NEW PROCEDURES FOR THE SYNTHESIS AND ANALYSIS OF 5,10,15,20-TETRAKIS(SULPHOPHENYL)PORPHYRINS AND DERIVATIVES THROUGH CHLOROSULPHONATION

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Abstract – Tetrakisarylporphyrins are conveniently chlorosulphonated in high yields. These chlorosulphonyl compounds may be converted in high yield into sulphonic acid derivatives through reaction with a variety of nucleophiles so as to give, for example, the free sulphonic acid, a sulphonamide or a sulphonate ester.

INTRODUCTION

Either in natural systems[1-3] or newly devised applications,[4] porphyrins are frequently required to perform their roles in aqueous media. Various model porphyrins have been synthesised with the aim of mimicking enzymes, particularly the P450 types.[2,3] For these purposes, there has been major interest in the easily prepared 5,10,15,20-tetrakisarylporphyrins for which reasonably high yielding one-pot syntheses have been developed.[5] Many of the model porphyrins lack water solubility and do not possess the water solubilising properties of the proteins that surround natural heme enzymes. Examination of their behaviour as oxidation catalysts has been done largely under non-aqueous conditions.[6] More recently, interest has developed in the production of water soluble or partially water soluble porphyrins for use in molecular electronics,[7] studies in photodynamic therapy[4] and the mimicking of peroxidases.[8] In the latter instance, the solubilisation of water-insoluble porphyrins by water-soluble ampholytes that imitate protein coats has

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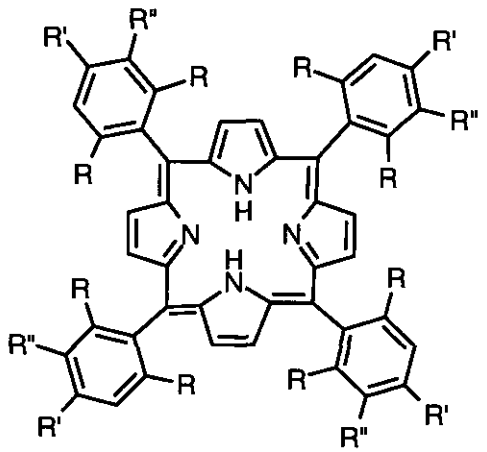
been described. For experiments in aqueous solution without a water-solubilising protein or ampholyte carrier, one important type of water-soluble 5,10,15,20-tetrakisarylporphyrin is based on sulphonic acid derivatives which are currently prepared by direct sulphonation with strong sulphuric acid.[9,10] Yields in such reactions are usually not good and the work-up needed to isolate the highly water-soluble porphyrin sulphonic acids from an excess of sulphuric acid is inconvenient and time-consuming. This problem is removed through the use of chlorosulphonic acid, as described below.[8,17] These experimental difficulties in handling water-soluble organic compounds when they must be isolated in a pure state from mixtures with other, often inorganic, water-soluble substances, is again observed during the preparation of water-soluble ionic metallo-porphyrins having a metal ion only at the center of the porphyrin ring and not on the sulphonic acid groups. To overcome this second problem, a convenient modification of a known heterogeneous metallation reaction[11] has allowed preparation of monometallo-5,10,15,20-tetrakis(sulphoaryl)porphyrins in high purity. Alternatively, the chlorosulphonyl intermediates resulting from chlorosufonation may be metallated directly and then hydrolysed to the corresponding metallated sulphonic acids. After initial reports of this chlorosulphonation had appeared, [8,13,14,17] there was a further report of the use of chlorosulphonic acid to produce an impure, uncharacterised water-soluble tetrabenzoporphyrin.[12]

RESULTS AND DISCUSSION

As with sulphuric acid, chlorosulphonic acid readily protonates a porphyrin ring, thereby deactivating the pyrrolic β-positions and directing electrophilic substitution to any meso-aryl groups which may be present. A major advantage of chlorosulphonation is that the initially formed chlorosulphonyl compounds are very easily isolated from the reaction medium because they are insoluble in water but soluble in water-immiscible organic solvents. Hydrolysis of the chlorosulphonyl derivatives with water alone is slow so that they can be separated easily by extraction from any excess of chlorosulphonic acid and its water soluble by-products and they may be chromatographed even on silica gel. However, the chlorosulphonyl group is susceptible to nucleophilic attack under suitable conditions. For example, isolated crystalline chlorosulphonyl derivatives can be cleanly and selectively converted into the corresponding sulphonic acids



(1)

by heating them with water for some time, thereby allowing simple isolation of the acids in crystalline form and high purity.[13] Similarly, sulphonate esters can be formed by reaction of the chlorosulphonyl derivative with an alcohol. Further, because of its susceptibility to attack by nucleophiles, the chlorosulphonyl group may be converted into other functionalities, giving access to novel porphyrins such as those having sulphonamido groups; these range from highly polar, hydrophilic compounds (**1**; R = R" = H, R' = SO_2NH_2) to amphiphilic surfactants suitable for formation of Langmuir films (**1**; R = R" = H, R' = $SO_2NHC_{12}H_{25}$).[14]

Treatment of 5,10,15,20-tetrakisphenylporphyrin (TPP) with chlorosulphonic acid gives a green solution which, on addition of ice-water, affords the dication of 5,10,15,20-tetrakis(4'-chlorosulphonylphenyl)porphyrin (**1**; R = H, R' = SO_2Cl, R" = H) as small bright green crystals. The chlorosulphonyl derivative can be purified if necessary by chromatography on silica gel. The chlorosulphonylporphyrin hydrolyses almost instantaneously on reaction with aqueous NaOH or KOH to form the corresponding alkali sulphonate (**1**; R = H; R' = SO_3Na or SO_3K, R" = H). This procedure leads to some difficulties in purification of the porphyrin salt from the water solution due to any excess of water soluble inorganic salts. To obtain the free sulphonic acid, ion exchange of the alkali metal can be used but it is much more convenient to accept the somewhat slower direct hydolysis with water alone because, after reaction, simple evaporation of the water gives the required 5,10,15,20-tetrakis(4'-sulphophenyl)porphyrin (TPPS; **1**; R = H, R' = SO_3H, R" = H) without tedious or laborious work-up. If necessary, purification of the resulting sulphonic acid can be effected rapidly by chromatography on Sephadex. Reaction of the chlorosulphonyl compound with ammonia or amines gave respectively sulphonamide (**1**; R = H, R' = SO_2NH_2, R" = H), *N*-n-butylsulphonamide (**1**; R = H, R' = $SO_2NHC_4H_9$, R" = H) and *N*-n-dodecylsulphonamide (**1**; R = H, R' = $SO_2NHC_{12}H_{25}$, R" = H).

Reaction of 5,10,15,20-tetrakis(2',6'-dichlorophenyl)porphyrin (TDCPP; **1**, R = Cl, R' = H, R" = H) with chlorosulphonic acid under the same conditions as for TPP gave a mixture of mono-, di- and tri-substituted chlorosulphonyl derivatives[17] and little of the required tetra-substituted compound but, if the reaction mixture be heated for 3 hours at 100 °C, 5,10,15,20-tetrakis(2',6'-dichoro-3'-chlorosulphonylphenyl)porphyrin (**1**; R = Cl, R' = H, R" = SO_2Cl) is obtained in 92% yield. Refluxing this chlorosulphonyl derivative with water gives the corresponding tetrasulphonic acid (**1**; R = Cl, R' = H,

R" = SO_3H). With n-butylamine at room temperature, the chlorosulphonyl compound yielded the corresponding sulphonamide (**1**; R = Cl, R' = H, R" = $SO_2NHC_4H_9$).

Metallation of the central ligand position and not the sulphonic acid groups of water-soluble porphyrins gives complicated work-up problems if standard methods[15] are used. While water-insoluble metalloporphyrins can be separated easily from the inorganic salts used in their preparation through partition between water and a suitable organic solvent, for the water-soluble porphyrins, all the components remain in the aqueous phase and purification becomes tedious and cumbersome. Additionally, these procedures lead to both the central ligand position and the substituent sulphonic acid groups becoming metallated. To overcome these difficulties, use was made of a reported[11] heterogeneous metallation of the sodium salts of water-soluble sulphonic acid derivatives of porphyrins, in which metallation of the ring is effected by stirring aqueous solutions of the sodium salts with the required finely divided metal or its oxide. The same method was applied to the sulphonic acids themselves after small modifications. With some easily oxidized metals such as copper, this method with sulphonic acids, while extremely convenient, can lead to degradation of the porphyrin if it is left in contact with metal for extended periods. It was found to be important to control the reaction by observing the shift of the Soret band during metallation. When the Soret band for the metal-free porphyrin had disappeared, the reaction was stopped. For copper this stage was reached after about 30 minutes but, for manganese it was about 2 hours. In contrast to the earlier similar use of the sodium salts,[10] this approach with free sulphonic acids leads to incorporation of metal into the sulphonic acid as well as at the center of the porphyrin ring and it is necessary to pass the resulting permetallated compound in water through an ion-exchange resin to obtain the required porphyrin having a central metal atom but no metal associated with the sulphonic acid groups. As a more convenient alternative, metallation of the chlorosulphonyl derivatives could be effected directly. Thus, refluxing 5,10,15,20-tetrakis(2',6'-dichloro-3'-chlorosulphonylphenyl)porphyrin with manganese(acac)$_2$ in THF gave the corresponding manganese derivative which could be hydrolysed in water to the corresponding metallated porphyrinsulphonic acid.

Elemental analysis of water-soluble porphyrins and metalloporphyrins can present difficulties. While elemental analysis is satisfactory for well-dried samples, these hydrophilic compounds tend to absorb water easily, making analysis difficult and the results somewhat problematical at times.[15] Analysis by ^{1}H-nmr

spectroscopy can also be difficult because of easy exchange of β-pyrrole protons with D_2O or because of formation of aggregates.[16] In the present work, the easiest methods of analysis for verifying the incorporation of the required number of sulpho groups were found to lie at the organic solvent soluble chlorosulphonyl stage, viz., after reaction with chlorosulphonic acid but before reaction of the chlorosulphonyl group with water. Chlorosulphonylarylporphyrins give excellent ^{1}H-nmr spectra in deuteriochloroform, good FAB mass spectra and reliable microanalyses. It was also found convenient to characterise the chlorosulphonyl compounds further by reacting them with alkylamines to give the corresponding stable *N*-alkylsulphonamides. Elemental analysis for the number of sulpho groups introduced during synthesis does not give unequivocal results. For example, in one instance a mixture of tri-, tetra- and penta-substituted sulphoporphyrins gave an elemental analysis correct for the solely tetra-substituted compound. One method that differentiates the number of sulphonic acid groups is negative ion electrospray mass spectrometry which gave excellent results. Series of well separated $[M - zH]^{z-}/z$ ions were observed, thereby affording ready discrimination between fully or partially sulphonated porphyrins.[17] This analytical procedure was used to optimise reaction conditions so as to achieve high yields of the correctly substituted sulphoporphyrins.

In conclusion, a convenient method for introducing sulphonic acid groups into the aryl rings of 5,10,15,20-tetrakisarylporphyrins has been developed through chlorosulphonation. The intermediate chlorosulphonyl compounds are easy to work with, simple to analyse, can be transformed readily into a variety of other compounds such as the free acids or sulphonamides and can be easily metallated. Methods for rapid analysis of water-soluble porphyrinsulphonic acids by electrospray mass spectrometry are described.

EXPERIMENTAL

All solvents and reagents were purified by standard methods before use. ^{1}H-Nmr spectra were recorded on a Bruker-AC 200 at 200 MHz and a Varian XL 200 at 200 MHz and were run in D_2O for water soluble porphyrins and $CDCl_3$ for the others. Mass spectra were obtained on a VG 7070E mass spectrometer in FAB positive ion mode with 3-nitrobenzyl alcohol as matrix and on a Fisons VG Bio-Q[17] or VG Platform instrument,[17] using electrospray ionization with water/acetonitrile/methanol (1:1:1) as matrix solvent.

Chlorosulphonation: (a) 5,10,15,20-Tetrakisphenylporphyrin (100 mg, 0.162 mmol) and chlorosulphonic acid (6 ml, 90 mmol) were stirred at room temperature for 1 h. To the resulting solution was added slowly, ground ice (30-40 g, caution!) to give a green crystalline precipitate of diprotonated 5,10,15,20-tetrakis(4'-chlorosulphonylphenyl)porphyrin. After addition of the ice, some water (30 ml) was added and the free base was liberated from this mixture through the gradual addition, with stirring, of a slight excess of saturated aqueous sodium bicarbonate. The required compound was extracted immediately into chloroform, which was then dried ($MgSO_4$) and evaporated to give the solid 5,10,15,20-tetrakis(4'-chlorosulphonylphenyl)porphyrin (**1**; R = H; R' = SO_2Cl, R" = H) (120 mg, 73%). *Anal.* Calcd for $C_{44}H_{26}N_4O_8Cl_4S_4$: C, 52.4; H, 2.6; N, 5.6. Found: C, 52.2; H, 3.0; N, 5.2. Ms (FAB), $[M+H]^+$ m/z 1007; λ_{max} ($CHCl_3$; % relative height of Soret band): 418 nm (100%), 516 (8.8), 554 (7.5), 590 (5.7), 650 (5.3); ^{1}H-nmr ($CDCl_3$), δ: 8.90 (8H, s), 8.20 (8H, d, *J* = 7.5 Hz), 7.50 (8H, d, *J* = 7.5 Hz), –2.70 (2H, s). Usually, the chlorosulphonyl compound is obtained pure by this process but, if it becomes necessary to purify the crude product this can be effected by chromatographing it on silica gel, using chlorofrom as eluant. (b) Similarly, 5,10,15,20-tetrakis(2',6'-dichlorophenyl)porphyrin (100 mg, 0.11 mmol) was stirred with neat chlorosulphonic acid (6 ml, 90 mmol) at 100 °C for 3 h. After cooling the solution to room temperature, ice/water was added as for the 5,10,15,20-tetrakis(4'-chlorosulphonylphenylporphyrin described above, to give the solid 5,10,15,20-tetrakis(2',6'-dichloro-3'-chlorosulphonylphenyl)porphyrin (**1**; R = Cl; R' = H, R" = SO_2Cl) directly; in this case, it was not necessary to free the dication of the chlorosulphonyl derivative with aqueous 10% sodium bicarbonate, extraction with chloroform being sufficient to obtain the chlorosulphonyl compound (115 mg, 89%). *Anal.* Calcd for $C_{44}H_{18}N_4O_8Cl_{12}S_4$: C, 41.1; H, 1.4; N, 4.4. Found: C, 40.6; H, 1.7; N, 4.1. Ms (FAB), $[M + H]^+$ m/z 1279; λ_{max} ($CHCl_3$; % relative height of Soret band): 422 nm (100%), 514 (6.2), 548 (2.9), 592 (1.7), 658 (1.6); ^{1}H-nmr ($CDCl_3$), δ: 8.65 (8H, s), 8.60 (4H, d, *J* = 8.6 Hz), 8.05 (4H, d, *J* = 8.6 Hz), –2.40 (2H, s).

Hydrolysis of chlorosulphonyl compounds to sulphonic acids. (a) A suspension of 5,10,15,20-tetrakis(4'-chlorosulphonylphenyl)porphyrin, (**1**; 70 mg, 69 mmol) in water (120 ml) was refluxed for 12 h. The resulting solution was concentrated by rotary evaporation to give the required 5,10,15,20-tetrakis(4'-sulphophenyl)porphyrin (**1**; R = H; R' = SO_3H, R" = H) which was further purified by passage through a Sephadex column (G25), using water as eluant. A purple band was eluted and the

collected fractions were reduced to a volume of about 2 ml by rotary evaporation at which stage addition of an excess of acetone precipitated the required solid tetrakis(4'-sulphophenyl)porphyrin (58 mg, 90%). *Anal.* Calcd for $C_{44}H_{30}N_4O_{12}S_4$: C, 56.5; H, 3.2; N, 6.0. Found: C, 56.0; H, 3.4; N, 5.8. Ms (electrospray), $[M - H]^-$, m/z 933; λ_{max} (H_2O; % relative height of Soret band): 418 nm (100%), 512 (6.8), 548 (4.6), 594 (3.6); ^{1}H-nmr (D_2O), δ: 8.75 (8H, s), 8.30 (8H, d, J = 7.7 Hz), 7.20 (8H, d, J = 7.7 Hz). (b) Similarly, a suspension of 5,10,15,20-tetrakis(2',6'-dichloro-3'-chlorosulphonylphenyl)-porphyrin (80 mg, 62 mmol) in water (120 ml) was refluxed for 20 h. The resulting solution was worked up as above to give 5,10,15,20-tetrakis(2',6'-dichloro-3'-sulphophenyl)porphyrin (**1**; R = Cl; R' = H, R" = SO_3H) (70 mg, 93%). *Anal.* Calcd for $C_{44}H_{26}N_4O_{12}Cl_8S_4$: C, 43.6; H, 1.8; N, 4.6. Found: C, 43.7; H, 2.3; N, 4.3. Ms (electrospray), $[M - H]^-$, m/z 1205; λ_{max} (H_2O; % relative height of Soret band): 418 nm (Soret; 100%), 517 (9.2), 550 (5.0), 588 (4.3), 656 (4.2); ^{1}H-nmr (CD_3OD), δ: 7.8–8.0 (4H, m), 8.2–8.5 (4H, m), 8.6–9.0 (8H, m).

Preparation of sulphonamides: (a) A sample of 5,10,15,20-tetrakis(4'-chlorosulphonyl-phenyl)porphyrin (100 mg, 99 mmol) was dissolved in dichloromethane (25 ml) and stirred with conc. aq. ammonia (35% w/v; 25 ml) for 1 h at room temperature. The precipitate so formed was filtered off to give the crude sulphonamide (72 mg, 78%). This solid was washed with dichloromethane (50 ml), crystallised from acetone/dichloromethane (1:1) and dried under vacuum to produce the solid 5,10,15,20-tetrakis(4'-sulphonamidophenyl)porphyrin (**1**; R = H; R' = SO_2NH_2, R" = H) (63 mg, 68%). *Anal.* Calcd for $C_{44}H_{34}N_8O_8S_4$: C, 56.6; H, 3.7; N, 12.0. Found: C, 56.7; H, 3.7; N, 11.8. Ms (FAB), $[M + H]^+$, m/z 931; λ_{max} (H_2O; % relative height of Soret band): 412 nm (100%), 515 (5), 550 (2), 580 (1.8), 610 (1.1); ^{1}H-nmr (D_2O), δ: 8.24 (8H, s), 8.20 (8H, d, J = 7.6 Hz), 7.72 (8H, d, J = 7.6 Hz). (b) A sample of 5,10,15,20-tetrakis(4'-chlorosulphonylphenyl)porphyrin (100 mg, 99 mmol) was suspended in dichloromethane (25 ml) and n-butylamine (12 molar equivalents) was added. The reaction mixture was stirred at room temperature for 4 h and was then concentrated by rotary evaporation. The resulting solid was passed through a column of silica gel (Silica Merck 9385) using $CHCl_3$/EtOAc (4:1) as eluant. Evaporation of the solvent and recrystallization of the residue from CH_2Cl_2/CH_3OH gave the solid 5,10,15,20-tetrakis(4'-*N*-n-butylsulphonamidophenyl)porphyrin (**1**; R = H, R' = n-$C_4H_9NHSO_2$, R" = H) (66 mg, 58%). *Anal.* Calcd for $C_{60}H_{66}N_8O_8S_4$: C, 62.4; H, 5.7; N, 9.7; S, 11.1. Found: C, 62.0; H, 5.7; N, 9.2; S, 11.0. Ms (FAB), $[M + H]^+$, m/z 1155; λ_{max} (MeOH; % relative height of

Soret band): 412nm (100%), 510 (4.5), 545 (2.0), 585 (1.9), 645 (0.8); ^{1}H-nmr (TFA), δ: 9.05 (8H, s), 8.98 (8H, d, *J* = 8 Hz), 8.77 (8H, d, *J* = 8 Hz), 5.32 (4H, s), 3.52 (8H, t, *J* = 7 Hz), 1.84 (8H, m), 1.66 (8H, m), 1.11 (12H, t, *J* = 7.1 Hz), –1.30 (4H, s). Similarly, the following sulphonamides were prepared from the requisite amines: 5,10,15,20-tetrakis(4'-*N*-n-dodecylsulphonamidophenyl)porphyrin (**1**; R = H, R' = n-$C_{12}H_{25}NHSO_2$, R" = H), in 41% yield, mp > 200 °C. *Anal.* Calcd for $C_{92}H_{130}N_8O_8S_4$: C, 68.9; H, 8.1; N, 7.0; S, 8.0. Found: C, 68.7; H, 8.6; N, 6.8; S, 7.8. Ms (FAB), $[M + H]^+$, m/z 1603 ; λ_{max} ($CHCl_3$; % relative height of Soret band): 418nm (100%), 515 (4.4), 550 (1.3), 635 (0.7), 690 (0.9); ^{1}H-nmr, δ: 8.78 (8H, s), 8.32 (8H, d, *J* = 8.4 Hz), 8.24 (8H, d, *J* = 8.4 Hz), 4.84 (4H, t, *J* = 6.7 Hz), 3.28 (8H, q, *J* = 6.7 Hz), 1.64 (8H, m), 1.23 (72H, m), 0.8 (12H, t, *J* = 6.5 Hz), –2.85 (2H, s); 5,10,15,20-tetrakis(2',6'-dichloro-3'-*N*-n-butylsulphonamidophenyl)porphyrin (**1**; R = Cl, R' = H, R" = n-$C_4H_9NHSO_2$) in 81% yield. *Anal.* Calcd for $C_{60}H_{58}N_8O_8Cl_8S_4$: C, 50.3; H, 4.1; N, 7.8, S 8.9. Found: C, 50.4; H, 4.3; N, 8.0, S 8.3. Ms (FAB), $[M + H]^+$, m/z 1427; λ_{max} ($CHCl_3$, % relative height of Soret band): 419 nm (100%), 512 (6), 587 (2), 653 (0.3); ^{1}H-nmr, δ: 8.59 (8H, s), 8.58 (4H, d, *J* = 8 Hz), 7.99 (4H, d, *J* = 8 Hz), 5.03 (4H, br s), 3.21 (8H, br q, *J* = 6.5 Hz), 1.58–1.25 (16H, m), 0.94 (12H, t, *J* = 7 Hz), –2.55 (2H, s).

Metallation of the central ring of porphyrin sulphonic acids: In a typical reaction, similar to that described in reference (10), 5,10,15,20-tetrakis(4'-sulphophenyl)porphyrin (**1**; R = H, R' = SO_3H, R" = H; 100 mg) was refluxed in water with copper powder (1 g; cleaned by stirring it with very dilute aqueous HCl at room temperarure for 1 h and then washing it well with distilled water). After 30 min the Soret band at 418 nm had been replaced by one at 414 nm for the copper porphyrin and the Q-bands typical of free porphyrin had disappeared. Atomic absorption spectroscopy showed that more than one copper atom had been incorporated (Found, 13.4% copper; 1 copper requires 6.4%). The solution was filtered and the filtrate was evaporated to a small volume before being placed on a column of ion-exchange resin (30 g; Dowex CCR-2; H^+ form; 20-50 mesh). Elution with distilled water gave the required mono-copper meso-tetrakis(4'-sulphophenyl)porphyrin in 75% yield (Found, 6.6% copper, by atomic absorption spectroscopy). Use of too much ion exchange resin led to loss of copper from the central position also. The same method was applied with manganese and iron metal powders to give the corresponding mono-metallated derivatives, analysed by atomic absorption spectroscopy as Mn^{3+} and Fe^{3+} (since these metallo porphyrins were chromatographed on an acid ion-exchange resin on which any hydroxyl ligand would have

been converted into water, it was assumed that the ligand was a sulphonate group from another molecule; this is not unreasonable in view of the known strong aggregation properties of porphyrin sulphonic acids[18]).

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