

NOVEL MESO-SUBSTITUTION REACTIONS OF ZINC(II) OCTAETHYLPORPHYRIN

Brian Evans and Kevin M. Smith*

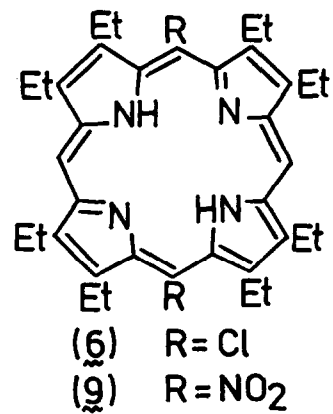
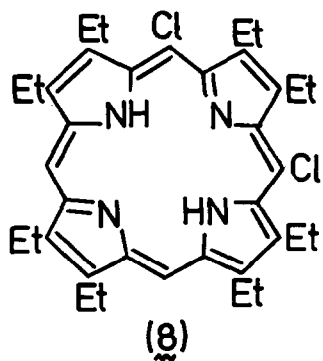
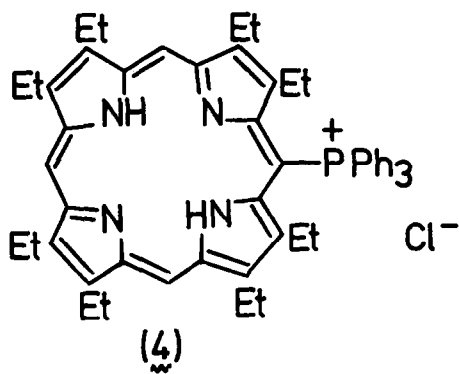
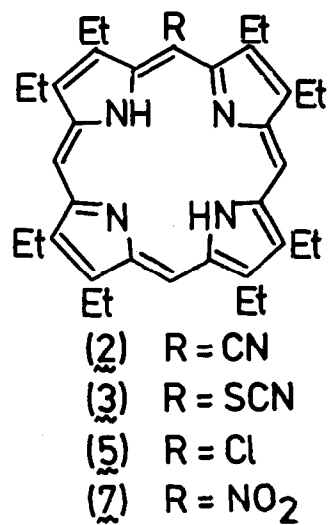
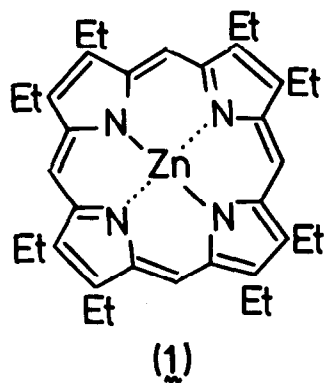
The Robert Robinson Laboratories, University of Liverpool,
P.O. Box 147, Liverpool L69 3BX, England.

(Received in UK 15 June 1977; accepted for publication 11 July 1977)

We have shown that solutions of π -cation radicals from some metalloporphyrins react rapidly with nitrite¹ or with pyridines² to afford good yields of the corresponding meso-substituted porphyrins. A similar reaction of magnesium(II) porphyrins with imidazole has been employed³ to fix porphyrins covalently into a polymeric matrix, and Shine *et al.* have reported⁴ that solutions of the π -cation radical perchlorate from zinc(II) meso-tetraphenylporphyrin react with pyridine to give the β -pyridinium substituted porphyrin. In this Letter we report preparatively convenient reactions involving solutions of zinc(II) octaethylporphyrin π -cation radical and common nucleophiles such as cyanide, thiocyanate, triphenylphosphine, and chloride, in which we underscore the usefulness of this route to meso-substituted porphyrins employing nucleophilic substitution.

Though several methods for formation of carbon-carbon bonds at meso positions of porphyrins are known,⁵ only one (the Vilsmeier formylation of copper or nickel complexes^{6,7}) has achieved a wide measure of application; other methods^{8,9,10} are either limited in generality, or else give prohibitively low yields. We have found that treatment of zinc(II) octaethylporphyrin (1) with 2 equiv of tris(p-bromophenyl)ammoniumyl hexachloroantimonate¹¹, (p-Br-C₆H₄)₃N⁺ SbCl₆⁻, (TBAH), or N-chlorobenzotriazole¹², (CBT), affords the π -cation radical which, after dropwise addition of a solution of sodium cyanide in methanol, and an acidic work-up, afforded good yields (68% using TBAH; 56% using CBT) of meso-cyano-octaethylporphyrin (2).¹³

Likewise, treatment of the π -cation radical (in THF/CH₂Cl₂) with thiocyanate or triphenylphosphine¹⁴ gave the corresponding meso-substituted



products [(3) and (4) respectively] after an appropriate work-up. These products were fully characterised, and the thiocyanate product (3) was identical with material prepared using Clezy's method.¹⁵

Preparation of mono and dichlorinated porphyrins is often a difficult process.¹⁶ However, treatment of zinc(II) octaethylporphyrin (in THF) with TBAH or CBT in CH_2Cl_2 , followed by dropwise addition of $\text{Et}_4\text{N}^+ \text{Cl}^-$ in MeOH gave a 31% yield of monochloro-octaethylporphyrin (5) after an acid work-up. If the $\text{Et}_4\text{N}^+ \text{Cl}^-$ was omitted¹⁷ then a 21% yield of the α,δ -dichloro porphyrin (6) was obtained merely by stirring (1) and TBAH together during 2 hours. Thus, the origin of the inserted chlorine is uncertain.

Since methanol is present in most of the nucleophilic reactions described above we can eliminate the possibility that metalloporphyrin π -dication species are intermediates because of the fact that no methoxy-substituted porphyrins were isolated.¹⁸ Metalloporphyrin π -cation radicals do react with NO_2 to give nitroporphyrins¹⁹ (e.g. 7), but our own virtually instantaneous reaction of nitrite¹ with solutions of metalloporphyrin π -cation radicals is totally unaffected by urea, which we have shown to be a moderately effective trap for NO_2 in its reaction with zinc(II) porphyrin π -cation radicals. Since the nitrite reaction does not produce any methoxyporphyrin when carried out in methanol, we conclude as previously,¹ that the presence of the π -cation radical in solution is essential under our conditions for reaction with nitrite.²⁰

We thank the S.R.C. for a studentship (to B.E.).

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- 13 meso-Cyanoporphyrins are usually prepared by Vilsmeier formylation of copper or nickel porphyrins, followed by treatment with hydroxylamine and dehydration of the resulting oxime.⁷
- 14 Triphenylphosphine and thiocyanate react⁴ with solutions of the π -cation radical perchlorate from zinc(II) meso-tetraphenylporphyrin, but full details of the products have not yet been published.
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- 17 Omission of the MeOH may be more important than omission of the chloride. We have observed that the type of solvent can have a critical effect upon the nature of the products. For example, treatment of zinc(II) octaethylporphyrin (1) with thallium(III) nitrate in THF/MeOH (dry) affords the meso-mononitroporphyrin (2) (B. Evans, K.M. Smith, and J.A.S. Cavaleiro, Tetrahedron Letters, 4863 (1976)). If damp solvents (MeOH, MeCN) are used then a good yield of a mixture of $\alpha\beta$ (3) and $\alpha\gamma$ (4) dinitroporphyrins is obtained (B. Evans, Ph.D. Thesis, Liverpool, 1977).
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