

## A Simplified Synthesis for *meso*-Tetraphenylporphin<sup>1</sup>

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As a result of our mechanistic studies on porphyrin synthesis,<sup>2</sup> we have developed a modified synthesis which represents an improvement over previous literature methods<sup>3-11</sup> for *meso*-tetraphenylporphin (TPP). The yield and rate of the condensation of pyrrole and benzaldehyde to TPP have been found to depend on the acidity, the solvent, the temperature, the availability of atmospheric oxygen, and the initial concentration of the reagents.<sup>2</sup> Hence, while the following procedure does not represent the conditions for the highest yield, it does represent the most convenient method for rapidly and reproducibly obtaining a  $20 \pm 3\%$  yield of crystalline TPP of relatively high purity. In addition, the TPP is in such a form as to facilitate further purification.

This same procedure may also be adapted to the ready preparation of several other *meso*-substituted porphyrins (generally the aromatic derivatives); *e.g.*, substitution of *p*-chlorobenzaldehyde gives a 20% yield of the *meso*-tetra-*p*-chlorophenylporphin. Not all condensations are successful. Although 70 different aldehydes have all given porphyrins under these conditions, the increased solubility due to the formation of the porphyrin acid salts for many of the other *meso* derivatives prevents the use of this method as a convenient procedure for the preparation of these types of porphyrins. Isolation of product in these cases is not as simple as above, but still may be achieved. As a general rule, the alkyl derivatives and those aromatic derivatives which bear ionizable functional groups have a greater tendency to form the porphyrin acid salts.

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## Experimental Section

Freshly distilled pyrrole (56 ml, 0.8 mole) and 80 ml (0.8 mole) of reagent grade benzaldehyde are added to 3 l. of refluxing reagent grade propionic acid. (Note: crystalline material is not directly obtained if acetic acid is used.) After refluxing for 30 min, the solution is cooled to room temperature and filtered, and the filter cake is washed thoroughly with methanol. After a hot water wash, the resulting purple crystals are air dried, and finally dried *in vacuo* to remove adsorbed acid<sup>12</sup> to yield 25 g (20% yield) of TPP. Spectrophotometric analysis shows that only 1% of the TPP yield remains in the filtrate and also that the filtered material is about 3% tetraphenylchlorin (TPC) by weight. (Note that longer reaction times in propionic acid do not appreciably improve the yield, but actually decrease the purity of the products.)

*Anal.* Calcd for C<sub>44</sub>H<sub>30</sub>N<sub>4</sub>: C, 85.90; H, 4.92; N, 9.12. Found: C, 85.16; H, 4.99; N, 9.60.

A study<sup>13</sup> of previous chromatographic purification techniques<sup>4,7,10,11</sup> shows that the product obtained by the above procedure is easily purified by a simple batchwise technique. TPP (1.0 g) and 100 g of fuller's earth (Florex) are stirred with enough 1,1,1-trichloroethane to make about 1 l. of mixture. This is immediately passed through a 0.25-in. bed of solvent-washed fuller's earth on a 6-in. sintered-glass vacuum funnel. The eluent is passed through a fresh bed of Florex three or four times. This eliminates the TPC contamination as indicated by the optical spectrum. Due to adsorption, there is a loss of approximately 80% of the starting material in this purification procedure.

Another reliable purification method for the crude TPP was found to be entrainment sublimation using purified nitrogen gas as the carrier. A horizontal furnace with one or two hot zones was used with the temperature of the hotter zone adjusted to 325°, while the cooler zone was maintained at 250°. During the sublimation process, nitrogen gas was allowed to flow at a rate of 1 ft<sup>3</sup>/hr. against atmospheric pressure. In this method, large, single-crystal needles of TPP were obtained. Combustion analysis of the sublimed product gave good agreement with the theoretical values, and the electronic adsorption spectrum of a solution of this product in benzene was in excellent agreement with that reported by other workers.<sup>10,11,14</sup>

*Anal.* Calcd for C<sub>44</sub>H<sub>30</sub>N<sub>4</sub>: C, 85.90; H, 4.92; N, 9.12. Found: C, 86.10; H, 4.91; N, 9.12.

Alternatively, the TPP can also be purified by vacuum sublimation in a horizontal furnace using vacuum ion pumping and a thermal gradient. The material is sublimed through a 12-in. diffusion path (325–350° at position of initial material to 150–200° at the collection region) at a pressure which must be maintained at less than  $1 \times 10^{-7}$  torr. This method yields octahedral or rhombohedral crystals, rather than needles.

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## Liquid Crystals. I. Fluorinated Anils

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The presence of mesomorphism in 2,2',6,6'-tetrafluoro-4,4'-di(*p*-*n*-alkoxybenzylidenamino)biphenyls has been deemed to be "extremely doubtful."<sup>1</sup> This assumption was based on the fact that the corresponding tetrachloro derivatives were not mesomorphic.

We wish to report that we have prepared dianils of 2,2',3,3',5,5',6,6'-octafluorobenzidine and have found them to be liquid crystals. Specifically, dianisylidene-

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