

meso-TETRAPHENYLPORPHYRIN PURIFICATION

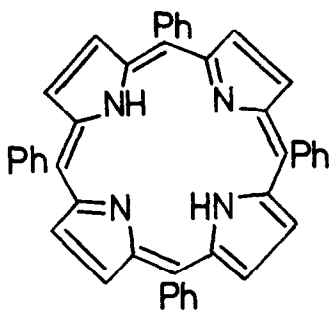
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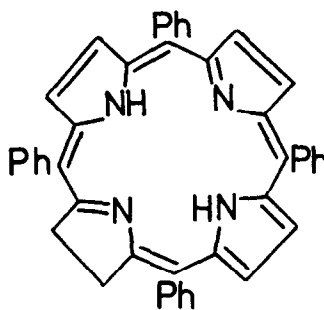
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meso-Tetraphenylporphyrin (TPP; 1) is by far the most commonly used porphyrin for investigation of the physical properties of the macrocycle and its diverse metallic complexes. There can be little doubt that the popularity of TPP as a substrate stems from the ease of its preparation from pyrrole and benzaldehyde by means of the Rothmund reaction.¹ The optimum conditions for this reaction have been developed by Adler and his co-workers² and involve the heating of an equimolar mixture of the two reagents in propionic acid. However, this and all other modifications of the Rothmund reaction furnish TPP which is contaminated (2 - 10%) with meso-tetraphenylchlorin (TPC; 2); the



(1)



(2)

latter is extremely difficult and tedious to remove.³ Recommended purification procedures involve either repeated filtration through a bed of fuller's earth, (which results in loss of about 80% of the product),² or else sublimation (for which a yield or recovery was not quoted).² Alternatively, the crude TPP/TPC mixture can be heated under reflux during several hours in dimethylsulphoxide (yield not quoted),⁴ or

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chromatographed on Florisil.⁵

We now report a rapid and convenient method for purification of the crude TPP/TPC mixture, involving treatment with 2,3-dichloro-5,6-dicyanobenzoquinone⁶ (DDQ), followed by chromatography on alumina. Thus, crude TPP/TPC mixture⁷ (1.0 g) was dissolved in refluxing dichloromethane (250 ml) and then treated with a solution of DDQ (250 mg) in benzene (15 ml). After refluxing for a further 30 min, the solution was evaporated to dryness, and the residue was chromatographed on neutral alumina (ca. 200 g; Merck, Brockmann Grade III) in hot chloroform. The TPP eluates were evaporated to a bulk of ca. 100 ml and then an equal volume of methanol was added; after further evaporation, the pure TPP (940 mg; 94%) was collected by filtration. (Found: C, 86.06; H, 5.14; N, 9.02. Calc. for $C_{44}H_{30}N_4$: C, 85.97; H, 4.92; N, 9.11%). The mass spectrum showed no evidence of TPC and the visible absorption spectrum [in benzene, λ_{max} 418.5 nm (ϵ 468,000), 481 (3400), 515(19,000), 548(7900), 592.5(5300), and 648.5(3400)] showed no evidence of TPC on the basis of the established calculation.⁸

REFERENCES

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3. This is emphasised by the fact that commercially available "chlorin-free" TPP (from Strem Chemicals Inc., Catalogue 6) is 72 times more expensive than the crude material.
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5. W. Bhatti, M. Bhatti, P. Imbler, A. Lee, and B. Lorenzen, *J. Pharm. Sci.*, 1972, 61, 307. This paper reports that the product TPP is of high purity, on the basis of elemental analyses; the figures reported are, however, erroneous.
6. For earlier reports of oxidation of chlorins to porphyrins with high-potential quinones, see U. Eisner and R.P. Linstead, *J. Chem. Soc.*, 1955, 3749.
7. This material contained ca. 5% TPC⁸ and gave an elemental analysis (Found: C, 85.09; H, 4.92; N, 9.21%) similar to that of the crude material described by Adler.²
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