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# SYNTHESIS OF MESO-PYRIDINIUM PORPHYRIN SALTS

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We recently reported[1] that solutions of metalloporphyrin π-cation radicals react with nitrite to provide good yields of meso-nitroporphyrins. Such reactions of π-cation radicals[2] with nucleophiles have been questioned[3] on the grounds that in the transition state an electron has to be promoted to an antibonding orbital; notwithstanding this, the literature documents an abundance of well-substantiated reactions[4] of nucleophiles with π-cation radicals from aromatics. In this Letter we report the reactions of various pyridines with metalloporphyrin π-cation radicals to afford good yields of adducts in which a bond has been formed between the porphyrin meso-position and the pyridine nitrogen atom.

Treatment of magnesium(II) octaethylporphyrin (1)(or the corresponding complex of aetioporphyrin-I) with iodine gave the π-cation radical which was stable in methanol but reverted slowly to a red solution upon addition of an excess of pyridine.[5,6] Demetallation and chromatography on alumina gave, apart from recovered octaethylporphyrin, a polar product which could only be removed from the column by elution with chloroform containing methanol. The product was shown, after a work-up using $Cl^-$, to be meso-(N-pyridinium)-octaethylporphyrin chloride (2) using the usual analytical and spectroscopic

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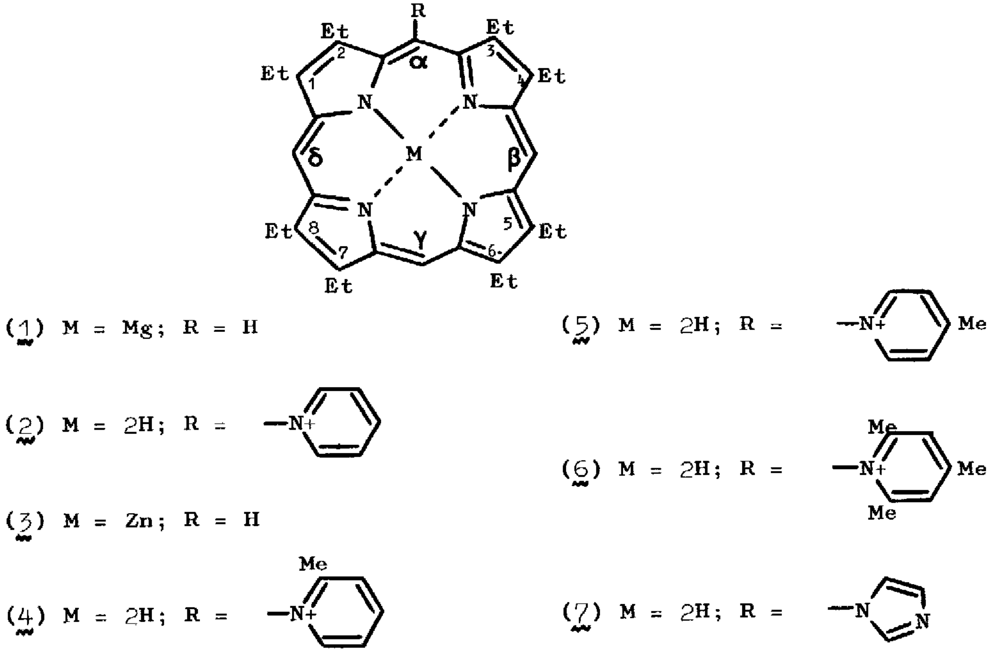

(1) M = Mg; R = H

(2) M = 2H; R =

(3) M = Zn; R = H

(4) M = 2H; R =

(5) M = 2H; R =

(6) M = 2H; R =

(7) M = 2H; R =

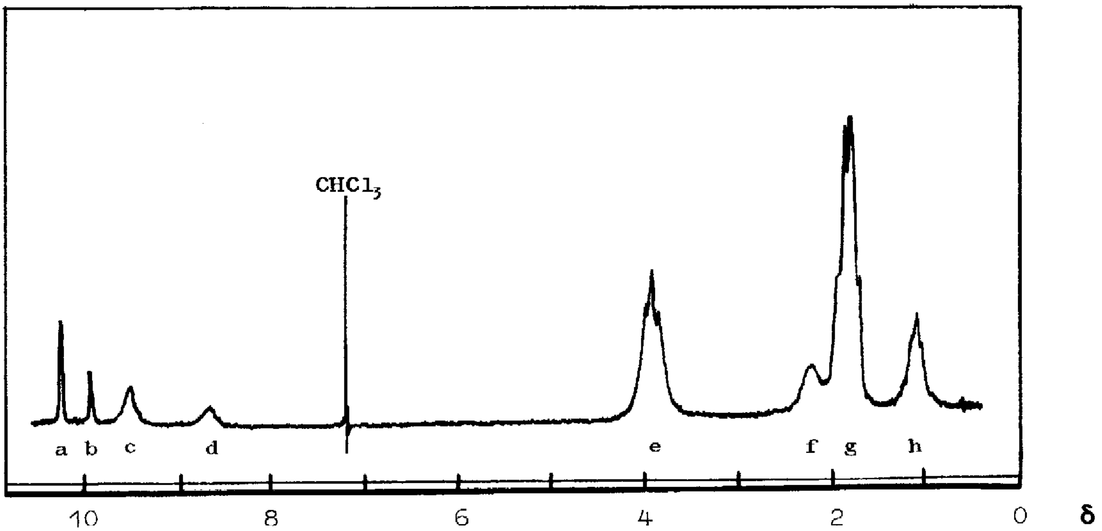

FIGURE: $^1$H NMR Spectrum (HA-100) of Compound (2) in CDCl$_3$

a, β,δ meso-H; b, γ meso-H; c, 3,4,5-pyridinium-H; d, 2,6-pyridinium-H; e, 1,4,5,6,7,8-C$\underline{H_2}$ CH$_3$ ; f, 2,3-C$\underline{H_2}$ CH$_3$ ; g, 1,4,5,6,7,8-CH$_2$ C$\underline{H_3}$ ; h, 2,3-CH$_2$ C$\underline{H_3}$ .

techniques (e.g. $^1$H NMR; Figure).

Zinc(II) octaethylporphyrin (3) is a more convenient substrate owing to the ease of zinc insertion into the porphyrin macrocycle. However, the π-cation radical from the zinc complex cannot be prepared using iodine as oxidant. Thus we have devised the more general procedure which follows:

Zinc(II) octaethylporphyrin (3)(300 mg) in dry THF (30 ml) was flushed with $N_2$ for 10 min. To the stirred soln was added a soln of thallium (III) nitrate (234 mg) in dry MeOH (25 ml). After 30 sec, pyridine (10 ml) was added and the mixture was stirred under $N_2$ for 30 min, during which time the green soln once again became red in colour. $SO_2$ gas was bubbled through the soln for 30 sec (excess $Tl^{+++}$ to $Tl^{+}$) before evaporation to dryness and then addition of $CHCl_3$ (300 ml). This soln was washed with brine, dried ($CaCl_2$) and then evaporated to give a purple residue which was dissolved in THF (25 ml) and MeOH (25 ml) before being treated with conc HCl (20 ml) and stirred for 5 min. $CHCl_3$ (300 ml) was added and the soln was washed with brine, dried ($CaCl_2$), and evaporated to give a red solid which was chromatographed (Fluka, Grade V neutral alumina). Elution with $CHCl_3$ gave mainly octaethylporphyrin (74 mg from $CH_2Cl_2$ -MeOH); further elution with $CHCl_3$ - MeOH (19:1) afforded red-brown eluates which were washed with brine, dried ($CaCl_2$), and evaporated to give a residue which was crystallised from $CH_2Cl_2$ - n-hexane to give purple fluffy needles of (2)(147 mg; 45% but 60% based on consumed octaethylporphyrin), mp > 300°. (Found: C, 74.03; H, 7.85; Cl, 5.24; N, 10.62. $C_{41}H_{50}ClN_5.H_2O$ requires: C, 73.90; H, 7.86; Cl, 5.32; N, 10.51%). $\lambda_{max}$(in $CHCl_3$) 402 (ε 150,100), 505 (14,400), 537 (11,500), 566 (8500), and 616 nm (8300); $\lambda_{max}$(in $CHCl_3$ + 1% TFA) 420 (ε 238,400), 556 (16,200), and 599 nm (9700). *M/e* 611 (15%) and 534 (100). NMR (see Figure on facing page).

Similar reactions were also carried out with 2-picoline (to give 4), 4-picoline (to give 5), and 2,4,6-collidine (to give 6). The reaction with imidazole, which allows porphyrins to be incorporated into a polymeric matrix, has been described elsewhere.[7]

Since the oxidation potential of pyridine (in $CH_3CN$ at Pt vs SCE) is greater than 2.0 V,[8] we do not consider pyridine cation radicals or radicals to be intermediates in this reaction; in any case, these might be expected to couple through carbon rather than nitrogen.[9] Though it is possible that imidazole radicals could be formed under the conditions used in the analogous reaction[7], consultation of the corresponding spin densities for the imidazole radical[10] in which most of the spin density resides on C-2 with the remainder on C-4(5), now leads us to suggest that the imidazole adduct (7) might likewise arise by reaction of imidazole (as a nucleophile) with the magnesium(II) porphyrin π-cation radical.

## REFERENCES AND NOTES

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2 The mechanism of the nitrite reaction will be fully discussed in a forthcoming publication.

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5 The title compounds were first isolated and characterised in 1972. They were observed as polar bands on chromatography columns from reactions of π-cation radicals from *dipyridine* magnesium(II) porphyrins in which a satisfactory mass balance could not be obtained. We thank Dr. S.W. McCombie for these initial experiments.

6 Publication of this work was partly prompted by the recent report that the cation radical from zinc(II) *meso*-tetraphenylporphyrin reacts with pyridine to give the β-substituted pyridinium salt: A.G. Padilla, S.-M. Wu, and H.J. Shine, J.C.S. Chem. Comm., 236 (1976).

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