

Synthesis of Axial Dialkoxy Phosphorus(v)porphyrin Derivatives—Novel Hypervalent Phosphorus Compounds

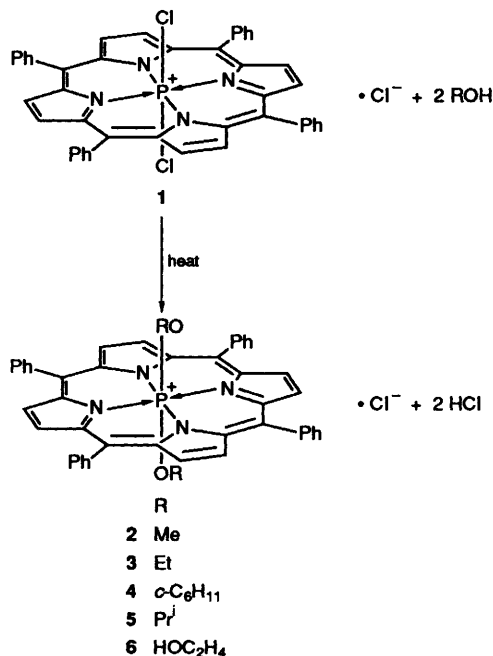
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Water-stable, axial dialkoxy hypervalent phosphorus(v)tetraphenylporphyrins have been synthesised in a novel fashion by efficient substitution of axial chloride ligands of dichlorophosphorus(v)-tetraphenylporphyrin.

Phosphorus(v)porphyrin, with a central six-co-ordinated phosphorus, is both a unique nonmetal porphyrin¹ and an unusual hypervalent compound with a large π -electron system.² The redox chemistry, photochemistry and the structure of phosphorus porphyrins have been reported,^{3–5} but the known compounds are unstable especially in redox reactions. We report here an efficient method of protection for the central phosphorus atom by formation of a stable P–O–R bond at the axial position. The synthetic strategy adopted was based not on the dehydration of dihydroxyphosphorus(v)porphyrin, but on substitution of the halogenated phosphorus atom of dichlorophosphorus(v)porphyrin with an alcohol.

The dichlorophosphorus(v)tetraphenylporphyrin chloride **1**^{5b} was dissolved in a series of dried alcohols (MeOH, EtOH,



Scheme 1

o-C₆H₁₁OH, PrⁱOH or HOCH₂CH₂OH) and refluxed for several hours. The excess of alcohol was evaporated at the end of the reaction and the product was purified using a column of neutral alumina (chloroform eluent); after impurities a main product was eluted with 5% methanol–chloroform and this was dried *in vacuo*. The derivatives **2–6** have normal porphyrin absorption spectra. Five typical derivatives **2–6** are reported here and many others were obtained by the same procedure.

Fig. 1 shows the ¹H NMR spectrum of product **3**. Peripheral proton signals of **3** [δ_{H} 9.07 (pyrrole β , d, 8 H), 7.7–8.1 (Ph, m,

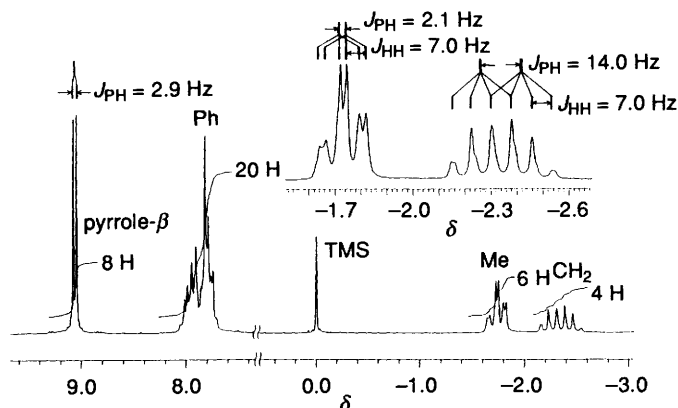


Fig. 1 ¹H NMR (90 MHz, CDCl₃) spectrum of diethoxy derivative **3**

20 H)] are similar to those of known phosphorus(v)-tetraphenylporphyrin (PTPP) derivatives.^{5b} The signals δ_{H} -1.73 (CH₃, dt, 6 H) and -2.34 (CH₂, dq, 4 H) are assigned to ethoxy groups. The $J_{\text{P-H}}$ couplings and the strong ring-current shifts of the ethoxy protons imply that the ethoxy groups are attached to the central phosphorus atom.⁶ This assignment is supported by the $J_{\text{P-C}}$ values of the ethoxy groups [δ_{C} 56.9 (CH₃, $J_{\text{P-C}}$ 15.3), 13.0 (CH₂, $J_{\text{P-C}}$ 16.6)]. The alkoxy substitutions are also confirmed by the P–O–C stretch in the IR spectra.⁷ The integrated intensities of the ¹H NMR spectra indicate that there are two equivalent ethoxy groups per phosphorus porphyrin moiety. Compound **3** has δ_{P} -180.1 , which is typical for a six-co-ordinate phosphorus compound⁸ and suggests that the two ethoxy groups are attached to the central phosphorus atom at the fifth and sixth co-ordination positions. It is concluded that compound **3** is diethoxyphosphorus(v)tetraphenylporphyrin chloride which is disubstituted as shown in Scheme 1. The MS (FAB, M⁺, 733) coincided with the expected molecular weight of the diethoxy derivatives without the counter ion.

Yields of products **2–6** listed in Table 1 exceeded 90% (based on the porphyrin units); diphenoxy and diacyloxy derivatives were also obtained. The substitution by primary (**2**, **3**, **6**) and secondary (**4**, **5**) alcohols occurred efficiently, but substitution by tertiary alcohols did not occur because of steric hindrance. An interesting feature of the reactions is that mono-substituted phosphorus porphyrins were not obtained as stable products but the di-substituted phosphorus porphyrins were selectively obtained even when the starting compound **1** remained.

Two features of the di-substituted products were observed: they resisted demetallation even in acidic solution in contrast to the unstable dihydroxy complexes indicating steric protection; exchange of axial groups was resisted even upon use of alkoxide, although nucleophilic addition on the porphyrin ring

Table 1 NMR data of axial dialkoxyporphorus(v)tetraphenylporphyrins^a

| | R | δ_{H} | | | δ_{P} (central atom) |
|---|--|---------------------|-------------------|--|------------------------------------|
| | | pyrrole- β | phenyl | axial substituent | |
| 2 | Me | 9.08 (d, 8 H) | 7.7–8.0 (m, 20 H) | –1.85 (d, J_{PH} 26, 6 H) | –178.1 |
| 3 | Et | 9.07 (d, 8 H) | 7.7–8.1 (m, 20 H) | –1.73 (dt, J_{PH} 2.1, 6 H) –2.34 (dq, J_{PH} 14, 4 H) | –180.1 |
| 4 | <i>c</i> -C ₆ H ₁₁ | 9.14 (d, 8 H) | 7.8–8.1 (m, 20 H) | 0.21 (m, 4 H), –0.39 (m, 8 H), –2.21 (m, 8 H), –3.07 (d, J_{PH} 26, 2 H) | –176.2 |
| 5 | Me ₂ CH | 9.14 (d, 8 H) | 7.8–8.1 (m, 20 H) | –2.19 (d, 12 H), –2.72 (m, J_{PH} 32, 2 H) | –176.7 |
| 6 | HOC ₂ H ₄ | 9.01 (d, 8 H) | 7.7–8.0 (m, 20 H) | 0.75 (br m, 4 H), –2.21 (dt, J_{PH} 11.9, 4 H) | –180.9 |

^a ¹H NMR and ³¹P NMR are relative to Me₄Si (internal) and H₃PO₄ (85%) (external), respectively.

occurred.⁹ The dihydroxy derivative **6** is water-soluble and very stable even under acidic and basic aqueous conditions. The stable axial bond is useful in photoredox catalysis and in the construction of hybridized porphyrins with axial functional groups.

Experimental

Selected Spectral Data.—NMR data are shown in Table 1. The derivatives **2–6** have normal porphyrin absorption spectra: $\lambda_{\text{max}}(\text{CHCl}_3)/\text{nm}$ **2**, 430, 560, 602; **3**, 431, 560, 602; **4**, 427, 552, 594; **5**, 426, 552, 593; **6**, 431, 560, 600. IR absorptions originating from P–O–C stretch were distinguished: primary alkoxy derivatives (ν/cm^{-1} **2**, 1057; **3**, 1054; **6**, 1054); and secondary alkoxy derivatives (**4**, 1092; **5**, 1092). In each case the P–O–C stretching bands were in the region of known hypervalent phosphorus compounds.⁷

Diphenoxy and Diacyloxy Derivatives.—(PhO)₂PTPP: δ_{H} 2.21 (*ortho*, d, 4 H, axial) and δ 6.01 (*meta* and *para*, m, 6 H, axial); δ_{P} –194.7 (central P); the absorption spectrum was also normal, $\lambda_{\text{max}}(\text{CHCl}_3)/\text{nm}$ 436, 562 and 604.

(MeCO₂)₂PTPP: δ_{H} –0.61 (d, 6 H, axial); δ_{P} –210.3 (central P); the absorption spectrum was also normal, $\lambda_{\text{max}}(\text{CHCl}_3)/\text{nm}$ 431, 560 and 603.

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