

# Efficient Preparation of the $\alpha,\alpha,\alpha,\alpha$ -Atropoisomer of *meso*-Tetrakis[2-(2,3,4,6-tetraacetyl-*O*- $\beta$ -glucosyl)phenyl]porphyrin

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Received December 1, 1993

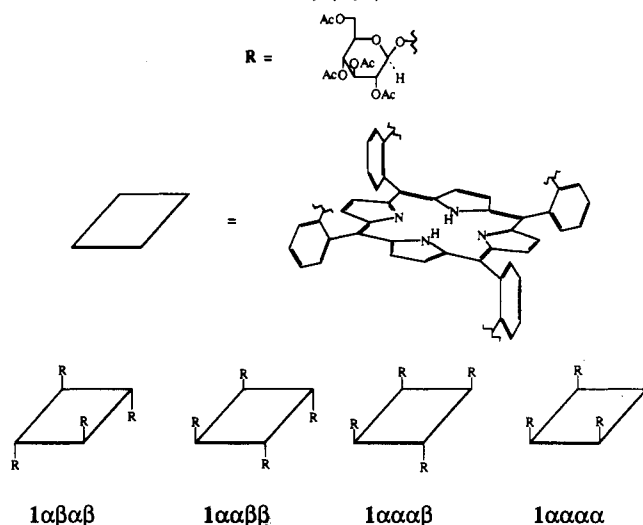
## Introduction

Collman's picket-fence porphyrin,<sup>3</sup> the first superstructured porphyrin, was prepared from the pure  $\alpha,\alpha,\alpha,\alpha$ -atropoisomer of *meso*-tetrakis(2-aminophenyl)porphyrin. Other pure atropoisomers of *meso*-tetraarylporphyrins have been employed to design various superstructured tetrapyrrolic compounds, including basket-handle,<sup>4</sup> jellyfish,<sup>5</sup> and gyroscope<sup>6</sup> porphyrins. Recently, we have described the synthesis<sup>7</sup> of *meso*-tetrakis[2-(2,3,4,6-tetraacetyl-*O*- $\beta$ -glucosyl)phenyl]porphyrin (1, Chart 1) using Lindsey's method.<sup>8</sup> However, only three atropoisomers ( $1\alpha,\beta,\alpha,\beta$ ,  $1\alpha,\alpha,\beta,\beta$ , and  $1\alpha,\alpha,\alpha,\beta$ ) were obtained. The catalytic activities of manganese and iron complexes of these compounds indicate that the chiral environment in the vicinity of the catalytic site and the proper molecular geometry are critical for the induction of an asymmetric oxidation of an alkene.<sup>9</sup> The  $\alpha,\alpha,\alpha,\alpha$ -atropoisomer's metal derivatives should be promising candidates for such catalytic activity. Herein, we report an efficient preparation of the latter from other atropoisomers that avoids thermal isomerization.

## Results and Discussion

Atropoisomerization of various *ortho*-substituted tetraphenylporphyrins has been the subject of several reports.<sup>10</sup> Nishino *et al.*<sup>11</sup> have prepared the  $\alpha,\beta,\alpha,\beta$ -

Chart 1. Isomers of *meso*-tetrakis[2-(2,3,4,6-tetraacetyl-*O*- $\beta$ -glucosyl)phenyl]porphyrin ( $1\alpha,\beta,\alpha,\beta$ ,  $1\alpha,\alpha,\beta,\beta$ ,  $1\alpha,\alpha,\alpha,\beta$ , and  $1\alpha,\alpha,\alpha,\alpha$ )



atropoisomer of *meso*-5,10,15,20-tetrakis(*o*-nitrophenyl)porphyrin in toluene at 80 °C. Recently, Rose *et al.*<sup>12</sup> reported the preparation of  $\alpha,\beta,\alpha,\beta$ -*meso*-5,10,15,20-tetrakis(*o*-aminophenyl)porphyrin by reduction of  $\alpha,\beta,\alpha,\beta$ -*meso*-5,10,15,20-tetrakis(*o*-nitrophenyl)porphyrin in 72% abundance as determined by HPLC, and in 39% yield, by a thermal isomerization in naphthalene at 130 °C. In contrast, the same treatment in acetonitrile gave a random statistical abundance of isomers as shown by Gottwald *et al.*<sup>13</sup> for *meso*-5,10,15,20-tetrakis(*o*-hydroxyphenyl)porphyrin.

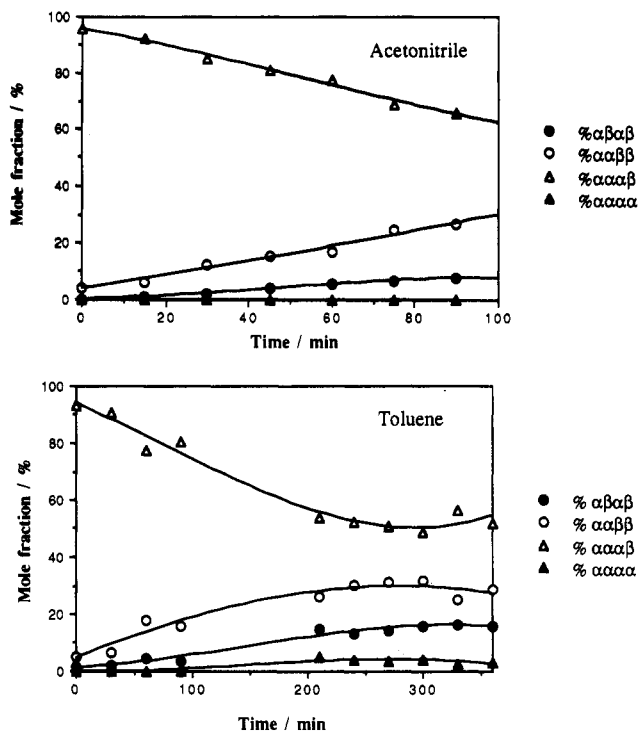
The equilibration of the atropoisomers of the mixture of glucosylated porphyrin 1 can be carried out between 50 and 100 °C. Partial destruction is observed upon heating under refluxing toluene (111 °C), even under argon. The atropoisomerization was investigated in toluene and in acetonitrile at 80 °C by using the purified  $\alpha,\alpha,\alpha,\beta$ -*meso*-tetrakis[2-(2,3,4,6-tetraacetyl-*O*- $\beta$ -glucosyl)phenyl]porphyrin.<sup>7b</sup> Figure 1 shows the mole fractions of the four isomers. Equilibration was reached after 4 h in toluene at 80 °C and the  $\alpha,\alpha,\alpha,\alpha$ -isomer was obtained in 8% yield. In contrast, isomerization of  $1\alpha,\alpha,\alpha,\beta$  in CH<sub>3</sub>CN at 80 °C is swift and the  $\alpha,\alpha,\alpha,\alpha$ -atropoisomer is not obtained ( $1\alpha,\beta,\alpha,\beta$ , 8%;  $1\alpha,\alpha,\beta,\beta$ , 26%;  $1\alpha,\alpha,\alpha,\beta$ , 66%;  $1\alpha,\alpha,\alpha,\alpha$ , 0%). The isomerization first-order rate constant of  $1\alpha,\alpha,\alpha,\beta$  is  $4 \times 10^{-5} \text{ s}^{-1}$  in toluene and  $7.2 \times 10^{-5} \text{ s}^{-1}$  in acetonitrile. These results show the crucial effect of solvent on the equilibrium of atropoisomerization.

In order to find the best enrichment conditions for the  $\alpha,\alpha,\alpha,\alpha$ -isomer, the atropoisomerization of a mixture of three atropoisomers of *meso*-tetrakis[2-(2,3,4,6-tetraacetyl-*O*- $\beta$ -glucosyl)phenyl]porphyrin was investigated by using various solvents at 80 °C with or without a small quantity of silica gel, as reported by Lindsey for the preparation of the  $\alpha,\alpha,\alpha,\alpha$ -isomer of *meso*-tetrakis(*o*-aminophenyl)porphyrin.<sup>14</sup> The results are reported in Table 1.

Because the atropoisomerization of the *ortho*-substituted tetraphenylporphyrins is an equilibrium process and

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(3) Collman, P. *J. Acc. Chem. Res.* 1977, 10, 265.  
(4) (a) Groves, J. T.; Myeres, R. S. *J. Am. Chem. Soc.* 1983, 105, 5791.  
(b) Momenteau, M.; Mispelter, J.; Loock, B.; Lhoste, J. M. *J. Chem. Soc., Perkin Trans. 1* 1985, 221. (c) Mansuy, D.; Battioni, P.; Renaud, J. P.; Guerin, P. *Chem. Commun.* 1985, 155. (d) Groves, J. T.; Viski, P. *J. Org. Chem.* 1990, 55, 3628. (e) Boitrel, B.; Lecas-Nawrocka, A.; Rose, E. *Tetrahedron Lett.* 1992, 33, 227.  
(5) (a) Uemori, Y.; Miyakawa, H.; Kyuno, E. *Inorg. Chem.* 1988, 27, 377. (b) Uemori, Y.; Kyuno, E. *Inorg. Chem.* 1989, 28, 1690.  
(6) (a) Boitrel, B.; Lecas-Nawrocka, A.; Renko, Z.; Rose, E. *Chem. Commun.* 1985, 1820. (b) Boitrel, B.; Lecas-Nawrocka, A.; Renko, Z.; Rose, E. *New J. Chem.* 1989, 13, 73.  
(7) (a) Maillard, Ph.; Guerin-Kern, J. L.; Momenteau, M.; Gaspard, S. *J. Am. Chem. Soc.* 1989, 111, 9125. (b) Maillard, Ph.; Guerin-Kern, J. L.; Huel, C.; Momenteau, M. *J. Org. Chem.* 1993, 58, 2774.  
(8) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguaretz, A. M. *J. Org. Chem.* 1987, 52, 827.  
(9) (a) Maillard, Ph.; Momenteau, M. *Tetrahedron Lett.* 1992, 33, 8081. (b) Collman, J. P.; Zhang, X.; Lee, V. J.; Uffelman, E. S.; Brauman, J. I. *Science* 1993, 261, 1404.  
(10) (a) Freitag, R. A.; Mercer-Smith, J. A.; Whitten, D. G. *J. Am. Chem. Soc.* 1981, 103, 1226. (b) Hatano, K.; Anzai, K.; Kubo, T.; Tamai, S. *Bull. Chem. Soc. Jpn.* 1981, 54, 3518. (c) Freitag, R. A.; Whitten, D. G. *J. Phys. Chem.* 1983, 87, 3918. (d) Miyamoto, T. K.; Hasegawa, T.; Takagi, S.; Sasaki, Y. *Chem. Lett.* 1983, 1181. (e) Hanato, K.; Kawasaki, K.; Munakata, S.; Iitaka, Y. *Bull. Chem. Soc. Jpn.* 1985, 60, 1985. (f) Crossley, M. J.; Field, L. D.; Forster, A. J.; Harding, M. M.; Sternhell, S. *J. Am. Chem. Soc.* 1987, 109, 341.  
(11) (a) Nishino, N.; Kobata, K.; Mihara, H.; Fujimoto, T. *Chem. Lett.* 1992, 1991. (b) Nishino, N.; Mihara, H.; Kiyota, H.; Kobata, K.; Fujimoto, T. *Chem. Commun.* 1993, 162.

- (12) Rose, E.; Quelquejeu, M.; Pochet, C.; Julien, N.; Kossanyi, A.; Hamon, L. *J. Org. Chem.* 1993, 58, 5030.  
(13) Gottwald, L. K.; Ullman, E. F. *Tetrahedron Lett.* 1969, 36, 3071.  
(14) Lindsey, J. *J. Org. Chem.* 1980, 45, 5215.



**Figure 1.** Time course of atropoisomerization from  $\alpha,\alpha,\alpha,\beta$ -*meso*-tetrakis[2-(2,3,4,6-tetraacetyl-*O*- $\beta$ -glucosyl)phenyl]porphyrin at 80 °C.

**Table 1. Relative Abundance of Atropoisomers of *meso*-Tetrakis[2-(2,3,4,6-tetraacetyl-*O*- $\beta$ -glucosyl)phenyl]porphyrin (1) Obtained upon Heating at 80 °C in Different Solvents**

solvent	time (h)	$1\alpha,\beta,\alpha,\beta$ (%)	$1\alpha,\alpha,\beta,\beta$ (%)	$1\alpha,\alpha,\alpha,\beta$ (%)	$1\alpha,\alpha,\alpha,\alpha$ (%)
toluene	5	10	28	55	8
acetonitrile	1.5	8	26	66	0
toluene/acetonitrile 10/3, v/v	4	20	31.5	48.5	trace
toluene + silica gel	4	6.5	26	55	12.5
toluene/acetonitrile 10/3, v/v + silica gel	4	6.5	20.5	51	22
toluene/ethanol 100/5, v/v + silica gel	4	22	25	53	0
toluene/ethanol 100/10, v/v + silica gel	4	7	22.5	66.5	4
toluene/ethanol 100/15 v/v + silica gel	4	21	21.5	55.5	2

the  $\alpha,\alpha,\alpha,\alpha$ -isomer is the most polar, the isomerization in the presence of silica gel and a suitable solvent or mixture of solvents should afford the  $\alpha,\alpha,\alpha,\alpha$ -isomer in a relatively high yield. The use of a mixture of toluene and silica gel increased the yield of  $\alpha,\alpha,\alpha,\alpha$ -isomer (12.5%) relative to that observed in pure toluene. In the latter case, the polarity of the glycosylated porphyrin was too high to permit desorption of the less polar isomers ( $1\alpha,\beta,\alpha,\beta$ ,  $1\alpha,\alpha,\beta,\beta$ ,  $1\alpha,\alpha,\alpha,\beta$ ). The polarity of the solvent (or mixture of solvents) used in this process appears crucial since it must support both preferred adsorption of the  $\alpha,\alpha,\alpha,\alpha$ -isomer and good desorption of the other isomers. The use of acetonitrile as cosolvent with toluene increases the formation of the  $\alpha,\alpha,\alpha,\alpha$ -compound to 22% which is higher than the random statistical mole fraction (12.5%) that would be obtained in pure solvent by a simple theoretical equilibrium.<sup>13</sup> The use of a very polar cosolvent such as ethanol gives a very poor yield of  $\alpha,\alpha,\alpha,\alpha$ -*meso*-tetrakis[2-(2,3,4,6-tetraacetyl-*O*- $\beta$ -glucosyl)phenyl]porphyrin. By using this cosolvent, maximum  $\alpha,\alpha,\alpha,\alpha$ -isomer formation

(4%) occurred in 10% ethanol in toluene, in the presence of silica gel.

The large-scale preparation of  $\alpha,\alpha,\alpha,\alpha$ -atropoisomer was performed in toluene/acetonitrile (10/3, v/v), with silica gel, at 80 °C. It was recovered by simple chromatography on a silica gel column, eluted by a mixture of methylene chloride/acetone (5/1, v/v) as the fourth red band. The isomerization of  $\alpha,\alpha,\alpha,\alpha$ -atropoisomer  $1\alpha,\alpha,\alpha,\alpha$  occurred at temperatures above 50 °C. The incorporation of zinc into this compound has been accomplished overnight at room temperature in a mixture of chloroform and acetic acid (1/1, v/v), in the presence of a large excess of zinc acetate.

<sup>1</sup>H NMR spectroscopy (200 MHz) was used for characterization of the  $\alpha,\alpha,\alpha,\alpha$ -atropoisomer of *meso*-tetrakis[2-(2,3,4,6-tetraacetyl-*O*- $\beta$ -glucosyl)phenyl]porphyrin and the zinc complex (Figure 2). The <sup>1</sup>H NMR spectra of porphyrins are governed by the symmetry properties of the tetrapyrrolic macrocycle.<sup>15</sup> The spectra of compounds  $1\alpha,\alpha,\alpha,\alpha$  and Zn- $1\alpha,\alpha,\alpha,\alpha$ , which contain a C<sub>4</sub> axis perpendicular to the porphyrin plane, are relatively simple, each resonance system corresponding to four equivalent protons. For example, the resonance peaks of the  $\beta$ -pyrrolic protons, at 8.71 and 8.61 ppm for the free base and 8.62 and 8.53 for zinc complex, as an AB system, appear as two doublets and are split by about 0.10 ppm. This splitting arises from the existence of two different environments for the  $\beta$ -pyrrolic protons in the  $\alpha,\alpha,\alpha,\alpha$ -isomer, understandable by consideration of the geometry of sugar moieties. Similar splitting of the  $\beta$ -pyrrolic proton resonances, due to nonequivalence, has been reported for the same atropoisomers of *meso*-tetrakis(2-methoxy-1-naphthyl)porphyrin<sup>15</sup> and *meso*-tetrakis(2-pivalamidophenyl)porphyrin.<sup>16</sup> The resonance of the anomeric C-1 proton of the glucosyl group appears as a single well-defined doublet ( $J = 8$  Hz) at 5.40 ppm or 5.38 ppm, indicative of a pure  $\beta$ -configuration and the perfect symmetry of the sugar groups around the macrocycle. In the case of the free base, one peak corresponding to the protons of one protecting acetyl group is shifted to -0.20 ppm. This upfield shift can reach -2.25 ppm for the  $\alpha,\alpha,\beta,\beta$ -isomer.<sup>7a,b</sup> This suggests that the glycosylated groups of the  $\alpha,\alpha,\alpha,\alpha$ -isomer bend over the ring in spite of less spatial congestion than in the other three isomers. This phenomena must be due to considerable steric interaction between the glucosyl groups in  $1\alpha,\alpha,\alpha,\alpha$ .

The UV-vis spectrum of the  $\alpha,\alpha,\alpha,\alpha$ -isomer was measured. The wavelengths of the absorption maxima do not vary from those of the other isomers; however, the extinction coefficients are different.<sup>7a,b</sup> The relative intensities of Q-band I-IV (Falk's notation<sup>17</sup>) of  $1\alpha,\beta,\alpha,\beta$  and  $1\alpha,\alpha,\alpha,\beta$  are of the etio type (IV > III > II > I) in chloroform, while those of  $1\alpha,\alpha,\beta,\beta$  and  $1\alpha,\alpha,\alpha,\alpha$  are of the phyllo type (IV > II > III > I).<sup>17</sup> The phyllo-type tendency, which is defined in terms of the ratio of the intensity of II/III bands, is greater in  $1\alpha,\alpha,\alpha,\alpha$  (1.19) than in  $1\alpha,\alpha,\beta,\beta$  (1.13). Similar effects have been reported by Anzai *et al.*<sup>16</sup> for the  $\alpha,\alpha,\alpha,\alpha$ -,  $\alpha,\alpha,\beta,\beta$ -, and  $\alpha,\alpha,\alpha,\beta$ -atropoisomers of the *meso*-tetrakis(*o*-pivalamidophenyl)porphyrin.

As do all zinc complexes of *ortho*-substituted glucosyl tetraphenylporphyrins  $1\alpha,\beta,\alpha,\beta$ ,  $1\alpha,\alpha,\beta,\beta$ , and  $1\alpha,\alpha,\alpha,\beta$ ,

(15) Abraham, R. J.; Plant, J.; Bedford, G. R. *Org. Magn. Res.* 1982, 19, 204.

(16) Anzai, K.; Hatano, K. *Chem. Pharm. Bull.* 1984, 32, 1273.

(17) Falk, J. E. *Porphyrins and Metalloporphyrins*; Elsevier: Amsterdam, 1964.

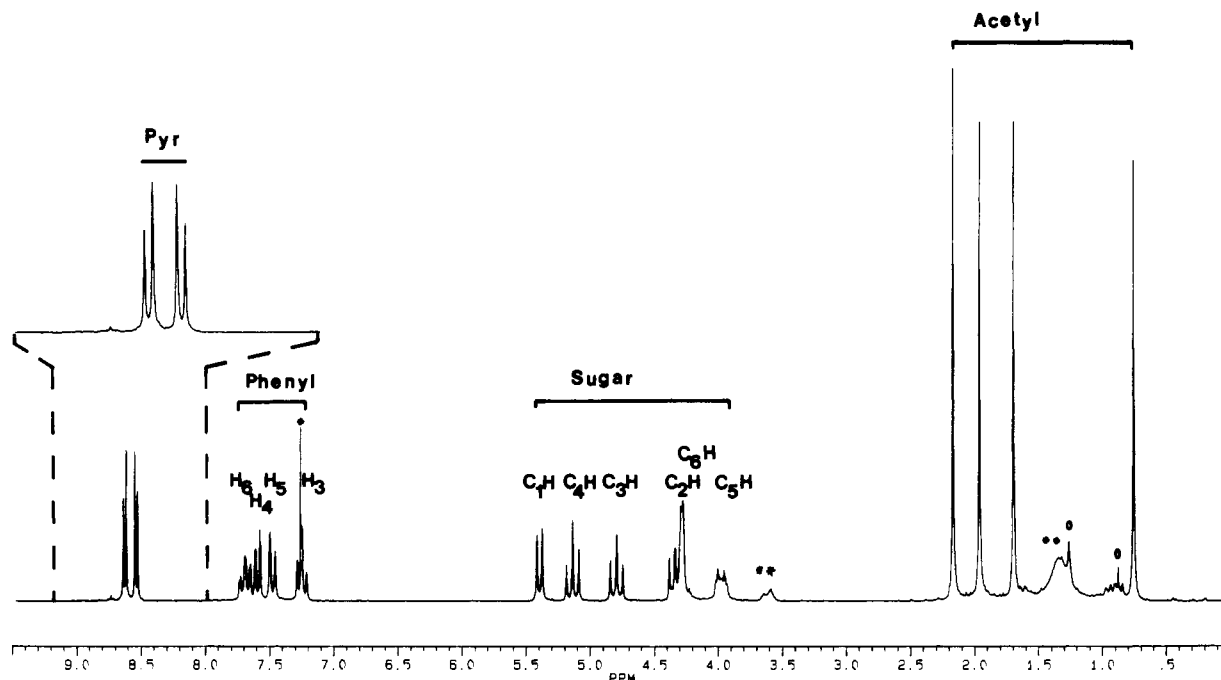


Figure 2.  $^1\text{H}$  NMR spectrum of compound  $\text{Zn-1}\alpha,\alpha,\alpha,\alpha$  in  $\text{CDCl}_3$ : \*,  $\text{CHCl}_3$ ; \*\*, HOD; O, impurities.

Table 2. UV-Vis Spectra in  $\text{CHCl}_3$

compd	$\lambda$ max, nm ( $\epsilon$ , $\text{mmol}^{-1}$ )
$1\alpha,\beta,\alpha,\beta$	418 (370.5), 515 (17), 544 (6), 588 (7), 654.5 (3.5)
$1\alpha,\alpha,\beta,\beta$	419.5 (421.5), 514.5 (18.5), 551 (8.5), 589 (7.5), 655.5 (5.5)
$1\alpha,\alpha,\alpha,\beta$	418.5 (418.5), 513.5 (19), 546 (7.5), 588 (8), 653 (3.3)
$1\alpha,\alpha,\alpha,\alpha$	418 (411.6), 513 (20.2), 545 (6.3), 589 (7.5), 644 (3.9)

compound  $\text{Zn-1}\alpha,\alpha,\alpha,\alpha$  showed a Soret band intensity much greater than that of zinc tetraphenylporphyrin.<sup>7b</sup>

The formation of pentacoordinated species of  $\text{Zn-1}\alpha,\alpha,\alpha,\alpha$  in the presence of pyridine in chloroform is very difficult.<sup>18</sup> The affinity constant of binding of pyridine ( $2.5 \text{ L}\cdot\text{mol}^{-1}$ ) at  $25^\circ\text{C}$  is less by a factor of 2000, compared to zinc tetraphenylporphyrin ( $5900 \text{ L}\cdot\text{mol}^{-1}$ ). This point indicates that the pyridine is linked to zinc on the constrained face of the macrocycle. The  $^1\text{H}$  NMR spectrum of  $\text{Zn-1}\alpha,\alpha,\alpha,\alpha$  confirms the binding of the pyridine in the hindered cavity. The spectrum of this complex in a mixture of  $\text{CDCl}_3/\text{pyridine-}d_5$  (1/1, v/v) shows that the "ose" proton resonances are shifted downfield or upfield relative to those of the unligated compound. No significant shift of the porphyrin proton resonances was observed, indicating no change in the geometry of the macrocycle upon ligation. This general behavior can be explained by a change in the conformation of the sugar in the pentacoordinated species. Chemical shifts of each "ose" proton could result from a possible rotation of the sugars when pyridine binds in the hindered cavity. But the ring current effect of the pyridine ring cannot be also excluded.

The feasibility of the preparation of the  $\alpha,\alpha,\alpha,\alpha$ -atropoisomer of *meso*-tetrakis[2-(2,3,4,6-tetraacetyl-*O*- $\beta$ -glucosyl)phenyl]porphyrin (1) from other isomers by a thermal process has been investigated under a variety of conditions. The best procedure for formation of this compound employs a solvent mixture of toluene/acetonitrile (10/3, v/v) in the presence of silica gel. Future goals

include an investigation of the preparation of manganese(III) or iron(III) complexes as asymmetrical catalysts for alkene oxidation.

## Experimental Section

**General.** General preparation of *meso*-tetrakis-5,10,15,20-[2-(2,3,4,6-tetraacetyl-*O*- $\beta$ -glucosyl)phenyl]porphyrin have been previously reported.<sup>7a,b</sup> Toluene, methylene chloride, and acetonitrile were analytical reagent grade and were purchased from Prolabo. Silica gel used for the atropoisomerization experiment was Macherey-Nagel silica gel 60 70–230-Mesh ASTM. Chromatography was carried out with Macherey-Nagel precoated TLC plates SIL G-200 (2 mm).  $^1\text{H}$  NMR spectra were recorded at 200 MHz for  $\text{CDCl}_3$  or  $\text{CDCl}_3/\text{pyridine-}d_5$  solutions with Bruker AM-200 instruments. Chemical shift values were given in ppm relative to TMS. Coupling constants were given in Hz. Optical spectra in the Soret and visible regions were recorded with a Varian DMS 200 spectrometer. HPLC analysis was performed with a Gilson apparatus with a dynamic mixer module Gilson 811, a manometric module Gilson 802, a pump Gilson 303, and a holochrome module Gilson (detection at 410 nm). Column: HiBar Lichrosorb SI 60 5- $\mu\text{m}$  Merck.

**General Procedure for the Atropoisomerization Reaction.** Typical experiment: 50 mg of porphyrin (pure isomer or mixture of three isomers) was heated at  $80^\circ\text{C}$  in 10 mL of solvent (or mixture of solvents) and 1 g of silica gel with stirring under argon. The molar fraction of isomers was measured by HPLC analysis with a column HiBar Lichrosorb SI 60 5- $\mu\text{m}$  Merck eluted with a mixture of methylene chloride/acetone 100/15, v/v, flow rate 1.30 mL/min, retention time:  $1\alpha,\beta,\alpha,\beta$ , 4.2 min;  $1\alpha,\alpha,\beta,\beta$ , 5.2 min,  $1\alpha,\alpha,\alpha,\beta$ , 6.6 min. A mixture of methylene chloride/acetone 100/17.5, v/v, was used for the  $\alpha,\alpha,\alpha,\alpha$ -isomer, flow rate 1.30 mL/min, retention time 27 min. Compound  $1\alpha,\alpha,\alpha,\alpha$  was purified by preparative thin-layer chromatography on silica gel eluted by a mixture of methylene chloride/ether (1/1, v/v) and crystallized from a mixture of methylene chloride/heptane. Anal. Calcd for  $\text{C}_{100}\text{H}_{102}\text{N}_4\text{O}_{40}\cdot\text{H}_2\text{O}$ : C, 59.72; H, 5.19; N, 2.78. Found: C, 59.29; H, 5.28; N, 2.60. UV-vis spectrum in  $\text{CHCl}_3$   $\lambda$  max, nm ( $\epsilon$ ,  $\text{mmol}^{-1}$ ): 418 (411.6), 513 (20.2), 545 (6.3), 589 (7.5), 644 (3.9).  $^1\text{H}$  NMR in  $\text{CDCl}_3$   $\delta$  ppm: 8.71 d (4H, pyr), 8.61 d (4H, pyr), 7.65 m (12H, phenyl), 7.31 m (4H, phenyl), 5.40 d (4H, H, ose,  $J = 8 \text{ Hz}$ ), 5.05 t (4H, H<sub>4</sub> ose), 4.90 t (4H, H<sub>3</sub> ose), 4.24 m (12H, H<sub>2</sub>, H<sub>6</sub> ose), 3.90 m (4H, H<sub>5</sub> ose), 2.16 s (12H, H acetyl), 1.92 s (12H, H acetyl), 1.60 s (12H, H acetyl), -0.2 s (12H, H acetyl), -2.82 s (2H, NH).

(18) Affinity constant of pyridine binding in methylene chloride at  $25^\circ\text{C}$  ( $K$  in  $\text{L}\cdot\text{mol}^{-1}$ ):  $\text{ZnTPP}$ , 5900;  $\text{Zn-1}\alpha,\beta,\alpha,\beta$ , 15;  $\text{Zn-1}\alpha,\alpha,\beta,\beta$ , 39;  $\text{Zn-1}\alpha,\alpha,\alpha,\beta$ , 14;  $\text{Zn-1}\alpha,\alpha,\alpha,\alpha$ , 2.5.

**Zinc meso-5,10,15,20-Tetrakis-[2-(2,3,4,6-tetraacetyl-O- $\beta$ -glucosyl)phenyl]porphyrin (Zn-1 $\alpha,\alpha,\alpha,\alpha$ ).** The zinc complex was prepared and purified as previously described<sup>19</sup> in a mixture of chloroform/acetic acid (1/1, v/v) at room temperature under argon overnight in the presence of zinc acetate. The compound was purified by preparative thin-layer chromatography on silica gel eluted by a mixture of methylene chloride/ether (1/1, v/v). The pure complex crystallized from methylene chloride/heptane (yield 95%). UV-vis spectrum of CHCl<sub>3</sub>  $\lambda$  max, nm ( $\epsilon$ , mmol<sup>-1</sup>): 404 (87), 425 (693.3), 557 (25.1), 592 (7). <sup>1</sup>H NMR in CDCl<sub>3</sub>  $\delta$  ppm: 8.62 d (4H, pyr), 8.53 d (4H, pyr), 7.68 d t, 7.58, 7.46 d d, 7.24 t (16H, H<sub>6</sub>, H<sub>4</sub>, H<sub>5</sub>, H<sub>3</sub> phenyl), 5.38 d (4H, H<sub>1</sub> ose,  $J$  = 8 Hz),

5.13 t (4H, H<sub>4</sub> ose), 4.78 t (4H, H<sub>3</sub> ose), 4.33 t (4H, H<sub>2</sub> ose), 4.27 m (8H, H<sub>6</sub> ose), 3.95 m (4H, H<sub>5</sub> ose), 2.16 s (12H, H acetyl), 1.95 s (12H, H acetyl), 1.69 s (12H, H acetyl), 0.75 s (12H, H acetyl). <sup>1</sup>H NMR in CDCl<sub>3</sub>/pyridine-*d*<sub>5</sub> (1/1, v/v)  $\delta$  ppm: 8.75 broad (8H, pyr), 7.71 d t (4H), 7.90 d d (4H), 7.56 d d (4H), 7.34 t (4H) (H<sub>6</sub>, H<sub>4</sub>, H<sub>5</sub>, H<sub>3</sub> phenyl), 6.08 d (4H, H<sub>1</sub> ose,  $J$  = 8 Hz), 5.40 t (4H, H<sub>3</sub> ose), 4.85 t (4H, H<sub>4</sub> ose), 4.06 t (4H, H<sub>2</sub> ose), 4.41-4.17 m (8H, H<sub>6</sub> ose), 3.79 m (4H, H<sub>5</sub> ose), 2.10 s (12H, H acetyl), 1.85 s (12H, H acetyl), 1.81 s (12H, H acetyl), 1.20 s (12H, H acetyl).

**Acknowledgment.** This work was supported by the Centre National de la Recherche Scientifique. The authors wish to thank Miss Marine Laforgue for kinetic experiments.

(19) Alder, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Org. Chem.* 1970, 32, 2445.