# β-Substitutions on *meso*-Tetraphenylporphyrin by Direct Electrochemical Oxidation in the Presence of Nucleophiles

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The electrochemical oxidation of *meso*-tetraphenylporphyrin in chloroform–acetonitrile in the presence of various nucleophiles leads to the formation of the corresponding β-substituted salt.

Previous studies have demonstrated that porphyrin π-cation radicals react in solution with various nucleophiles to provide β-substituted porphyrins.[1,2] In order to obtain good yields for this reaction, the chemical route generally needs the metalloporphyin ZnTPP (TPP = tetraphenylporphyrin) as starting material because of its low oxidation potential[3] and the high stability of the π-cation radical $ZnTPP^{+\bullet}$.[4,5] These characteristics facilitate obtaining the corresponding salt required for the nucleophilic β-substitutions.

The higher oxidation potential of the corresponding free base $H_2TPP$,[6,7] and the very low stability of its π-cation radical[5] prevented carrying out such β-substitutions chemically, until now.

We described recently an alternative oxidation pathway for obtaining β-substituted porphyrins through direct electrochemical oxidation of ZnTPP in the presence of various nucleophiles.[8,9] This electrochemical route is of particular interest considering the good yield of substitution reaction compared to the chemical route.

We now report the first evidence for β-substitution of the *meso*-tetraphenylporphyrin $H_2TPP$ by a one-pot reaction, *viz.* by electrochemical oxidation of the free base $H_2TPP$ in the presence of nucleophiles.

*meso*-Tetraphenylporphyrin $H_2TPP$, prepared by the method of Adler *et al.*[10] and purified as described by Smith,[11] had spectroscopic properties consistent with the literature.

The exhaustive electrochemical oxidation of $H_2TPP$ was performed under nitrogen in a three-electrode two-compartment cell. The working and counter electrodes were platinum wires. The reference electrode was a saturated calomel electrode (S.C.E.). The electrochemical solution contained $H_2TPP$ (40 mg) and pyridine (4 ml) in $MeCN$–$CHCl_3$ (1:4) (250 ml) with tetraethylammonium perchlorate (TEAP 0.1 M) as supporting electrolyte.

The solvents and pyridine were commercial products (Fluka Puriss.), used without further purification. TEAP was purified by known procedures.[12]

After the working electrode had been maintained for 1 h at +1.01 V *vs.* S.C.E., the initial violet solution turned yellow-brown. Further evaporation under reduced pressure, washing, and extraction with $H_2O$–$CH_2Cl_2$ (5:1) gave a dark solid which was chromatographed on an alumina column (activity III, Merck). Elution with $CHCl_3$ gave a yellow clear solution (unidentified product). Further elution with $CHCl_3$–$MeOH$ (95:5) afforded the desired product which was recrystallised from $CH_2Cl_2$–n-pentane to produce dark crystals (39 mg). Thus the net yield of the substitution was 86% whereas the yield was only 70% when the metallated porphyrin (ZnTPP) was the starting material. Elemental analyses were consistent with the product being the monoperchlorate $(H_2TPP\text{-}\beta\ Py)^+$ $ClO_4^-$ and its visible spectrum† fitted well with the known characteristics[2] of the β-pyridinium derivative of $H_2TPP$. The $^1H$ n.m.r. spectrum‡ is also consistent with the structure assigned; the pyrrolic protons all appear downfield from those of the phenyl ring, thus demonstrating that the aromaticity of the porphyrin ring was not interrupted[2] and, therefore, that the substitution had not taken place at a *meso*-position.

We successfully carried out similar reactions with various substituted pyridines: for instance, in the presence of 2-picoline the substitution reaction generated the species $(H_2TPP\text{-}\beta\text{-}Pic_2)^+$ $ClO_4^-$ (Pic = picoline)§¶ whereas no substitution occurred when the starting material was the metalloporphyrin ZnTPP. The net yield of the reaction was 61%.

This possibility of forming β-substituted porphyrins by direct electrochemical oxidation of the free base $H_2TPP$ in the presence of the appropriate nucleophiles presents major advantages. It eliminates the metallation step of the free base (necessary when the chemical route is taken), it generates the β-substituted porphyrin with a better yield than that observed when the starting material is the metalloporphyrin, and it allows some β-substitution reactions which do not take place with the metalloporphyrin, as documented above with 2-picoline, and the yield of the reaction is good (61%).

*Received, 8th December 1988; Com. 8/04854A*

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† $\lambda_{max}$ ($CH_2Cl_2$) ($10^{-4}$ ε) 658 (0.93), 600 (0.45), 564 (0.39), 526 (1.52), 426 (24.9) nm.

‡ $^1H$ N.m.r. $(CD_3)_2C=O$, δ9.53 (d, 2 H, *J* 5 Hz, pyridinium H) 9.39 (s, 1 H, β-H adjacent to pyridinium$^+$), 9.07 (s, 2 H, β-H), 8.98 (d, 1 H, *J* 5 Hz, pyridinium H), 8.83—8.77 (m, 4 H, β-H), 8.33—8.09 (m, 10 H, 8 *o*-H and pyridinium H), 7.90—7.83 (m, 9 H, *m*- and *p*-H of phenyl), 7.58—7.49 (m, 3 H, *m*- and *p*-H of phenyl nearest pyridinium).

§ $\lambda_{max}$ ($CH_2Cl_2$) ($10^{-4}$ ε) 656 (0.65), 600 (0.35), 564 (0.33), 527 (1.21), 426 (19.8) nm.

¶ $^1H$ N.m.r. $(CD_3)_2C=O$, δ 9.49 (d, 1 H, *J* 5 Hz, picolinium H), 9.32 (s, 1 H, β-H adjacent to picolinium), 9.08 (s, 2 H, β-H), 8.96 (d, 1 H, *J* 5 Hz, picolinium H), 8.83—8.77 (m, 2 H, β-H), 8.70—8.63 (m, 2 H, β-H), 8.35—8.00 (m, 10 H, 8 *o*-H and picolinium H), 7.90—7.85 (m, 9 H, *m*- and *p*-H of phenyl), 7.59—7.48 (m, 3 H, *m*- and *p*-H of phenyl nearest picolinium) 2.76 (s, 3 H, methyl H).