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Selective Synthesis of Unsymmetrical Dialkoxyphosphorus(V)tetraphenylporphine Derivatives by Stepwise Substitution of Axial Position

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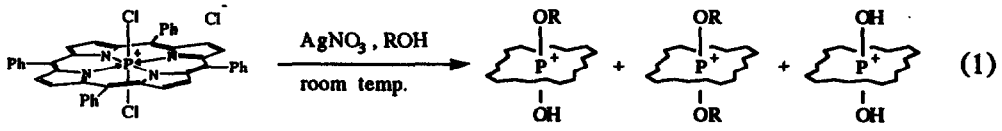
Key Words: Phosphorus(V)porphyrin; Stepwise Alkoxylation; O-Alkylation; Unsymmetrical Substitution; Hybridized Molecular System.

Abstract: *Unsymmetrical dialkoxyP(V)TPPs are synthesized by treatment of dichloroP(V)TPP with silver nitrate in appropriate alcohols and successive treatment with alkylating reagents under mild conditions at room temperature.*

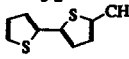
Phosphorus(V)porphyrins(P(V)porphyrins) with the unique properties as a non-metal porphyrin[1] are able to form stable axial bond and to fix various functional molecules on both sides of the porphyrin π-electron system.[2,3] Thus, the P(V)porphyrin is a very interesting compound for the construction of molecular hybridized systems. However, the axial substitution method of P(V)porphyrin reported so far is inconvenient to obtain unsymmetrical derivatives.[1-3] Especially, it should be noted that the monoalkoxylated derivative was not observed even as an intermediate in the thermal reactions of dichlorophosphorus(V)-tetraphenylporphine chloride (1, $[Cl_2P(V)TPP]^+Cl^-$) with appropriate alcohols.[2] To extend the application for construction of the molecular hybridized systems with the P(V)porphyrin, it is indispensable to open up the new methodology for the unsymmetrical substitution of the axial group. In this paper, we report new synthetic methods for axial P-O-alkyl bond formation from both dichloroP(V)TPP 1 and dihydroxyP(V)TPP 4 as starting materials. By the combination of the two methods, novel unsymmetrical dialkoxyP(V)TPP derivatives can be obtained.

The important strategy for the synthesis of unsymmetrically substituted P(V)TPP derivative is unsymmetrical activation of the P-Cl bond by a treatment of 1 with silver nitrate in an alcoholic solution. The nitrate anion could be a nucleophile lying on one side where silver cation activates the P-Cl bond, and the solvent alcohol could be a nucleophile lying on the other side. As a result, it is expected that the unsymmetrically substituted P(V)TPP derivatives is preferentially formed by this treatment. The reaction of 1 with excess amount of silver nitrate in methanol at room temperature afforded three products as shown in



1 2 3 4

Table 1. Alkoxylation with Silver Nitrate at Room Temperature[a)]

	ROH	yield (%)[b)] 2	3	4
(a)	CH_3OH	73	19	8
(b)	C_2H_5OH	79	12	9
(c)	$HOCH_2CH_2CH_2OH$	74	16	10
(d)	CF_3CH_2OH[c)]	49	19	32
(e)	$(CF_3)_2CHOH$[c)]	0	0	100
(f)	 [c)]	47	14	39

[a)] compound 1 (13 - 18 mM) was treated with silver nitrate (380 - 800 mM) in the corresponding alcohol.

[b)] yields were determined by ^1H NMR. [c)] reaction was carried out in acetonitrile solution.

(1). The ^1H NMR signals of the reaction mixture showed three doublets at δ 9.01 (J_{P-H} = 2.9 Hz), 8.90 (2.9 Hz), and 8.81 (2.6 Hz) ppm as β-H of porphyrin ring and two doublets at δ -1.91 (25.7 Hz) and -1.97 (26.2 Hz) as CH_3 of axial groups. The ^{31}P NMR signals also showed the formation of the three products (δ -177.8, -184.2, and -193.1 ppm). Two minor products were assigned to be already known dimethoxy derivative **3a** and dihydroxy one **4** by the data of ^1H and ^{31}P NMR.[4] The β-H and phosphorus signals of the major product appeared halfway between **3a** and **4**. Moreover, it was clarified by the integrated intensities of ^1H NMR that there existed only one methoxyl group per one porphyrin. Consequently, we concluded that this major product was hydroxy(methoxy)P(V)TPP **2a** as depicted in (1). The **2a** is difficult to be isolated, and further analytical data of **2a** was not obtained. Analogous treatments with other alcohols afforded the corresponding monoalkoxylated derivatives **2** in high yields (Table 1). In the case of 2,2,2-

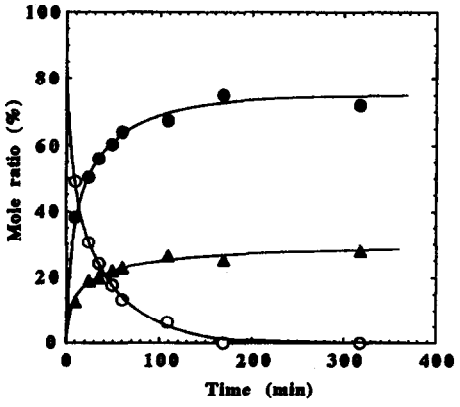
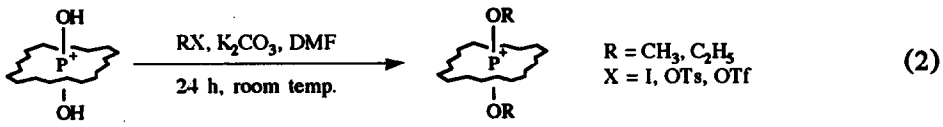


Fig. 1. Time-course for Alkoxylation of **1** (13 mM, ○) with Silver Nitrate (38 mM) in CD_3OD; Monoalkoxylated (**2**, ●) and Dialkoxylated (**3**, ▲) derivatives were produced and detected by ^1H NMR.

trifluoroethanol, the yield of the monoalkoxylated derivative decreased, whereas that of the dihydroxy derivative increased. Hexafluoropropane-2-ol was not substituted and only dihydroxy derivative was obtained. These observations indicate that monoalkoxylated derivatives **2** are unstable in the acidic conditions and decompose into the dihydroxyP(V)TPP **4**. The reaction mechanism is inferred from the time-course of methoxylation in CD_3OD by the use of ^1H NMR. As shown in Fig. 1, both **2** and **3** simultaneously began to produce and the concentration ratio was almost constant during the reaction. These results suggest that both **2** and **3** were independently produced from **1**. In the similar time-course experiment in CD_3CN, only dihydroxyP(V)TPP **4** was detected. This observation indicates that O atom was originated from nitrate anion, and it is considered that NO_3 group was considerably unstable and immediately decomposed under the reaction condition to give hydroxyl group by the successive protonation. In fact, dihydroxyP(V)TPP **4** was not detected in the condition of Fig. 1, because the concentration ratio of silver nitrate to the starting material was 3-fold and less than that of the preparative reaction which was 100-fold.

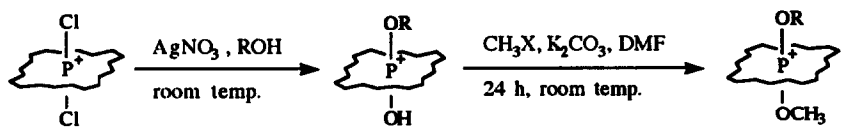
On the other hand, the treatments of dihydroxyP(V)TPP **4** with alkylating reagents under room temperature afforded O-alkylated derivatives in high yield as shown in (2). O-Methylation by methyl iodide or tosylate for 1day afforded **3a**, quantitatively. O-Methylation by methyl triflate in chloroform also afforded **3a** in 30 % yield for 30 min. O-Ethylation also proceeded in high yield as the same way (76 % with C_2H_5I). These O-alkylations under mild condition is useful for the application to the substitution with thermodynamically unstable alkoxyl groups.



(2)

From the standpoint of construction of molecular hybridized system with P(V)porphyrin as a main unit, unsymmetrical fixation of the functional molecules via stable bonds in the axial direction of the porphyrin ring is important. We developed the stepwise derivation with different alkoxyl groups by the combination of the monoalkoxylation and the O-alkylation as shown in (3).[5] By the use of the present method, we synthesized unsymmetrically dialkoxylated derivatives **5**,[6] where **5f** possesses bithienyl group as a precursor for polymerization on a single side of the porphyrin ring.[3] It should be noted that the ^{31}P NMR signal of **5d** was observed at δ -182.6 ppm halfway between the corresponding symmetrical derivatives **3a** and **3d** (δ -187.9 ppm). This implies that the electronic property of an unsymmetrically dialkoxylated derivative lies at the middle of those of the corresponding symmetrically dialkoxylated ones.[7]

In summary, we have opened up the new methodologies to connect the alkoxyl groups as axial substituents of P(V)TPP. Such a new synthetic method will facilitate and extend further investigation for construction of molecular hybridized systems with porphyrins.



(3)

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4. Derivatives **3a** and **4** showed the following: for **3a**, ^{1}H NMR ($CDCl_3$, TMS): δ 9.08 (d, 8H, $J_{P\text{-}H}$ = 2.9 Hz, β-H), 8.0 - 7.7 (m, 20H, phenyl-H), -1.85 (d, 6H, $J_{P\text{-}H}$ = 26 Hz); ^{31}P NMR ($CDCl_3$, 85% H_3PO_4): δ -178.1; for **4**, ^{1}H NMR ($CDCl_3$, TMS): δ 8.89 (d, 8H, $J_{P\text{-}H}$ = 2.9 Hz, β-H), 7.8 - 7.6 (m, 12H, m, p-phenyl H), 8.1 - 7.9 (m, 8H,o-phenyl H); ^{31}P NMR ($CDCl_3$, 85% H_3PO_4): δ -193.0. Both ^{1}H and ^{31}P NMR chemical shifts of **4** and **2** suffered from small change in basic or neutral condition because of the acid-base equilibrium of axial hydroxyl groups.
5. Among three products, dialkoxy derivative was easily separable from the other two by column chromatography on alumina with chloroform as an eluent. The mixture of **2** and **4** was used for the next reaction without further purification.
6. Each unsymmetrically dialkoxylated derivative was obtained as the mixture with dimethoxy derivative **3a**. **5c** was purified by column chromatography on silica gel with chloroform - methanol (20:1) mixture as an eluent. **5d** and **5f**, however, were very hard to be separated from **3a**, and spectral data were obtained as the mixture. For **5c**, ^{1}H NMR ($CDCl_3$, TMS): δ 9.00 (d, 8H, $J_{P\text{-}H}$ = 2.9 Hz, β-H), 8.3 - 7.6 (m, 20H, phenyl-H), 1.55 (t, 2H, $POCCCH_2O$), -1.1 - -1.3 (m, 2H, $POCCH_2CO$), -1.98 (d, 3H, $J_{P\text{-}H}$ = 25.9 Hz), -2.17 (dt, 2H, $J_{P\text{-}H}$ = 12.7 Hz); ^{31}P NMR ($CDCl_3$, 85% H_3PO_4): δ -178.5. For **5f**, ^{1}H NMR ($CDCl_3$, TMS): δ 9.08 (d, 8H, $J_{P\text{-}H}$ = 2.9 Hz, β-H), 8.1 - 7.6 (m, 20H, phenyl-H), 7.00 (d, 1H, bithiophene $C^{5'}$-H), 6.78 (dd, 1H, bithiophene $C^{4'}$-H), 6.58 (d, 1H, bithiophene $C^{3'}$-H), 6.15 (d, 1H, bithiophene C^4-H), 4.72 (d, 1H, bithiophene C^3-H), -1.10 (d, 2H, $J_{P\text{-}H}$ = 16.5 Hz, OCH_2), -1.88 (d, 3H, $J_{P\text{-}H}$ = 25.9 Hz, OCH_3).
7. First reduction potentials and ^{31}P NMR signals of dialkoxylated P(V)TPP derivatives were correlated with the pKa value of the corresponding alcohol, by which the electron-donating properties of axial substituents were represented. We will report on such contents elsewhere.

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