

- [4] Cf. M. S. Newman, P. G. Scheurer, *J. Am. Chem. Soc.* 78, 5004 (1956). Reaction of phthalic anhydride with phenyllithium: W. E. Parham, R. M. Piccirilli, *J. Org. Chem.* 41, 1268 (1976).
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- [7] According to the  $^1\text{H-NMR}$  spectrum, formation of up to a maximum of 5% of the isomer—by addition of (6b) to the sterically more hindered carbonyl group of (5)—cannot be ruled out.
- [8] Correct analytical values were obtained for the new compounds.

## The Synthesis of Unsymmetrical Tetraarylporphyrins on Solid Phases<sup>[\*\*]</sup>

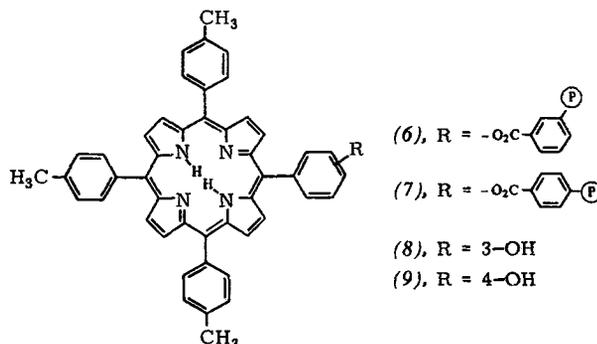
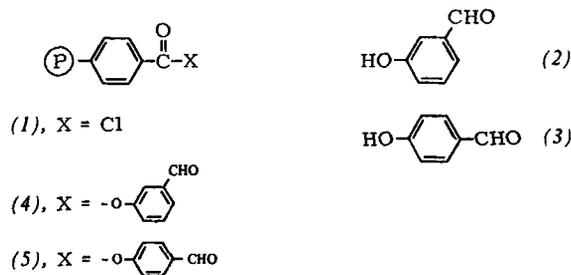
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There has been tremendous interest recently directed toward the synthesis of model porphyrin systems related to the oxygen-binding proteins<sup>[1]</sup>. In addition, the synthesis of model dimers and higher aggregates of porphyrins are of particular interest in studies of the photo-oxidation of water to oxygen during photosynthesis<sup>[2]</sup>. The *symmetrical* tetraarylporphyrins had long been widely used as models in both of these systems due to their ease of preparation<sup>[3]</sup>, but some more recent sophisticated work required the synthesis of *unsymmetrical* tetraarylporphyrins, which were synthesized in yields ranging from 0.5—5%<sup>[4]</sup>. Furthermore, the desired product could only be isolated from the many other compounds produced by extensive chromatographic separations.

Although preformed hemes and porphyrin models have been attached to insoluble supports<sup>[5]</sup> and unusual synthetic polymers incorporating the heme function have been described<sup>[6]</sup>, the actual synthesis of a porphyrin on polymer supports from its simple precursors has not been described. Insoluble polymer supports provide a suitable means of "fishing out" a minor component from a complex reaction mixture<sup>[7a]</sup> and we have utilized these supports in this way to prepare monoblocked derivatives of a wide variety of symmetrical difunctional compounds<sup>[7b]</sup>.

We now report that insoluble polymer supports can be used to prepare unsymmetrical tetraarylporphyrins and aid in their isolation. Thus a 2% crosslinked divinylbenzene-styrene copolymer (1) containing 1.7 mmol of benzoyl chloride functional groups per g polymer<sup>[8]</sup>, was treated with 3-hydroxybenzaldehyde (2) or 4-hydroxybenzaldehyde (3) to give the polymer-bound benzoylbenzaldehydes (4) and (5), respectively. Cleavage of (4) and (5) with 0.5 M sodium hydroxide/dioxane (1:1) at room temperature for 20 h liberated 0.73 mmol of (2) and 1.06 mmol of (3)/g of (4) and (5), respectively. Treatment of (4) and (5) with *p*-tolualdehyde and pyrrole in hot propionic acid for 1 h yielded upon filtration black polymers which were readily washed free of tetratolylporphyrin by extraction in a Soxhlet extractor with chloroform for 2 h to yield the polymer-bound unsymmetrical tetraarylporphyrins (6) and (7), respectively. Cleavage of (6) and (7) with potassium carbonate in methanol for 24 h yielded black powders essentially free of tetratolylporphyrin present in large amounts in a comparable solution synthesis<sup>[4a]</sup>.

The black powders can be readily purified by a quick filtration through a silica column using chloroform as eluant followed by preparative thin-layer chromatography using benzene/ether/chloroform (7:2:1) as eluant to give 5-(3-hydroxyphenyl)-10,15,20-tritolylporphyrin (8) in 2% yield and 5-(4-hydroxyphenyl)-10,15,20-tritolylporphyrin (9) in 4.5% yield,



both as purple crystals. The NMR spectra of (8) and (9) were identical with the published spectra<sup>[4a]</sup> and the mass spectra exhibited peaks of 672 ( $M^+$ ) and 336 ( $M^{2+}$ ) typical of tetraarylporphyrins<sup>[9]</sup>.

### CAS Registry numbers:

(2), 100-83-4; (3), 123-08-0; (8), 57412-06-3; (9), 57412-08-5; *p*-tolualdehyde, 104-87-0; pyrrole, 109-97-7

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## Addition of Water to *o*-Phenylethynyl-Substituted Triphenylphosphanes

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Surprisingly, on recrystallization of the *o*-phenylethynyl-substituted triphenylphosphane (1a)<sup>[1a]</sup> from commercial ethanol, the triphenylphosphane oxide (2a) containing a stereo-

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