The Synthesis of Unsymmetrical Tetraarylporphyrins on Solid Phases

By Clifford C. Leznoff and Polina I. Svirskaya

There has been tremendous interest recently directed toward the synthesis of model porphyrin systems related to the oxygen-binding proteins\(^\text{[1]}\). 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\(^\text{[2]}\). The *symmetrical* tetraarylporphyrins had long been widely used as models in both of these systems due to their ease of preparation\(^\text{[3]}\), but some more recent sophisticated work required the synthesis of *unsymmetrical* tetraarylporphyrins, which were synthesized in yields ranging from 0.5—5%\(^\text{[4]}\). 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\(^\text{[5]}\) and unusual synthetic polymers incorporating the heme function have been described\(^\text{[6]}\), 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\(^\text{[7]}\) and we have utilized these supports in this way to prepare monoblocked derivatives of a wide variety of symmetrical difunctional compounds\(^\text{[8]}\).

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 benzyl chloride functional groups per g polymer\(^\text{[9]}\) was treated with 3-hydroxybenzaldehyde (2) or 4-hydroxybenzaldehyde (3) to give the polymer-bound benzylbenzaldehydes (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) 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 powders which were readily washed free of tetraloloyporphyrin 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 tetralolyoporphyrin present in large amounts in a comparable solution synthesis\(^\text{[10]}\).

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,

![Diagram](https://via.placeholder.com/150)

both as purple crystals. The NMR spectra of (8) and (9) were identical with the published spectra\(^\text{[11]}\) and the mass spectra exhibited peaks of 672 (M\(^+\)) and 336 (M\(^2+\)) typical of tetraarylporphyrins\(^\text{[12]}\).

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

Addition of Water to o-Phenylethynyl-Substituted Triphenylphosphines

By Werner Winter\(^\text{[*]}\)

Surprisingly, on recrystallization of the o-phenylethynyl-substituted triphenylphosphine (1a)\(^\text{[13]}\) from commercial ethanol, the triphenylphosphine oxide (2a) containing a stereo-

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