y = H
29 M = 2H, X = H, Y = $NHCOCMe_3$

Diagram 3. Efficient peripheral functionalization of porphyrins.

is consistent with the assignment of structure **4** to this compound. The origin of these shifts is no doubt due to polarization by the nitro group of the field due to the porphyrin ring current.

Demetalation of **4** and **5** with anhydrous HBr proceeded smoothly and gave the corresponding β-nitroporphyrins **6** and **7**, δ 5.07, 5.54, 5.63, 6.00 in 97% yield. This mixture could be separated with difficulty by hplc into the individual isomers **6** and **7**. Compound **6**, δ 5.01 and 5.91, was also obtained by demetallion of isomerically pure **4** thereby substantiating the assignments of **4** and **5**.

Direct nitration of the free-base, "$C_2$-capped"-porphyrin **2**, was also achieved by this method, although at a slower rate. A reaction time of 3.5 hr was required for complete consumption of **2**. Pernitrated compounds were detected and a dinitroporphyrin was isolated in low yield.[12] By far the major product however was the β-nitro-"$C_2$-capped"-porphyrin which was isolated in 81% yield. Analysis of the p.m.r. spectrum showed that it was a mixture consisting of 55% of **6** and 45% of **7**. This suggests that in the non-metalated porphyrin **2**, the end-on positions 2 and 3 are more susceptible to nucleophilic attack. This would seem to be borne out in the X-ray structure[13] of **2** although the *meso*-substituents would be expected to be conformationally more mobile in solution.

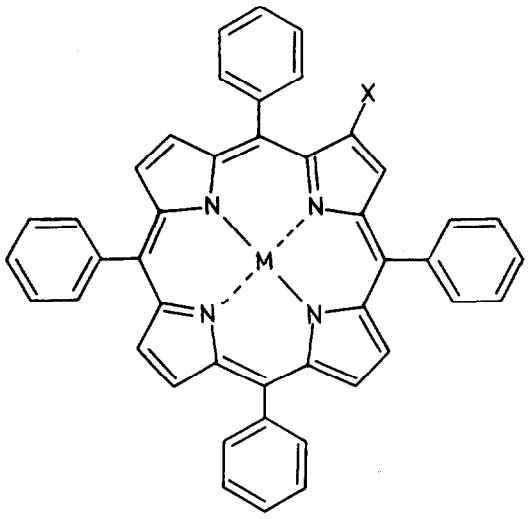
Other zinc porphyrins were also readily nitrated by this method. Treatment of zinc "naphthyl-$C_2$-capped"-porphyrin[8] **8** gave a 45:55 mixture of zinc β-nitroporphyrins **9** and **10** in 87% yield. Demetalation with HBr afforded the corresponding β-nitroporphyrins **11** and **12** in 91% yield.

Similarly zinc *meso*-tetraphenylporphyrin **13** was nitrated to give **14** in 51% yield. However in this case the reaction was somewhat slower than reaction on **3**, probably because the *meso*-phenyl substituents have greater rotational freedom than the *meso*-substituents in **3**, and thus attack on $ZnTPP^{+\cdot}$ by the nucleophile $NO_2^-$ is more hindered at the β-pyrrolic positions through interaction with the phenyl substituents. Some polar ring-opened products were also obtained from this reaction.[9,10] Removal of zinc from **14** as before gave 2-nitro-*meso*-tetraphenylporphyrin **15** in 90% yield. Attempts to directly nitrate TPP gave no **15** and resulted in recovery of TPP.

Two other reports of nitration of TPP in low yield have appeared recently.[9,10]

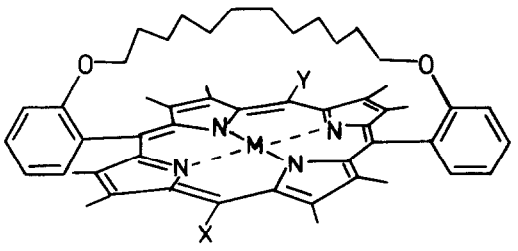
Treatment of the zinc "strapped"-porphyrin[14] **16** with the nitration mixture very rapidly gave the zinc *meso*-nitroporphyrin **17**, demetallation of which gave **18**. Treatment of **16** with excess nitrating mixture for 15 min gave the zinc *meso*-dinitroporphyrin **19**.

In each of the above nitrations the reaction proceeded until all the starting porphyrin had been consumed. Thus the one pot "*in situ*" generation and reaction of π-cation radical avoids the limitation of other work[10] in which the π-cation radical is generated as a separate step. Of synthetic importance is the fact that irreversible quenching of the π-cation radical to unsubstituted zinc porphyrin is also avoided. This reaction invariably occurs under the two step method.[10] The lack of β-pernitration of zinc porphyrins must be a consequence of zinc β-nitroporphyrins having higher oxidation potentials than unsubstituted zinc porphyrins. The mechanism of nitra-



13 M = Zn, X = H
14 M = Zn, X = $NO_2$
15 M = 2H, X = $NO_2$
24 M = 2H, X = $NH_2$
27 M = 2H, X = $NHCOCH_3$
35 M = 2H, X = SPh
36 M = 2H, X = SEt

Diagram 4. Efficient peripheral functionalization of porphyrins.



16 M = Zn, X = Y = H
17 M = Zn, X = $NO_2$, Y = H
18 M = 2H, X = $NO_2$, Y = H
19 M = Zn, X = Y = $NO_2$
41 M = 2H, X = Y = H

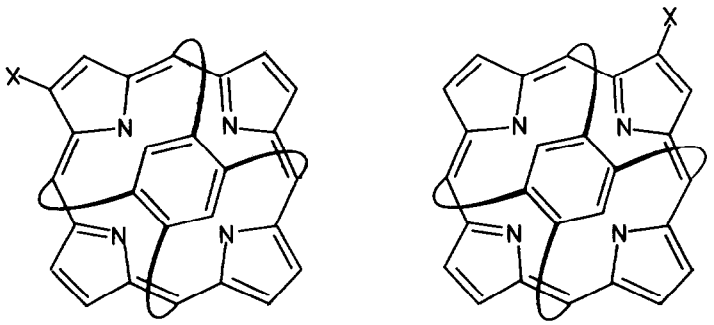
Diagram 5. Efficient peripheral functionalization of porphyrins.

tion of porphyrins has been discussed at length by others.[2,10,15,16]

The transformation of nitroporphyrins into other useful substituted porphyrins is described below.

*β-Aminoporphyrins*

The β-nitroporphyrins **6** and **7**, **11** and **12**, and **15**, were hydrogenated to the corresponding β-aminoporphyrins **20** and **21**, **22** and **23**, and **24** in almost quantitative yields with sodium borohydride in methanol in the presence of a 10% palladium on carbon catalyst. This controlled microhydrogenation method has previously found application in the reduction of *meso*-nitrodeuteropor-



6 AND 7 X = $NO_2$
20 AND 21 X = $NH_2$
25 AND 26 X = $NHCOCH_3$
30 AND 31 X = NCO
32 AND 33 X = $NHCO_2Et$
37 AND 38 X = SPh
39 AND 40 X = SEt

Diagram 6. Efficient peripheral functionalization of porphyrins.

phyrin.[17] Conventional hydrogenation of **6** and **7** resulted in over-reduction to mixtures of porphyrins and chlorins, while reductions with tin(II) chloride in HCl gave β-keto compounds.[7]

All the β-aminoporphyrins **20–24** proved to be unstable to chromatography on silica or alumina, and indeed to hydrolysis conditions generally. In this respect the β-aminoporphyrins behave as enamines or imines rather than aromatic amines. The lability of β-aminoporphyrins is in contrast to the *meso*-aminoporphyrins which have been prepared by tin(II) chloride/HCl reduction of the corresponding *meso*-nitroporphyrins.[18] Under strongly acidic conditions protonated *meso*-imine tautomers are formed and phlorin-type spectra are observed[18] but it appears that otherwise *meso*-aminoporphyrins behave as aromatic amines, forming diazonium salts cleanly for example.[17] The difference in behaviour of the aminoporphyrins is no doubt a consequence of the fact that aromatic 18-π electron delocalization of the porphyrin system does not require full conjugation of β,β-pyrrolic double bonds,[19] thereby the β-aminoporphyrins have some enamine character unlike the case of double bonds at the *meso*-positions which must be fully delocalized.

In other respects however the β-aminoporphyrins show amine reactivity. The aminoporphyrins **20–24** were all smoothly acylated on the amino nitrogen, with no β-acylenamines or derivatives thereof being detected. Thus treatment of **20** and **21** and **24** with acetic anhydride and pyridine gave the acetaminodoporphyrins **25**, **26** and **27** in high yields, while pivolylation of **22** and **23–28** and **29** proceeded smoothly. Similarly treatment of **20** and **21** with phosgene afforded the corresponding isocyanates **30** and **31** which on treatment with ethanol gave the ethylurethanes **32** and **33**. The conversion of amino and isocyanatoporphyrins to pentadentate ligands of the type **1** will be reported separately.

*β-Pyridiniumporphyrin salts and related compounds*

Our approach followed from the observation of Shine[1] that pyridine reacted with $ZnTPP^{+\cdot}$, $ClO_4^-$ to afford zinc β-pyridinium-*meso*-tetraphenylporphyrin perchlorate in 25–33% yield. We reasoned that other nucleophilic nitrogen heterocycles might react similarly. In particular 8-substituted quinolines would be expected to form compounds of the type **1** when reacted with "capped"-porphyrin derivatives, the orientation being controlled through steric interactions with the capping structure.

Thus zinc "$C_2$-capped"-porphyrin **3** was converted to its π-cation radical perchlorate [$Zn(CP)^{+\cdot}$, $ClO_4^-$].[20] All of **3** was consumed in the reaction and subsequent reactions of $Zn(CP)^{+\cdot}$, $ClO_4^-$ were consistent with a purity of at least 88% of the cation radical.[10]

Pyridine reacted with $Zn(CP)^{+\cdot}$, $ClO_4^-$ to give **3** in 56% yield and a mixture of polar salts which were further fractionated with difficulty by normal-phase chromatography. Reverse-phase chromatography proved to be unsuccessful since the pyridinium porphyrin salts were too hydrophobic. Zinc (±)7-pyridinium-"$C_2$-capped"-porphyrin perchlorate **34** was obtained in 16%. The structure was assigned as above by the chemical shifts of the capping aromatic protons in the PMR spectrum which appeared as one-proton singlets at δ 5.20 and 5.72. A second fraction was obtained in 22% yield and proved to be an approximately equimolar mixture of the (±)2-pyridinium and (±)7-pyridinium salts. In this case the capping protons appeared with equal intensity as singlets at δ 4.94, 5.20, 5.72, and 6.26. The visible electronic spectra of these compounds showed a bathochromic shift (*ca.* 10 nm) as the solvent polarity was increased ($CH_2Cl_2$ to methanol) indicating the presence of a polarized π-system and an increase in hydrogen-bonding interactions. The neutral zinc porphyrins did not show this effect.

Attempts to effect an analogous reaction with 2-picoline, 2,6-lutidine, quinoline, 8-nitroquinoline and 8-hydroxyquinoline were not encouraging, substantial mixtures of compounds being obtained in each case, together with a higher recovery of **3** resulting from reduction of the π-cation radical.

Attempts to increase yields of the pyridinium salts by the "in situ" generation of π-cation radical using $I_2/AgNO_3$/pyridine were unsuccessful, since the starting porphyrin **3** was not all consumed, presumably because the generated iodonium ion is stabilized as $(Pyr_2I)^+NO_3^-$.[21] In addition, the small amount of zinc β-pyridinium porphyrin nitrates so obtained proved harder to separate than the corresponding perchlorate salts. The use of this approach to β-substituted porphyrins thus has limited synthetic utility.

*β-Porphyrin sulphides and denitration of nitroporphyrins*

Treatment of 2-nitro-*meso*-tetraphenylporphyrin **15** with thiophenolate ion (thiophenol and anhydrous lithium hydroxide) in dry DMF at 0°→25° gave 2-phenylthio-*meso*-tetraphenylporphyrin **35** in 89% isolated yield. The field desorption mass spectrum of **35** showed only the molecular ion, *m/e* 722, and the infrared spectrum lacked nitro absorptions. The visible spectrum of **35**, $\lambda_{max}$ 419, 523, 554, 594, 651 nm, showed a hypsochromic shift compared with the starting material **15**, $\lambda_{max}$ 427, 526, 560, 605, 665 nm, and a small bathochromic shift by comparison with the unsubstituted porphyrin TPP, $\lambda_{max}$ 417, 514, 548, 590, 647 nm.

Similar treatment of **15** with ethanethiol and anhydrous lithium hydroxide gave 2-ethylthio-*meso*-tetraphenylporphyrin **36** in 41% isolated yield; this compound in solution is especially sensitive to light. The sulphide **36** had virtually the same visible chromophore as the phenylthioporphyrin **35** and the ethyl group resonances appeared in the PMR spectrum as a three-proton triplet at δ 1.38, J 7 Hz and a two-proton quartet at δ 3.08, J 7 Hz. In addition to **36**, TPP was obtained in 11% yield from the reaction, clearly from denitration of the starting material **15**.

When the β-nitro-"$C_2$-capped"-porphyrins **6** and **7** were similarly treated with thiophenol and anhydrous lithium hydroxide varying yields of β-phenylthio-"$C_2$-capped"-porphyrins **37** and **38** and denitrated porphyrin **2** were obtained. Treatment of **6** and **7** with ethanethiol and lithium hydroxide yielded an intractable mixture consisting chiefly of **2** together with some of the putative ethylthioporphyrins **39** and **40**.

The concurrence of porphyrin sulphides and reduced porphyrins suggested that conditions could be found in which complete denitration of nitroporphyrins occurs. Indeed treatment of 2-nitro-*meso*-tetraphenylporphyrin **15** with o-aminothiophenol and lithium hydroxide gave TPP in 85% yield.

The *meso*-nitroprophyrin **18** was also smoothly denitrated with thiophenolate ion to give the "strapped" porphyrin **41** in 83% yield. Fischer has previously observed that *meso*-nitroporphyrins can be reduced to the parent porphyrin when heated with succinic acid or

when treated with zinc amalgam.[22] Since treatment of the thiophenylporphyrin **35** with o-aminothiophenol and lithium hydroxide under the standard condition resulted in quantitative recovery of **35** a common pathway to porphyrin sulphides and denitrated porphyrins from nitroporphyrins seems implicated.

Extension of this displacement reaction to other nucleophiles and other substituted porphyrins is at present under active investigation.[23] The application of these efficient, mild methods for porphyrin functionalization in the synthesis of compounds designed to mimic the haemoprotons will be described in due course.

## EXPERIMENTAL

The general experimental details have been described previously.[8]

### *Synthesis of nitroprophyrins*

*β-Nitration of zinc "$C_2$-capped"-porphyrin* **3**

Zinc "$C_2$-capped"-porphyrin[8] (**3**) (308 mg, 0.28 mmol) was dissolved in a mixture of dry $CH_2Cl_2$ (30 ml) and dry acetonitrile (30 ml) under nitrogen. A solution of iodine (49 mg, 0.19 mmol) in dry dichloromethane (5 ml) was added, followed by a solution of silver nitrite (65 mg, 0.42 mmol) in dry acetonitrile (5 ml). The colour of the solution changed from red to green. The mixture was stirred at room temperature for 35 min, filtered and the filtrate was evaporated to dryness. The resultant solid was extracted with dichloromethane, and the extract filtered and evaporated to dryness to give an equal mixture of the two isomeric, racemic zinc β-nitroporphyrins **4** and **5** as a purple crystalline solid (314 mg, 98%), m.p. > 300°. IR: (KBr) $\nu_{max}$: 1720(br), 1520, 1380, 1340 $cm^{-1}$; VIS: ($CHCl_3$) $\lambda_{max}$ (log ε): 396(sh) (4.57), 433(br) (5.14), 530(3.81), 561(4.06), 606 nm (3.99). NMR ($CDCl_3$) δ: 3.5–4.6 (m, 16 H), 5.03 (s, 0.5 H), 5.43 (s, 0.5 H), 5.57 (s, 0.5 H), 5.78 (s, 0.5 H), 7.17–8.00 (m, 16 H), 8.57–8.77 (m, 7H). MS (FD) *m/e*: 1143/1145 (M, $^{64}Zn^{66}Zn$).

*Separation of isomers* **4** *and* **5**

Compounds **4** and **5** were separated by recycle hplc on a Waters Associates Porasil A column (7 mm ID × 183 cm) using a flow rate of 8 ml/min. The solvent system employed was benzene/ethyl acetate (17:3), and 100 mg samples of the above porphyrin mixture in dichloromethane (2 ml) were applied to the column. A less polar porphyrin fraction (t = 20.75 → 25.0 min), and a more polar porphyrin fraction (t = 29.75 → 38.25 min) were collected and the intermediate fraction was recycled once and collected in three fractions as above.

Work-up of the less polar fraction from three separate runs gave [(±)7 - nitro - 5,10,15,20 - [*pyromellitoyl - (tetrakis - o - oxyethoxyphenyl)*]-*porphyrin*]*zinc(II)* **5** *as a purple solid* (131 *mg*), *m.p.* > 300° (*from methanol/chloroform*) *VIS*: ($CHCl_3$) $\lambda_{max}$ (log ε): 395(sh) (4.59), 429(5.24), 525(3.71), 556(4.15), 602 nm (3.93). NMR: ($CDCl_3$) δ 3.5 → 4.6 (m, 16H), 5.42 (s, 1H), 5.58 (s, 1H), 7.1 → 8.0 (m 16H), 8.70 (m, 6H), 8.97 (s, 1H, pyrrolic proton adjacent to $NO_2$ group). MS: (FD) *m/e*; 1143/1145 (M). Solutions of this compound have a bronze hue. Work up of the more polar fraction gave [(±)2 - nitro - 5,10,15,20 - [pyromellitoyl - (tetrakis - o - oxyethoxyphenyl)] - porphyrin]zinc(II) **4** as a purple solid (126 mg) m.p. > 300° (from methanol/chloroform). IR: (KBr) $\nu_{max}$: 1730(br), 1520, 1510, 1495, 1445, 1330 $cm^{-1}$. VIS: ($CHCl_3$) $\lambda_{max}$ (log ε): 395(sh) (4.59), 438 (5.12), 530(sh) (3.71), 562 (4.04), 607 nm (4.05). NMR: ($CDCl_3$) δ: 3.5 → 4.6 (m, 16 H), 5.00 (s, 1 H), 5.78 (s, 1 H), 7.0 → 8.0 (m, 16 H), 8.70 (m, 6 H), 9.04 (s, 1 H, pyrrolic proton adjacent to the $NO_2$ group). MS: (FD) *m/e*: 1143–1145 (M). Solutions of this compound have a green hue.

*Removal of zinc from* **4** *and* **5**

The foregoing mixture of zinc nitro-"$C_2$-capped"-porphyrins **4** and **5** (2.53 g, 2.21 mmol) was dissolved in dry dichloromethane (400 ml) and anhydrous HBr bubbled through the solution for 7 min, followed by a stream of nitrogen for 5 min. The green solution was washed with water (200 ml), saturated sodium bicarbonate solution (2 × 200 ml), water (200 ml) and dried over sodium sulphate. Workup and crystallization of the resultant solid from petroleum ether/$CH_2Cl_2$ gave an equal mixture of the two isomeric racemic nitroporphyrins **6** and **7** as a purple solid (2.32 g, 97%), m.p. > 300°. IR: (KBr) $\nu_{max}$: 1723, 1510, 1342 $cm^{-1}$. VIS: ($CHCl_3$) $\lambda_{max}$ (log ε): 434(5.47), 532(4.04), 605(3.64), 667 nm (3.75). NMR: ($CDCl_3$) δ: − 3.23 (br s, 2 H), 3.8 → 4.7 (br m, 16 H), 5.07 (s, 0.5 H), 5.54 (s, 0.5 H), 5.63 (s, 0.5 H), 6.00 (s, 0.5 H), 7.2 → 7.9 (m, 16 H), 8.6 → 9.0 (m, 7 H). MS: (FD) *m/e*: 1081(M).

(±)2 - *Nitro* - 5,10,15,20 - [*pyromellitoyl* - (*tetrakis* - *o* - *oxyethoxyphenyl*) - *porphyrin* **6**

The zinc nitroporphyrin **4** (65 mg, 0.057 mmol), was demetalated as above to give the porphyrin **6** as a brown-yellow solid (56.5 mg, 92%), m.p. > 300°. IR: (KBr) $\nu_{max}$: 3300, 1728 br s, 1600, 1510, 1490, 1445, 1345 $cm^{-1}$. VIS: ($CHCl_3$) $\lambda_{max}$ (log ε): 437(4.71), 533 (3.61), 608 (3.20), 671 nm (3.30). NMR: ($CDCl_3$) δ − 3.10(br s, 2 H), 3.4 → 4.8 (m, 16 H), 5.01(s, 1 H), 5.91(s, 1 H), 7.1 → 8.1(m, 16 H), 8.5(br s, 2 H), 8.7(br s, 4 H), 8.90 (s, 1 H), MS: (FD): Found *m/e* 1081.2810; $C_{62}H_{43}N_5O_{14}$ requires *m/e* 1081.2812.

*Nitroporphyrins* **6** *and* **7** *by direct nitration of "$C_2$-capped"-porphyrin* **2**

"$C_2$-capped"-porphyrin[8] α (1.10 g, 1.06 mmol) was nitrated with silver nitrite and iodine in the same way as the corresponding zinc porphyrin **3** above. Workup of the reaction after 3.5 h gave a mixture of the nitro porphyrins **6** and **7** as a purple solid (926 mg, 81%) m.p. > 300° after chromatography on silica gel using benzene/ethyl acetate as eluant. The mixture of compounds was identical with that obtained above (IR, NMR, chromatography). Minor fractions from chromatography yielded pernitrated compounds and unchanged starting material (*ca.* 2%).

*Nitration of zinc "naphthyl-$C_2$-capped"-porphyrin* **8**

The zinc porphyrin[8] **8** (50 mg, 0.038 mmol) was nitrated with silver nitrite (10 mg, 0.08 mmol) and iodine (10 mg, 0.04 mmol) over 30 min as for the nitration of **3**. The product was purified by chromatography on silica gel, eluted by toluene/ethyl acetate (1:1) and was crystallized from hexane/$CH_2Cl_2$ to give **9** and **10** as a green microcrystalline solid (45 mg, 87%), m.p. > 300°. VIS: ($CHCl_3$) $\lambda_{max}$ (log ε): 405(sh) (4.63), 427(5.31), 533(4.20), 604 nm (3.93), NMR: ($CDCl_3$) δ: 3.8–4.8 (m, 16 H), 5.51(s, 0.45 H), 5.73(s, 0.55 H), 5.89(s, 0.55 H), 5.91(s, 0.45 H), 6.0–8.85 (m, 31 H). MS: (FD) *m/e*: 1343/1345 (M).

*Demetalation of* **9** *and* **10**

The foregoing zinc porphyrin (39 mg, 0.03 mmol) was demetalated with anhydrous HBr as for **4** to yield **11** and **12** as a brown-yellow solid (34 mg, 91%), m.p. > 300°. VIS: ($CHCl_3$) $\lambda_{max}$ (log ε): 4.27(5.14), 525(4.08), 597(3.66), 662 nm (3.55). MS: (FD) *m/e*: 1281 (M).

*Zinc* 2 - *nitro* - 5,10,15,20 - *tetraphenylporphyrin* **14**

ZnTPP **13** (400 mg, 0.59 mmol) was dissolved in a mixture of dry dichloromethane (60 ml) and dry MeCN (20 ml) and stirred under nitrogen, protected from light. Silver nitrite (130 mg, 0.83 mmol) in acetonitrile (20 ml) was added to the solution followed by iodine (100 mg, 0.4 mmol) in $CH_2Cl_2$ (20 ml). After 2 hr the reaction mixture was filtered and the filtrate evaporated to dryness and the product chromatographed over silica gel using dichloromethane as eluant. The green band was collected and worked up to yield **14** as a purple solid (220 mg, 51%), m.p. > 300°; lit.[9] m.p. > 360°. IR: (KBr) $\nu_{max}$: 1520, 1340 $cm^{-1}$. VIS: ($CHCl_3$) $\lambda_{max}$ (log ε): 425 (5.28), 558(4.20), 603 nm (4.14). NMR ($CDCl_3$) δ: 7.5 → 7.85 (m, 12 H), 7.95 → 8.25 (m, 8 H), 8.80 (br s, 6 H), 9.18 (s, 1 H, pyrrolic proton adjacent to $NO_2$ group). MS: (FD) *m/e*: 721/723 (M).

2 - *Nitro* - 5,10,15,20 - *tetraphenylporphyrin* **15**

The foregoing zinc porphyrin **14** (420 mg, 0.58 mmol) was demetalated with anhydrous HBr in the usual way to give **15** as a purple solid from hexane/$CH_2Cl_2$ (345 mg, 90%), m.p. > 300°. IR:

($CHCl_3$) $\nu_{max}$: 3340, 1530, 1520, 1360 $cm^{-1}$. VIS: ($CHCl_3$) $\lambda_{max}$ (log $\epsilon$): 427(5.30), 526(4.22), 560(3.63), 605(3.63), 665 nm (3.97). NMR: ($CdCl_3$) $\delta$: −2.54(br s, 2 H), 7.65(m, 12 H), 8.10(m, 8 H), 8.6→9.0(m, 7 H). MS: (FD) *m/e*: 659 (M).

*Zinc* 10 - *nitro* - 2,3,7,8,12,13,17,18 - *octamethyl* - 5,15 - (*o,o'* - 1,14 - *dioxatetradecamethylene*)*diphenylporphyrin* **17**

The zinc porphyrin[14] **16** (50 mg, 0.06 mmol) was taken up in dry $CH_2Cl_2$ (250 ml) and dry MeCN (100 ml). Iodine (12 mg, 0.05 mmol) in dichloromethane (100 ml) was added and the solution stirred for 5 min. A solution of silver nitrite (14 mg, 0.09 mmol) in MeCN (20 ml) was added and the red-brown solution stirred for 5 min, filtered and the filtrate evaporated to dryness. The resultant solid was chromatographed on silica gel plates (3 of 1 mm, 20 × 20 cm) using hexane/$CH_2Cl_2$ as eluant. The top pink band ($R_f$ 0.8) gave unchanged starting material (6 mg). The red-brown major band ($R_f$ 0.6) yielded the title zinc nitroporphyrin **17** as a red-brown solid (43 mg, 93% of reacted material). IR: ($CHCl_3$) $\nu_{max}$: 1605, 1585, 1495, 1450, 1375 $cm^{-1}$. VIS: ($CHCl_3$) $\lambda_{max}$ (log $\epsilon$): 413(5.18), 510(3.72), 547(4.36), 580 nm (4.18). NMR: ($CDCl_3$) $\delta$: −0.58 (br s, $W_H$ 6 Hz, 8 H), −0.01 (br m, 8 H), 0.91(br m, 4 H), 2.37(s, 6 H), 2.40(s, 6 H), 3.16(s, 6 H), 3.37(s, 6 H), 3.92(br t, J *ca.* 7 Hz, 4 H), 7.1→7.85(m, 8H), 9.92(s, 1H, $H_{20}$) MS: (FD) *m/e* 879/881 (M).

A more polar green band ($R_f$ 0.45) yielded a small amount of 10,20-dinitrated product (see also below).

*Zinc* 10,20 - *dinitro* - 2,3,7,8,12,13,17,18 - *octamethyl* - 5,15, (*o,o'* - 1,14 - *dioxatetradecamethylene*)*diphenylporphyrin* **19**

The above reaction was repeated with 40 mg of **16** but otherwise the same and the reaction mixture was stirred for 15 min. In this case work up of the green band ($R_f$ 0.45) yielded the dinitrated porphyrin **19** as a purple-blue solid (15 mg, 34%) m.p. 295°. VIS: ($CHCl_3$) $\lambda_{max}$ (log $\epsilon$): 422(5.09), 558(4.04), 595 nm (3.96). NMR: ($CDCl_3$) $\delta$: −0.86(br s, $W_H$ 7 Hz, 8 H), 0.08(m, 8 H), 1.1(br m, 4 H), 2.23(s, 6 H), 2.97(s, 6 H), 3.91(br t, J *ca.* 6 *Hz*, 4 *H*), 7.1→7.8 (m, 8 H). MS (FD) *m/e*: 924/926 (M).

The mononitrated porphyrin **17** was obtained as a red-brown solid (15 mg, 35%).

10 - *Nitro* - 2,3,7,8,12,13,17,18 - *octamethyl* - 5,15 - (*o,o'* - 1,14 - *dioxatetradecamethylene*)*diphenylporphyrin* **18**

The zinc nitroporphyrin **17** (37 mg, 0.042 mmol) was demetalated with anhydrous HBr in the usual way to give **18** as a purple-red solid (32.5 mg, 95%) m.p. > 300°. IR: ($CHCl_3$) $\nu_{max}$: 3260, 1595, 1560, 1490, 1440, 1350 $cm^{-1}$, VIS: ($CHCl_3$) $\lambda_{max}$ (A): 410(8.0), 514(1.2), 587(5.4), 612(sh) (2.4), 642 nm (1.2). NMR: ($CDCl_3$) $\delta$: −2.61(br s, 2 H), −0.68(br s, 8 H), −0.01(br s, 8 H), 0.90(br m, 4 H), 2.36 (s, 12 H), 3.08(s, 6 H), 3.36(s, 6 H), 3.85(t, 4 H), 7.05→7.9 (m, 8 H), 9.90(s, 1 H). MS: (FD) *m/e*: 817 (M).

### *Synthesis of β-aminoporphyrins*

*β-Amino-*"$C_2$-*capped*"-*porphyrin*: **20** *and* **21**

The mixture of β-nitro-"$C_2$-capped" porphyrin isomers **6** and **7** (300 mg, 0.28 mmol) was dissolved in a mixture of dry $CH_2Cl_2$ (30 ml) and dry methanol (30 ml) and 10% palladium on carbon (240 mg) added and the mixture purged with argon. Sodium borohydride (260 mg, 6.8 mmol) was added in portions over 10 min, and the resultant red-brown mixture was stirred under argon for 45 min then dry $CH_2Cl_2$ (50 ml) was added. The mixture was filtered and the filtrate evaporated to dryness. The residue was extracted with dry $CH_2Cl_2$ (30 ml) which was then filtered and the filtrate evaporated to dryness to afford the β-amino-"$C_2$-capped" porphyrins **20** and **21** as a yellow-purple solid (282 mg, 96%), m.p. > 300°. The porphyrin was obtained with sufficient purity to be used without purification. IR: (KBr) $\nu_{max}$: 3420, 3350, 1725 $cm^{-1}$. VIS: ($CHC_2Cl_2$) $\lambda_{max}$ (A) 420 (9.7), 522 (0.69), 545(sh) (0.25), 595 (0.23), 651 nm (0.18). NMR: ($CDCl_3$) $\delta$: −3.27(br s, 1H), −2.72 (br s, 1 H), 3.8–4.7 (m, 16 H), 5.5(s, 0.5 H), 5.6(s, 0.5 H), 5.8(s, 0.5 H), 5.95(s, 0.5 H), 7.2→7.8 (m, 16 H, 8.3→8.8 (m, 7 H).

*β - Amino - "naphthyl - $C_2$ - capped" - porphyrins* **22** *and* **23**

The mixture of nitroporphyrin isomers **11** and **12** (30 mg, 0.023 mmol) in dry $CH_2Cl_2$ (15 ml) and dry methanol (5 ml) was reduced and worked up as above to give the mixture of isomeric aminoporphyrins **22** and **23** as a yellow solid (25 mg, 85%) which was used without purification. VIS: ($CHCl_3$) $\lambda_{max}$ (A): 412(sh) (4.29), 424(5.5), 520(0.26), 550(0.11), 663 nm (0.22).

2 - *Amino* - 5,10,15,20 - *tetraphenylporphyrin* **24**

Compound **15** (200 mg, 0.30 mmol) was reduced as above to give porphyrin **24** as an unstable purple solid (166 mg, 87%), VIS: ($CH_2Cl_2$) $\lambda_{max}$: 425, 522, 555(sh), 594, 651 nm.

### *Derivatives of aminoporphyrins*

*Acetylation of β-amino-*"$C_2$-*capped*"-*porphyrins* **20** *and* **21**

A solution of the isomeric β-aminoporphyrin mixture **20** and **21** (30 mg, 0.03 mmol) in acetic anhydride (1 ml) containing pyridine (0.1 ml) was warmed for 1.5 hr and then poured into water. After 0.5 hr the mixture was extracted with $CH_2Cl_2$ and the organic layer dried and evaporated to dryness. The resulting crude porphyrin was purified by preparative chromatography on silica gel eluted by $CH_2Cl_2$/MeOH (97:3). The major band yielded the isomeric mixture of acetamidoporphyrins (**25**) and **26**), as a purple solid (22 mg, 70%) IR: ($CH_2Cl_2$) $\nu_{max}$: 3400, 1722, 1697 $cm^{-1}$. VIS: ($CH_2Cl_2$) $\lambda_{max}$: 423, 519, 550(sh), 595, 648 nm. NMR: ($CDCl_3$) $\delta$ 1.98(s, 3 H), 3.8–4.7(m, 16 H), 5.32, 5.45, 5.50, 5.55(4s, 2 H), 7.3–8.0(m, 16 H), 8.3–8.8 (m, 7 H). MS: (FD) *m/e*: 1093 ± 1 (M).

2 - *Acetamido* - 5,10,15,20 - *tetraphenylporphyrin* **27**

Compound **24** (35 mg, 0.056 mmol) was similarly acetylated at room temperature overnight. The resultant solid on workup was chromatographed on silica with $CH_2Cl_2$ and the red-purple major band ($R_f$ 0.45) collected. This band yielded porphyrin **27** as a purple-brown solid (28 mg, 75%) m.p. > 300° IR: (nujol) $\nu_{max}$: 3410, 3320, 1690 $cm^{-1}$. NMR: ($CDCl_3$) $\delta$: −2.7(br s, 2 H), 1.81(s, 3 H, 7.5→7.9 (m, 13 H), 7.9–8.3(m, 8 H), 8.5(m, 1 H), 8.7 (m, 5 H), 9.2(s, 1 H).

*β - Trimethylacetamido - "naphthyl - $C_2$ - capped" - porphyrin* **28** *and* **29**

The β-aminoporphyrin isomeric mixture **22** and **23** (25 mg, 0.02 mmol) in pyridine (0.3 ml) was treated with pivaloyl chloride (120 mg, 1.0 mmol) and triethylamine (10 ml) and allowed to stand overnight. The product was partitioned between water (25 ml) and chloroform (25 ml). The organic phase was retained and washed with water (20 ml), dried and evaporated to dryness. The crude amide was chromatographed on silica gel [toluene/ethyl acetate (7:3)] and the major band ($R_f$ 0.5) isolated and worked up to give the product **28** and **29** as a purple solid (15 mg, 56%), m.p. > 300°. VIS: ($CHCl_3$) $\lambda_{max}$(A): 425(87.8), 518(6.0), 546(sh) (1.3), 596(1.7), 654 nm (1.0). NMR: ($CDCl_3$) $\delta$:−2.78(br s, 2 H), 1.20(s, 9 H), 3.8→4.8 (m, 16 H), 5.75, 5.76, 5.82, 5.86(4s, 2 H), 6.1→8.4 (m, 23 H). MS: (FD) *m/e*: 1335 (M).

*β - Isocyanato - "$C_2$ - capped" - porphyrin* **30** *and* **31**

A toluene solution (250 ml) saturated with phosgene was prepared by bubbling phosgene (purified by passage through linseed oil and then conc. $H_2SO_4$) into dry toluene at 0°. The β - aminoporphyrin mixture **20** and **21** (250 mg, 0.24 mmol) in dry toluene (90 ml) was added dropwise to this solution at room temperature over 70 min. The resultant green solution was stirred at room temperature for 0.5 hr, then boiled for 1 hr. Removal of the solvent *in vacuo* gave the isomeric isocyanates **30** and **31** as a purple solid of sufficient purity for further reactions. IR: ($CHCl_3$) $\nu_{max}$: 2300(s), 1725 $cm^{-1}$. VIS: ($CH_2Cl_2$) $\lambda_{max}$: 424, 519, 550(sh), 594, 649 nm.

*β-Ethylurethanes* **32** *and* **33**

The foregoing isomeric isocyanates **30** and **31** (0.29 g, 0.27 mmol) were treated with excess ethanol in boiling ethyl acetate. The solvent was removed *in vacuo*. The solid was chromatographed over silica using a benzene/ethyl acetate gradient. The desired product was eluted with a 17:3 mixture of solvent. Workup gave the isomeric ethylurethanes **32** and **33** as a purple solid (125 mg, 41%). IR: 3300, 1720, 1670 $cm^{-1}$. VIS:

($CH_2Cl_2$) $\lambda_{max}$: 423, 518, 550, 595, 658 NM. MS: (FD) *m/e*: 1123 ± 1 (M).

*Pyridination and related reactions*

*Zinc "$C_2$-capped"-porphyrin π-cation radical perchlorate ($ZnCP^{+\cdot}$, $ClO_4^-$)*

Zinc "$C_2$-capped"-porphyrin **3** (220 mg, 0.2 mmol) was dissolved in dry $CH_2Cl_2$ (10 ml) under nitrogen and anhydrous silver perchlorate (52 mg, 0.25 mmol) in dry MeCN (3.5 ml) added, followed by iodine (40 mg, 0.3 mmol). The mixture was stirred for 15 min, filtered and the filtrate evaporated to dryness. The resultant porphyrin salt was purified by precipitation from a minimum volume of $CH_2Cl_2$ by addition of hexane to give $ZnCP^{+\cdot}$, $ClO_4^-$ as a green solid (235 mg, 98%) m.p. > 300°. VIS: ($CH_2Cl_2$) $\lambda_{max}$ (A): 417(6.5), 450(sh) (0.96), 550(0.18), 648(sh) (0.32), 688 nm (0.40).

*Reaction of $ZnCP^{+\cdot}$, $ClO_4^-$ with pyridine*

A solution of the foregoing salt (60 mg, 0.05 mmol in dry acetonitrile (5.0 ml) under nitrogen was treated with dry redistilled pyridine (250 mg, 2.7 mmol) and the solution stirred overnight and concentrated. Chromatography on silica gel [$CH_2Cl_2$/methanol, (5:1)] resulted in two bands. The top band ($R_f$ 0.9) afforded **3** (31 mg, 56%) on workup. The green band ($R_f$ 0.2) gave a mixture ($\lambda_{max}$ ($CH_2Cl_2$): 429, 440, 510(sh), 555, 582, 623 nm) which was fractionated over silica gel (30 g). Elution with $CH_2Cl_2$ and with $CH_2Cl_2$/ethyl acetate (10:1) gave only minor products which were discarded. Further elution with $CH_2Cl_2$/methanol (10:1) gave a broad green band which was collected in two portions. The first half gave on concentration an approximately equimolar mixture of the isomeric, racemic zinc β-pyridinium - "$C_2$-capped"-porphyrin perchlorates as a green–black solid (14 mg, 22%), m.p. > 300°. IR: ($CHCl_3$) $\nu_{max}$: 1725, 1600, 1500, 1450, 1250(br) $cm^{-1}$. VIS: ($CH_2Cl_2$) $\lambda_{max}$: 428, 518, 558, 586, 610(sh) nm; (methanol) $\lambda_{max}$: 431, 527, 565, 603 nm. NMR: ($CDCl_3$) δ: 3.6→4.6 (m, 16 H), 4.94(s, 0.5 H), 5.20(s, 0.5 H), 5.72(s, 0.5 H), 6.26(s, 0.5 H), 6.96→10.1 (m, 28 H). The latter part of the band on concentration gave the (±)7-pyridinium compound **34** as a blue–green solid (10 mg, 16%), m.p. > 300°. IR: ($CHCl_3$) $\nu_{max}$: 1725, 1630, 1600, 1580, 1500, 1450, 1250(br) $cm^{-1}$. VIS: ($CH_2Cl_2$) $\lambda_{max}$: 428, 518, 558, 586, 610(sh) nm; (methanol) $\lambda_{max}$: 431, 527, 565, 603 nm. NRM: ($CDCl_3$) δ: 3.6→4.6 (m, 16 H), 5.20 (s, 1 H), 5.72(s, 1 H), 6.9→8.57 (m, 21 H), 8.6→10.0 (m, 7 H).

*Nucleophilic substitution of nitro groups of nitroporphyrins*

2 - *Phenylthio* - 5,10,15,20 - *tetraphenylporphyrin* **35**. An ice-cold solution of **15** (66 mg, 0.1 mmol) and thiophenol (600 mg, 5.0 mmol) in dry DMF (10 ml) under argon was treated with anhydrous lithium hydroxide (102 mg, 4.4 mmol). The solution was stirred at 0° for 15 min and allowed to stand at room temperature for 15 hr. Chloroform (100 ml) and glacial acetic acid (1 ml) were added and the solution was washed with water (8 × 100 ml), dried ($MgSO_4$), filtered and evaporated to dryness *in vacuo* to yield a purple–brown solid. Chromatography on silica (dichloromethane/carbon tetrachloride, 1:2) gave a major yellow–brown band ($R_f$ 0.7) which on workup gave the 2-phenylthioporphyrin **35** as a purple–brown amorphous solid (64 mg, 89%), m.p. 180°, IR: (KBr) $\nu_{max}$ 3330 $cm^{-1}$. VIS: ($CHCl_3$) $\lambda_{max}$ (log ε): 419(5.24), 521(4.32), 552(3.79), 595(3.79), 650 nm (3.58). NMR: ($CDCl_3$) δ: −2.61(br s, 2 H), 7.1→7.9 (m, 17 H), 7.9→8.3 (m, 8 H), 8.7→8.9 (m, 7 H), MS: (FD) *m/e* 722 (M).

2 - *Ethylthio* - 5,10,15,20 - *tetraphenylporphyrin* **36**. Porphyrin **15** (66 mg, 0.1 mmol) was treated with ethanethiol (1.2 g, 5.0 mmol) and anhydrous lithium hydroxide (0.55 g, 23.9 mmol) in DMF as above. Chromatography of the crude reaction product on silica gel (hexane/$CH_2Cl_2$, 2:1) gave two bands. The top band (purple–pink $R_f$ 0.35) yielded TPP as a purple solid (7 mg, 11%), identical in all respects with authentic material. The bottom band (brown–yellow, $R_f$ 0.2) afforded **36** as a brown–yellow light-sensitive solid (28 mg, 41%), m.p. > 300°. IR: ($CHCl_3$) $\nu_{max}$: 3340, 3070, 3020, 1160 $cm^{-1}$. VIS: ($CH_2Cl_2$) $\lambda_{max}$ (log ε): 411 (5.06), 422(sh) (4.98), 522(4.12), 555(3.51), 594(3.62), 652 nm (3.37). NMR: ($CDCl_3$) δ: −2.63(br s, 2H), 1.38 (t, J 7 Hz, 3 H), 3.08(q, J 7 Hz, 2 H), 7.75(m, 12 H), 7.9→8.4 (m, 7 H). MS: (FD) *m/e*: 674 (M).

*Replacement of nitro group of* **15** *by hydrogen*

Porphyrin **15** (66 mg, 0.1 mmol) was treated with 2 - aminothiophenol (550 mg, 0.44 mol) and anhydrous lithium hydroxide (80 mg, 0.34 mmol) as above. Workup yielded TPP as a purple–pink solid (52 mg, 85%), m.p. > 300°, identical in all respects with authentic material.

*Treatment of β-nitro-"$C_2$-capped"-porphyrin with nucleophiles*

*Reaction with thiophenol.* (a) An ice-cold solution of thiophenol (320 mg, 2.9 mmol) and anhydrous lithium hydroxide (30 mg, 1.3 mmol) in dry DMF (10 ml) under argon was prepared. A solution of β-nitro-"$C_2$-capped"-porphyrin **6** and **7** (41.5 mg, 0.038 mmol) in dry DMF (5 ml) was added by canula and the solution stirred at 0° for 1 hr and the reaction worked up immediately by the method for the corresponding reaction with **15** above. The product was chromatographed on silica (benzene/ethyl acetate, 3:1). The bottom, major band ($R_f$ 0.5) yielded starting material as a purple solid, (25 mg). The top band ($R_f$ 0.6) yielded β-phenylthio-"$C_2$-capped"-porphyrin **37** and **38** as a yellow–purple solid (11 mg, 63% based on recovered starting material), m.p. > 300°. VIS: ($CH_2Cl_2$) $\lambda_{max}$ (A): 428(10.5), 524(0.60), 545(sh), (0.44), 598(0.30), 650 nm (0.44). MS: (FD) *m/e*: 1144 (M), small impurities at 1160, 1189.

(b) Thiophenol (118 mg, 1.07 mmol) and anhydrous lithium hydroxide (22 mg, 0.96 mmol) was added to the porphyrin mixture **6** and **7** (50 mg, 0.046 mmol) in dry DMF (5 ml) under argon and the solution stirred for 16 hr at room temperature. Workup as above gave "$C_2$-capped"-porphyrin **2** as a purple solid (25 mg, 52%), m.p. > 300°, identical with authentic material, and a complex mixture of products not resolved by PLC.

*Reaction with ethanethiol.* Treatment of β-nitro-"$C_2$-capped" porphyrin **6** and **7** (108 mg, 0.1 mmol) with ethanethiol (600 mg, 10 mmol) and lithium hydroxide (102 mg, 4.43 mmol) in dry DMF (10 ml) as in the corresponding reaction on **15** gave a mixture consisting largely of "$C_2$-capped" porphyrin and some putative ethylthioporphyrin **39** and **40** as a brown yellow solid. VIS ($CH_2Cl_2$): $\lambda_{max}$ 422, 519, 542(sh), 593, 649 nm. NMR: ($CDCl_3$) 1.38(t, J 7 Hz), 3.09 (q, J 7 Hz), 5.36, 5.58 (same intensity singlets) 5.48, 5.55 (same intensity singlets), 5.45 (high intensity singlet). Resolution of the mixture by chromatography was unsuccessful.

*Denitration of* **18** *with thiophenol*

Thiophenol (110 mg, 1.0 mmol) and anhydrous lithium hydroxide (23 mg, 1.0 mmol) were added to a solution of **18** (28 mg, 0.034 mmol) in dry DMF (2 ml) under argon and the solution stirred overnight. Workup in the usual way gave the denitrated "strapped"-porphyrin **41** as a purple–brown solid (22 mg, 83%), m.p. > 300°. The compound was identical in all respects with an authentic sample.[14]

*Acknowledgements*—We thank the National Institutes of Health and the S.R.C. for financial support and Dr. R. T. Alpin for mass spectra.

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