JOC*Article*

# Meso-Substituted [34]Octaphyrin(1.1.1.0.1.1.1.0) and Corrole Formation in Reactions of a Dipyrromethanedicarbinol with 2,2′-Bipyrrole

G. Richard Geier III* and Scott C. Grindrod

*Department of Chemistry, Colgate University, 13 Oak Drive, Hamilton, New York 13346*

*ggeier@mail.colgate.edu*

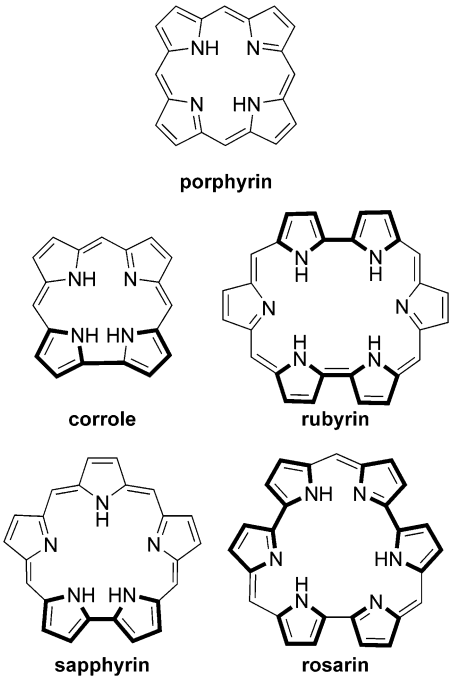
*Received May 24, 2004*

The reaction of a dipyrromethanedicarbinol with 2,2′-bipyrrole leading to meso-substituted [34]-octaphyrin(1.1.1.0.1.1.1.0) and/or corrole was investigated to determine the effect of key reaction parameters on the distribution of the two macrocycles. Solvent, acid catalyst, acid quantity, oxidant, oxidant quantity, and reaction time were surveyed for a model reaction affording 5,10,19,24,29,-38-hexaphenyl[34]octaphyrin(1.1.1.0.1.1.1.0) (HPO) and/or *meso*-triphenylcorrole (TPC). HPO was found to be a fairly ubiquitous product, produced in yields as high as 23% (UV−vis), while TPC was observed infrequently, in yields up to 10% (UV−vis). A preparative-scale reaction provided HPO in an isolated yield of 25%. The methodology was extended to the synthesis of an octaphyrin bearing two different substituents in defined locations and to an octaphyrin possessing electron-withdrawing pentafluorophenyl substituents. Preferential formation of octaphyrin instead of corrole suggests that the anti conformation of 2,2′-bipyrrole is the relevant form under the reaction conditions surveyed. The spectral properties of the novel meso-substituted [34]octaphyrin-(1.1.1.0.1.1.1.0) species are similar to those of the known $\beta$-substituted analogue, including spectra consistent with the absence of macrocycle aromaticity despite a main conjugation path of 34 $\pi$-electrons. Key to the overall study was the development of a refined synthesis of 2,2′-bipyrrole.

## Introduction

Porphyrinic macrocycles with contracted, expanded, or isomeric core structures relative to porphyrin have been of interest for some time.[1] A significant subset of these macrocycles shares the structural motif of one or more direct α,α-bipyrrole linkages (e.g., corrole, sapphyrin, rubyrin, and rosarin). Such species display interesting and potentially useful properties that complement those of porphyrin as illustrated by the two title compounds of this paper. [34]Octaphyrin(1.1.1.0.1.1.1.0) provides two sites for metal ion coordination, allowing the preparation of bimetallic complexes,[2] and corrole is known to stabilize metal ions in unusually high oxidation states.[3]

From a synthetic perspective, the incorporation of one or more bipyrrole linkages in a porphyrinic macrocycle presents a challenge. Of the possible approaches, routes involving a precursor possessing a preformed bipyrrole linkage (e.g., 2,2′-bipyrrole) have been attractive.[1] However, these reactions are not always without difficulty. For example, the preparation of corrole via $\beta$-substituted 2,2′-bipyrroles has been a classic challenge. Johnson's

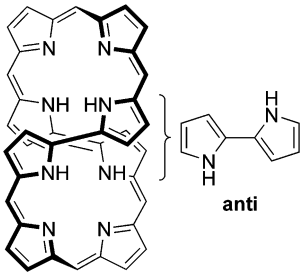



(1) (a) Sessler, J. L.; Seidel, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 5134−5175. (b) Sessler, J. L.; Gebauer, A.; Vogel, E. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 2, pp 1−54. (c) Sessler, J. L.; Gebauer, A.; Weghorn, S. J. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 2, pp 55−124. (d) Sessler, J. L.; Weghorn, S. *Expanded, Contracted, and Isomeric Porphyrins*; Elsevier: Oxford, U.K., 1997. (e) Jasat, A.; Dolphin, D. *Chem. Rev.* **1997**, *97*, 2267−2340.

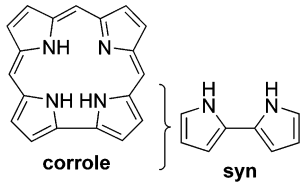
(2) (a) Gisselbrecht, J.-P.; Bley-Escrich, J.; Gross, M.; Zander, L.; Michels, M.; Vogel, E. *J. Electroanal. Chem.* **1999**, *469*, 170−175. (b) Werner, A.; Michels, M.; Zander, L.; Lex, J.; Vogel, E. *Angew. Chem., Int. Ed.* **1999**, *38*, 3650−3653. (c) Bley-Escrich, J.; Gisselbrecht, J.-P.; Vogel, E.; Gross, M. *Eur. J. Inorg. Chem.* **2002**, 2829−2837. (d) Bley-Escrich, J.; Gisselbrecht, J.-P.; Michels, M.; Zander, L.; Vogel, E.; Gross, M. *Eur. J. Inorg. Chem.* **2004**, 492−499.

10.1021/jo049131z CCC: $27.50 
Published on Web 08/17/2004

historic attempts required the presence of cobalt ions,[4] and related work by Vogel and co-workers afforded instead a novel [34]octaphyrin(1.1.1.0.1.1.1.0) that was found to have a chiral figure-eight structure.[5] To adopt a figure-eight structure, both bipyrrole linkages of the octaphyrin reside in an anti conformation, compared to the syn conformation present in corrole.

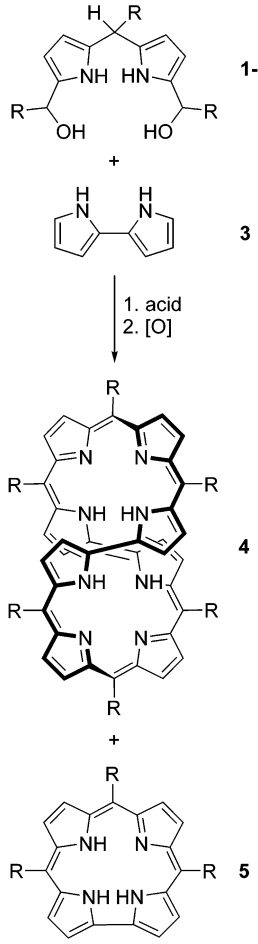



**[34]octaphyrin(1.1.1.0.1.1.1.0)**




By convention, 2,2′-bipyrrole is usually drawn in the syn conformation. However, it has been known for some time that the anti conformation is actually lower in energy.[6] Calculations pertaining to $\beta$-unsubstituted 2,2′-bipyrrole place the syn conformation at an energy maximum, ~12 kJ mol$^{-1}$ higher in energy than the anti form, which in turn is ~2 kJ mol$^{-1}$ higher in energy than an anti−gauche conformation.[6d−f] The Boltzmann population (298 K) for the anti−gauche/syn−gauche equilibrium calculated at a variety of levels of theory is ~94% in favor of the anti−gauche conformation.[6f] X-ray diffraction studies are in agreement with these findings.[7] This conformational preference may account, in part, for the formation of the octaphyrin over corrole in Vogel's work—especially given that a bipyrrole species bearing $\beta$-substituents, which might further destabilize the syn form on steric grounds, was employed. So although the barrier to rotation about the bipyrrole linkage is not particularly high, perhaps in some circumstances it is better to think of 2,2′-bipyrrole in the anti form. Yet

**SCHEME 1. Two-Step, One-Flask Reaction of a Dipyrromethanedicarbinol and 2,2′-Bipyrrole, Leading to a Meso-Substituted [34]Octaphyrin(1.1.1.0.1.1.1.0) and/or Corrole**




interestingly, expanded porphyrinic macrocycles bearing syn-orientated bipyrrole unit(s) have been prepared (sometimes very efficiently[8]) from 2,2′-bipyrroles.[1] Perhaps reaction conditions can alter the preferred conformation of the bipyrrole precursor (the syn and anti forms differ in polarity); perhaps expanded structures better tolerate a range of bipyrrole conformations during macrocycle formation; and/or perhaps in some cases facile alternative reaction pathways are absent, thereby allowing the reaction leading to a syn-oriented bipyrrole linkage.

To begin unraveling some of these issues, we sought to examine the effects of key reaction parameters on the formation of [34]octaphyrin(1.1.1.0.1.1.1.0) and corrole in the two-step, one-flask reaction of a dipyrromethanedicarbinol **1-OH** with 2,2′-bipyrrole **3** (Scheme 1).[9] In a

(3) (a) Vogel, E.; Will, S.; Schulze-Tilling, A.; Neumann, L.; Lex, J.; Bill, E.; Trautwein, A. X.; Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 731−735. (b) Gross, Z. *J. Biol. Inorg. Chem.* **2001**, *6*, 733−738. (c) Erben, C.; Will, S.; Kadish, K. M. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 2, pp 233−300.

(4) Conlon, M.; Johnson, A. W.; Overend, W. R.; Rajapaksa, D.; Elson, C. M. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2281−2288.

(5) Vogel, E.; Bröring, M.; Fink, J.; Rosen, D.; Schmickler, H.; Lex, J.; Chan, K. W. K.; Wu, Y.-D.; Plattner, D. A.; Nendel, M.; Houk, K. N. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2511−2514.

(6) (a) Orti, E.; Tomas, F.; Sanchez-Marin, J. *J. Mol. Struct. THEOCHEM* **1983**, *104*, 197−206. (b) Orti, E.; Sanchez-Marin, J.; Tomas, F. *Theor. Chim. Acta* **1986**, *69*, 41−49. (c) Orti, E.; Sanchez-Marin, J.; Tomas, F. *J. Chim. Phys.* **1987**, *84*, 729−734. (d) Kofranek, M.; Kovar, T.; Karpfen, A.; Lischka, H. *J. Chem. Phys.* **1992**, *96*, 4464−4473. (e) Padilla-Campos, L.; Toro-Labbe, A. *J. Mol. Struct. THEOCHEM* **1995**, *330*, 223−229. (f) Duarte, H. A.; Duani, H.; De Almeida, W. B. *Chem. Phys. Lett.* **2003**, *369*, 114−124.

(7) Street, G. B.; Lindsey, S. E.; Nazzal, A. I.; Wynne, K. J. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 137−148.

(8) Sessler, J. L.; Weghorn, S. J.; Morishima, T.; Rosingana, M.; Lynch, V.; Lee, V. *J. Am. Chem. Soc.* **1992**, *114*, 8306−8307.

(9) After a report of our preliminary results,[9a] Decreay and Collman published the observation of corrole formation in modest yield from a dipyrromethanedicarbinol + 2,2′-bipyrrole route.[9b] In a recent review article on corrole synthesis,[9c] Gryko reported that his group has also attempted to prepare meso-substituted corrole via 2,2′-bipyrrole but without success. To the best of our knowledge, the details of their work have not been published. (a) Geier, G. R., III; Grindrod, S. C.; Callinan, J. B.; Reid, C. G. *Abstr. Papers Am. Chem. Soc.* **2002**, *224*, 750. (b) Decreay, R. A.; Collman, J. P. *Tetrahedron Lett.* **2003**, *44* 3323−3327. (c) Gryko, D. T. *Eur. J. Org. Chem.* **2002**, 1735−1743.

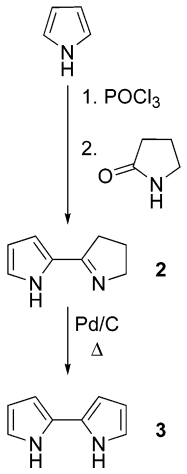
fundamental sense, we sought to gain insight into reactions involving 2,2′-bipyrrole leading to porphyrinic macrocycles bearing bipyrrole linkage(s). In a practical sense, we sought to determine whether either meso-substituted [34]octaphyrin(1.1.1.0.1.1.1.0) or corrole could be prepared efficiently via this route. Both macrocycles are of current interest, and the meso-substituted [34]-octaphyrin(1.1.1.0.1.1.1.0) has not yet been reported. This study is complementary to the work of Vogel and coworkers[5] in that the bipyrrole employed in our study lacks $\beta$-substituents, and the reaction conditions best suited for dipyrromethanecarbinol species differ from those employed in their work.

In this paper we describe our investigation of solvent, acid catalyst, acid catalyst quantity, time, oxidant, and oxidant quantity on a model reaction leading to 5,10,-19,24,29,38-hexaphenyl[34]octaphyrin(1.1.1.0.1.1.1.0)(HPO) and/or *meso*-triphenylcorrole (TPC) (Scheme 1, R = Ph). This model reaction allows comparison to data available from studies of the synthesis of *meso*-tetraphenylporphyrin (TPP)[10] and to our recent work involving the reaction of a dipyrromethanedicarbinol with excess pyrrole leading to TPC.[11] Trifluoroacetic acid (TFA) and mild acid catalysts of proven success in reactions of dipyrromethanecarbinol species leading to porphyrin[12] and corrole[11] were examined. The yield of HPO and TPC in analytical-scale reactions was assessed by a modification of the UV−vis spectrophotometric method commonly employed in porphyrin syntheses.[13] Results from analytical-scale experiments were confirmed by representative preparative-scale syntheses. Undesired reversibility (leading to scrambling) was assessed by UV−vis and thin-layer chromatographic (TLC) analysis for the presence of TPP. The suppression of scrambling was further confirmed by laser desorption mass spectrometry (LD-MS) analysis of a reaction involving a dipyrromethanedicarbinol bearing different substituents in defined locations. The effect of electron-withdrawing substituents was investigated via a reaction leading to 5,10,19,24,29,38-hexakis(pentafluorophenyl)[34]octaphyrin(1.1.1.0.1.1.1.0) (HpFPO) and/or 5,-10,15-tris(pentafluorophenyl)corrole (TpFPC) (Scheme 1, R = $C_6F_5$). Spectral properties and the stability toward light of the novel octaphyrins prepared in this study were investigated. Facilitating the overall study was a refinement of Rapoport and Castagnoli's synthesis of 2,2′-bipyrrole.[14]

## Results and Discussion

**Refined Synthesis of 2,2′-Bipyrrole (3).**[15] 2,2′-Bipyrrole was prepared by a refinement of the dehydrogenation of 2,2′-(1′-pyrrolinyl)pyrrole **2** reported by Rapoport and Castagnoli (Scheme 2).[14] The reaction of 2-pyrrolidone and pyrrole proceeded smoothly as described in the literature, affording **2** in a yield of 68%. Attempted dehydrogenation of **2** leading to **3** (treatment of **2** with 1 equiv of palladium on carbon in di-*n*-hexyl ether at 200 °C for 2 h, followed by filtration and precipitation in hexanes[14]) provided a poor result (~6% yield), primarily because the 2,2′-bipyrrole did not readily precipitate. Evaporation of the ether (bp 228 °C) under reduced pressure required heating, which caused some decomposition of **3**. The decomposition of **3** led us to wonder if similar damage occurred during the 2 h reaction at 200 °C.

**SCHEME 2. Synthesis of 2,2′-Bipyrrole**




Given those observations, we sought to refine the dehydrogenation of **2** so as to employ a solvent with a lower boiling point. The replacement of di-*n*-hexyl ether with triglyme (bp 216 °C) has been reported for this reaction,[16] so we focused attention on this family of solvents. Analytical-scale reactions monitored by gas chromatography/mass spectrometry (GC/MS) were performed at reflux in monoglyme (bp 85 °C), diglyme (bp 162 °C), or triglyme with palladium on carbon (0.0625−0.50 equiv relative to **2**). The best balance of solvent volatility, palladium quantity, and reaction time was provided by reflux in diglyme with palladium on carbon (0.125 equiv) for ~1.5 h (see Supporting Information for additional data). Preparative-scale reactions (12.8 mmol of **2**) afforded **3** as a while crystalline solid in a yield of 71% (1.2 g). The isolated yield compares favorably to the yield of 38% reported by Rapoport and Castagnoli[14] and to a yield of 54% obtained from a modified procedure with triglyme (which afforded **3** as a green solid).[16]

**Investigation of the Model Reaction Leading to 5,10,19,24,29,38-Hexaphenyl[34]Octaphyrin-(1.1.1.0.1.1.1.0) (4a) and/or *meso*-Triphenylcorrole (5a).** Studies of the model reaction of dipyrromethanedicarbinol **1a-OH** [prepared freshly via $NaBH_4$ reduction of 1,9-bis(benzoyl)-5-phenyldipyrromethane **1a**] with 2,2′-bipyrrole **3** involved the isolation of authentic HPO, development of a spectrophotometric method to quantify HPO and TPC in analytical-scale reactions, a survey of catalysis conditions, reaction time course experiments,

(10) (a) Geier, G. R., III; Lindsey, J. S. *J. Chem. Soc., Perkin Trans. 2* **2001**, 687−700. (b) Geier, G. R., III; Littler, B. J.; Lindsey, J. S. *J. Chem. Soc., Perkin Trans. 2* **2001**, 712−718.

(11) Geier, G. R., III; Chick, J. F. B.; Callinan, J. B.; Reid, C. G.; Auguscinski, W. P. *J. Org. Chem.* **2004**, *69*, 4159−4169.

(12) Geier, G. R., III; Callinan, J. B.; Rao, D. P.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **2001**, *5*, 810−823.

(13) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827−836.

(14) Rapoport, H.; Castagnoli, N. *J. Am. Chem. Soc.* **1962**, *84*, 2178−2181.

(15) Although 2,2′-bipyrrole is now commercially available (Alfa Aesar), its relatively high price (1 g, $224) provided the impetus to further improve its synthesis.

(16) Groenendaal, L.; Peerlings, H. W. I.; van Dongen, J. L. J.; Havinga, E. E.; Vekemans, J. A. J. M.; Meijer, E. W. *Macromolecules* **1995**, *28*, 116−123.

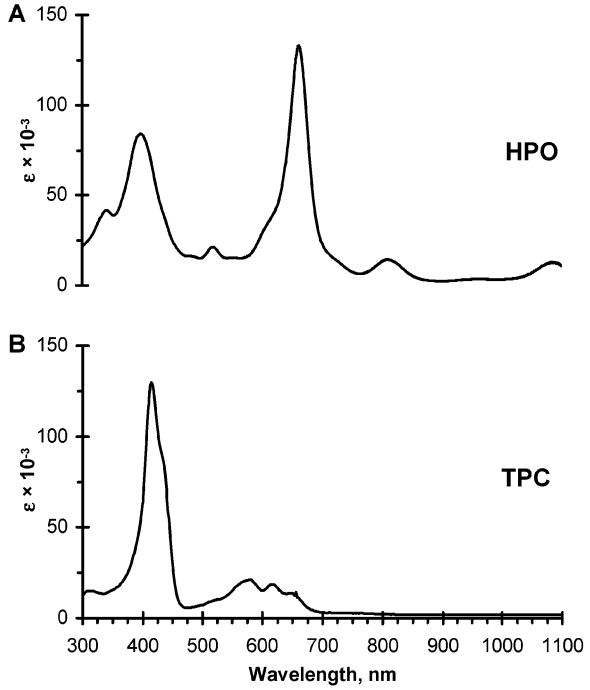



**FIGURE 1.** UV−Vis spectra of (A) HPO and (B) TPC ($CH_2Cl_2$). TPC was obtained from our earlier study of the reaction of a dipyrromethanedicarbinol with excess pyrrole, leading to corrole.[11]

an examination of oxidation conditions for the preparation of HPO, and a preparative-scale synthesis of HPO.

**1. Isolation of 5,10,19,24,29,38-Hexaphenyl[34]-Octaphyrin(1.1.1.0.1.1.1.0) (4a).** As the preparation of HPO had not been previously reported, reactions of dipyrromethanedicarbinol **1a-OH** with **3** were performed in the hopes of isolating HPO for preliminary characterization and for use in the development of a spectrophotometric method to quantify HPO and TPC in analytical-scale reactions. Published UV−vis data for the $\beta$-ethyl-substituted [34]octaphyrin(1.1.1.0.1.1.1.0)[1c,5] assisted our efforts. The spectrum of the octaphyrin is quite distinct from that of corrole and linear oligopyrrylmethenes. UV−vis analysis of the products obtained from our initial reactions revealed a promising dark green pigment (Figure 1A).[17] The pigment was more strongly retained ($R_f$ 0.070) on silica TLC than TPC ($R_f$ 0.60) ($CH_2Cl_2$). Further analysis of the pigment by LD-MS led to its provisional assignment as the desired HPO. Additional characterization was performed on HPO prepared later in the study, after methods for its synthesis and purification were further refined (vide infra).

**2. Determination of the Yield of HPO and TPC in Analytical-Scale Reactions.** In our recent study of the reaction of **1a-OH** with excess pyrrole leading to TPC,[11] a well-known spectrophotometric method for monitoring reactions leading to porphyrin[13] was modified to include an aqueous basic dithionite wash to eliminate interference caused by DDQ and filtration through a Pasteur pipet containing silica gel to remove absorbing polar byproducts (e.g., oligopyrrylmethenes). In the present study, experiments were performed to assess the detection of HPO in the presence of DDQ and to examine washing with aqueous basic dithionite and filtration through a silica pad. As with TPC, DDQ was found to strongly interfere with the detection of HPO. DDQ altered the appearance of the UV−vis spectrum, and it caused the pigment to bind tightly to silica. The interference was found to be reversible upon washing with aqueous basic dithionite. Quantitative elution of HPO from a silica pad required $CH_2Cl_2$/ethyl acetate (25:1).

A remaining challenge lay in quantitating HPO and TPC in a mixture containing both species.[18] The strong absorbance of HPO at 661 nm rendered the analysis of HPO straightforward as TPC provides little absorbance at that wavelength (Figure 1). However, both species absorb strongly at the wavelength of the Soret band of TPC (414 nm). To circumvent this problem, we first attempted to pass an aliquot of the mixture through a silica pad followed by elution with $CH_2Cl_2$ in the hopes that HPO would be retained and not interfere with the analysis of TPC. Unfortunately, HPO tended to streak on the silica pad, allowing a small but bothersome quantity to contaminate the TPC. Thus, we instead developed a baseline correction to account for the contribution of HPO absorbance at 414 nm. The absorbance of the mixture at 661 nm (due nearly entirely to HPO) is multiplied by the ratio of the absorbance at 414 and 661 nm from a purified sample of HPO; that result is then subtracted from the absorbance of the mixture at 414 nm (see Supporting Information for an example). Thus, the spectral yield of both HPO and TPC could be determined from oxidized reaction aliquots upon washing with aqueous basic dithionite, passing a portion of the washed mixture through a silica pad [$CH_2Cl_2$/ethyl acetate (25:1)], and recording the UV−vis spectrum of the eluent.

**3. Survey of Catalysis Conditions.** The distribution of HPO and TPC in analytical-scale reactions of **1a-OH** and **3** was investigated. Both reactants were employed at a concentration of 2.5 mM, in keeping with conditions previously identified for reactions of dipyrromethanecarbinol species leading to porphyrin.[12,19] Reactions were performed at room temperature in $CH_2Cl_2$, acetonitrile, toluene, or tetrahydrofuran (THF) to investigate the effect of solvent polarity on the product distribution.[20] Four mild acids [$Dy(OTf)_3$, $Yb(OTf)_3$, $Sc(OTf)_3$, and $InCl_3$] were investigated at concentrations of 0.32, 1.0, 3.2, 10, and 32 mM.[21] TFA catalysis was also explored as a control for reversible processes, as previous studies of analogous reactions leading to porphyrin[10,12] and corrole[11] detected scrambling under elevated concentrations of TFA in $CH_2Cl_2$. The yield of TPC and/or HPO was

(17) We considered the possibility that DDQ might interfere with the detection of HPO as we had observed to be the case in our previous studies involving the synthesis of TPC.[11] Thus, samples were washed with an aqueous basic dithionite solution prior to analysis by TLC and UV−vis.

(18) As it turned out, TPC was rarely produced in reactions of **1a-OH** with **3** according to TLC analysis; thus, it was not typically necessary to determine the yield of TPC in the presence of HPO.

(19) Rao, P. D.; Dhanalekshmi, S.; Littler, B. J.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7323−7344.

(20) The solubility of 2,2′-bipyrrole was adequate to afford 2.5 mM solutions in all of the solvents investigated. Reactions involving $CH_2Cl_2$ required brief sonication in order to produce a solution of bipyrrole that was not visibly light scattering.

(21) The quantity of acid is reported in concentration units of molarity for convenience of comparison of reaction conditions; however, these four acids are poorly soluble and the reaction mixtures were generally heterogeneous as reported previously.[12]

**TABLE 1. Highest Yield of HPO 4a and TPC 5a Observed from the Survey of Catalysis Conditions[a]**

| entry | solvent | acid | [acid],[b] mM | % yield of HPO[c] | [acid],[d] mM | % yield of TPC[c] |
|---|---|---|---|---|---|---|
| 1 | $CH_2Cl_2$ | $Dy(OTf)_3$ | 10 | 23 | | ND[e] |
| 2 | $CH_2Cl_2$ | $Yb(OTf)_3$ | 10 | 21 | | ND |
| 3 | $CH_2Cl_2$ | $Sc(OTf)_3$ | 0.32 | 18 | 1.0 | ~1% |
| 4 | $CH_2Cl_2$ | $InCl_3$ | 0.32 | 15 | | ND |
| 5 | $CH_2Cl_2$ | TFA | 0.32 | 9 | | ND |
| 6 | MeCN | $Dy(OTf)_3$ | 0.32 | 7 | | ND |
| 7 | MeCN | $Yb(OTf)_3$ | 0.32 | 8 | | ND |
| 8 | MeCN | $Sc(OTf)_3$ | 0.32 | 9 | | ND |
| 9 | MeCN | $InCl_3$ | 0.32 | 9 | | ND |
| 10 | MeCN | TFA | 0.32 | 11 | | ND |
| 11 | toluene | $Dy(OTf)_3$ | 0.32 | 6 | | ND |
| 12 | toluene | $Yb(OTf)_3$ | 0.32 | 5 | | ND |
| 13 | toluene | $Sc(OTf)_3$ | 3.2 | 7 | | ND |
| 14 | toluene | $InCl_3$ | 0.32 | 8 | | ND |
| 15 | toluene | TFA | 0.32 | 6 | | ND |
| 16 | THF | $Dy(OTf)_3$ | 0.32 | 9 | | ND |
| 17 | THF | $Yb(OTf)_3$ | 0.32 | 9 | | ND |
| 18 | THF | $Sc(OTf)_3$ | 0.32 | 8 | | ND |
| 19 | THF | $InCl_3$ | 10 | 7 | | ND |
| 20 | THF | TFA | 0.32 | 14 | 0.32 | 10 |

[a] The reactions were performed with **1a-OH** and **3** (2.5 mM each) on a 5−10-mL scale in the indicated solvent at room temperature. The reactions were monitored at 15 min and 1 h. Entries 11, 12, and 20 were also monitored at 4 h. [b] The lowest acid concentration that provided a near-maximal yield of HPO. Higher quantities of acid commonly provided yields of HPO similar to those reported here. [c] The highest yield (UV−vis) at any of the time points is reported. [d] The lowest acid concentration that provided a near-maximal yield of TPC. [e] ND, TPC was not detected at any acid quantity (limit of detection is ~1%).

determined spectrophotometrically at reaction times of 15 min and 1 h (and at 4 h for a subset of sluggish reactions). The presence of TPP (indicating undesired reversible processes) was assessed by TLC.

The highest yield of HPO and TPC obtained from each combination of solvent and acid is summarized in Table 1 (see Supporting Information for plots of the yield of HPO or TPC as a function of acid quantity). In the majority of conditions surveyed, HPO was the only macrocyclic product observed. This result is in accord with the reaction involving $\beta$-substituted 2,2′-bipyrrole reported by Vogel and co-workers.[5] HPO was a fairly ubiquitous product, commonly found in yields ranging from 5−10%. A subset of conditions in $CH_2Cl_2$ afforded respectable yields of 15−23% (Table 1, entries 1−4). The preferential formation of HPO suggests that the anti conformation of 2,2′-bipyrrole is the relevant form under the conditions surveyed and that the use of a $\beta$-unsubstituted bipyrrole does not sharply improve access to corrole. Acid quantity was found to have greater effect on the yield of HPO (Supporting Information) than previously reported for reactions of dipyrromethanedicarbinols leading to TPP[12] or TPC.[11] Thus, conditions for the formation of HPO are somewhat more exacting. Only TFA in THF (Table 1, entry 20) provided appreciable TPC (10%), accompanied by HPO (14%). Although the best yield of TPC was modest, it nearly matched the highest yield of corrole reported for any reaction of a 2,2′-bipyrrole precursor in the absence of metal ion templation (12%).[9b] As only TFA catalysis led to enhancement of TPC formation in THF, the solvent alone does not appear to be the origin of the elevated formation of TPC. Low levels of tetraphenylporphyrin (1−3%) were only detected under TFA catalysis (≥3.2 mM in $CH_2Cl_2$, acetonitrile, or toluene), and under $InCl_3$ catalysis (≥32 mM in $CH_2Cl_2$ or THF). This result is in accord with previous studies of reactions of dipyrromethanecarbinols leading to TPP.[12]

**TABLE 2. Summary of Results from Reaction Time Course Experiments[a]**

| entry | solvent | acid | [acid], mM | time,[b] h | % yield of HPO[c] | time,[d] h | % yield of TPC[e] |
|---|---|---|---|---|---|---|---|
| 1 | $CH_2Cl_2$ | $Dy(OTf)_3$ | 3.2 | 2 | 15 | | ND[f] |
| 2 | $CH_2Cl_2$ | $Dy(OTf)_3$ | 10 | 1 | 20 | | ND |
| 3 | $CH_2Cl_2$ | $Yb(OTf)_3$ | 3.2 | 1 | 18 | | ND |
| 4 | $CH_2Cl_2$ | $Yb(OTf)_3$ | 10 | 0.5 | 25 | | ND |
| 5 | $CH_2Cl_2$ | $Sc(OTf)_3$ | 1.0 | 0.5 | 16 | | ND |
| 6 | THF | TFA | 1.0 | 2 | 16 | 1 | 10 |

[a] The reactions were performed with **1a-OH** and **3** (2.5 mM each) on an 8-mL scale under the indicated conditions at room temperature. The reactions were monitored from 1 min to 8 h. [b] The reaction time that provided the maximum yield of HPO. [c] The highest yield of HPO (UV−vis) is reported. [d] The reaction time that provided the maximum yield of TPC. [e] The highest yield of TPC (UV−vis) is reported. [f] ND, TPC was not detected at any time point (limit of detection is ~1%).

Recently, Decreay and Collman reported the preparation of meso-substituted corrole in yields of 1−12% from reactions of dipyrromethanedicarbinols and 2,2′-bipyrrole.[9b] Their most successful condition is closely related to the "low scrambling" methodology developed for reactions of a dipyrromethane and an aldehyde leading to *trans*-$A_2B_2$-porphyrins ($BF_3{\cdot}OEt_2$, $NH_4Cl$, in acetonitrile).[22] Given the nearly ubiquitous presence of HPO in our experiments, we wondered if an octaphyrin might also be produced under their conditions. Thus, we treated **1a-OH** and **3** (1.06 mM each) according to the published procedure [$BF_3{\cdot}OEt_2$ (2.0 mM) and $NH_4Cl$ (24 mM) in acetonitrile (36 mL) at room temperature]. The reaction was monitored (UV−vis and TLC) from 1 to 24 h. The only macrocyclic product observed was tetraphenylporphyrin (~9%). The presence of TPP was not surprising as the "low scrambling" condition is known to allow a low level of undesired reversibility at long reaction times.[22,23] The absence of HPO may have been due, in part, to the ~2.5-fold lower reactant concentration employed in their procedure. A more dilute reaction mixture would be expected to shift the oligomer composition to smaller species.[24]

The survey of catalyst conditions in the reaction of **1a-OH** with **3** suggests that this reaction is more appropriate for the preparation of HPO than TPC. Thus, our subsequent work was directed toward probing the effects of additional key parameters on the preparation of HPO.

**4. Reaction Time Course Experiments.** Six reaction conditions were selected from the catalysis survey for detailed monitoring of the yield of HPO and TPC. Five of the conditions had provided good yields of HPO, and the sixth condition (TFA in THF) had provided a mixture of HPO and TPC. The reactions were monitored spectrophotometrically from 1 min to 8 h. The results of these experiments are summarized in Table 2, and illustrative plots of the yield of HPO or TPC as a function of time

(22) Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864−2872.
(23) Geier, G. R., III; Littler, B. J.; Lindsey, J. S. *J. Chem. Soc., Perkin Trans. 2* **2001**, 701−711.
(24) Geier, G. R., III; Lindsey, J. S. *J. Chem. Soc., Perkin Trans. 2* **2001**, 677−686.

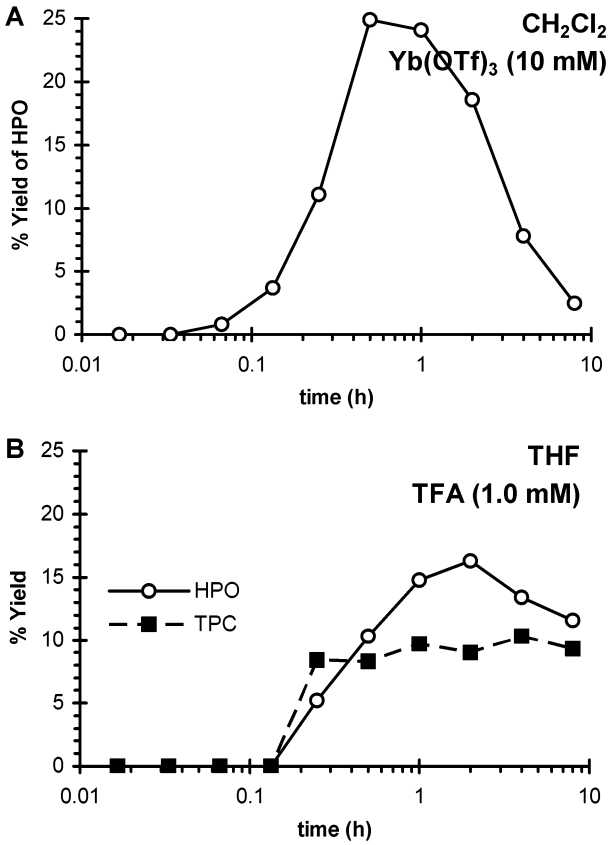



**FIGURE 2.** Yield of (A) HPO or (B) HPO and TPC as a function of condensation time for reactions of dipyrromethanedicarbinol **1a-OH** and **3** (2.5 mM each) at room temperature under the indicated conditions. The reactions were monitored spectrophotometrically. Note the log scale for time.

are provided in Figure 2 (see Supporting Information for the complete set of plots). The overall maximum yields of both HPO (~25%) and TPC (~10%) were in good agreement with results from the catalysis survey. Once again, TPC was only detected in the reaction involving TFA in THF. The yield of HPO as a function of time generally displayed an increase followed by a fairly sharp decline at longer reaction times (Figure 2A). In some cases (conditions for entries 3−5 in Table 2), the yield of HPO fell below 5%. This trajectory contrasts with the reaction of dipyrromethanecarbinol species leading to TPP[12] or TPC[11] under mild catalytic conditions, where the yield shows a fairly stable plateau before undergoing modest decline at long reaction times. The yield trajectory of TPC shown in Figure 2B displays such a plateau whereas the yield of HPO does not. The origin of the turnover in yield of HPO under the conditions examined is not clear, but as a practical matter, it suggests that these reactions need to be closely monitored in order to obtain a maximum yield of HPO. Finally, a trace level of tetraphenylporphyrin (<1%) was detected only under $Sc(OTf)_3$ catalysis at the 8 h time point.

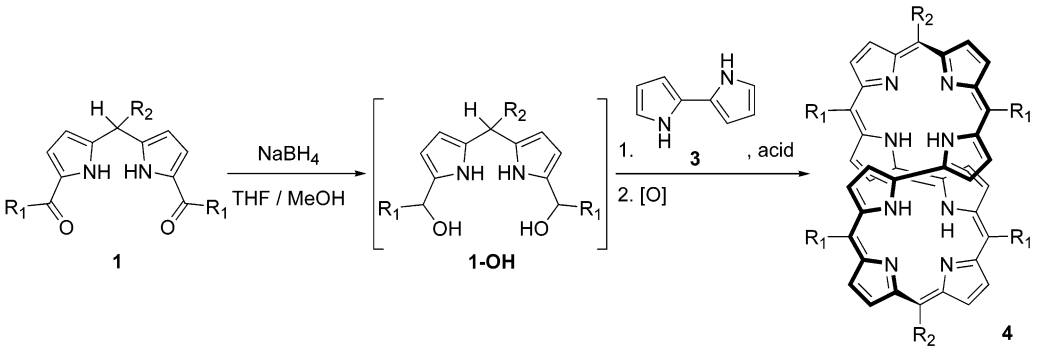
**5. Examination of Oxidation Conditions for Reactions Leading to HPO.** In our previous study of dipyrromethanedicarbinol reactions with excess pyrrole leading to meso-substituted corroles,[11] we found that judicious selection of oxidation conditions could be quite important for obtaining a maximum yield, minimizing byproducts, and facilitating isolation. Given our observation that DDQ interferes with the detection of HPO, we suspected that oxidation conditions leading to HPO might also be exacting.

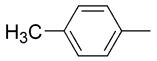
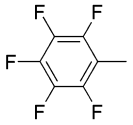
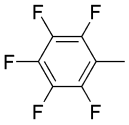
**(i) DDQ Oxidation.** Aliquots from the condensation of **1a-OH** and **3** (2.5 mM each) catalyzed by $Yb(OTf)_3$ (10 mM) in $CH_2Cl_2$ were treated with 0.5−40 equiv of DDQ relative to **1a-OH**. [The stoichiometric quantity of DDQ required for HPO synthesis is 2.5 equiv relative to **1a-OH**.] The yield of HPO was determined spectrophotometrically after a wash with aqueous dithionite, and the complexity of the mixtures was assessed by TLC. HPO was observed in aliquots treated with ≥2 equiv of DDQ, and the level of HPO gradually increased until a maximum yield of 24% was reached at 27 equiv (Supporting Information). Thus, HPO required a fairly large excess of DDQ to obtain the highest yield in contrast to reactions leading to porphyrin or corrole. TLC analysis of aliquots treated with lower than optimal levels of DDQ showed a small number of additional pigments. Those pigments were largely absent in aliquots treated with higher quantities of DDQ. The oxidation conditions employed in our protocol for spectrophotometric monitoring of the yield of HPO (6 equiv of DDQ relative to **1a-OH**) fall on the low end of the ideal oxidation conditions.

**(ii) *p*-Chloranil Oxidation.** Aliquots from the condensation of **1a-OH** and **3** (2.5 mM each) catalyzed by $Yb(OTf)_3$ (10 mM) in $CH_2Cl_2$ and quenched by the addition of triethylamine (5 equiv relative to the acid) were treated with 2.5−50 equiv of *p*-chloranil relative to **1a-OH**. The samples were heated to reflux and monitored from 30 min to 2 h by TLC and UV−vis. All of the conditions investigated provided yields of HPO in the range of 21−25% (Supporting Information). Thus, a wider range of *p*-chloranil quantity was tolerated compared to DDQ oxidation. None of the reactions produced detectable porphyrin, and *p*-chloranil did not affect the retention of HPO on silica. Nevertheless, *p*-chloranil was not a perfect oxidant, as a handful of pigments in addition to HPO were detected by TLC under all conditions. In general, *p*-chloranil afforded reaction mixtures of greater complexity than optimal conditions of DDQ oxidation. The presence of additional pigments (some of which were less polar than HPO) was expected to complicate purification of the HPO. Nevertheless, we favored *p*-chloranil over DDQ as *p*-chloranil did not cause HPO to bind tightly to silica. The best balance between yield of HPO and complexity of the reaction mixture was provided by ~5 equiv of *p*-chloranil relative to **1a-OH**.

**6. Preparative-Scale Synthesis of HPO.** Dipyrromethanedicarbinol **1a-OH** and 2,2′-bipyrrole **3** (0.50 mmol, 2.5 mM each) were treated with $Yb(OTf)_3$ (10 mM) in $CH_2Cl_2$ at room temperature (Scheme 3). The reaction was monitored spectrophotometrically at 15-min intervals. Consistent with analytical-scale reactions, a spectral yield of ~21% was obtained by 45 min. Triethylamine (5 equiv relative to acid) was added, followed by *p*-chloranil (2.5 mmol), and the mixture was heated to reflux for 45 min. HPO was isolated from other byproducts upon passage through a pad of silica gel. The pad was first washed with $CH_2Cl_2$ to elute a tan pigment followed by a brilliant blue pigment. TPC was not observed. HPO was eluted as a dark green band with $CH_2Cl_2$/ethyl acetate (25:2). HPO was further purified via a short silica gel

**SCHEME 3. Preparative Syntheses of Meso-Substituted [34]Octaphyrin(1.1.1.0.1.1.1.0)**




| Diacyl DPM | $R_1$ | $R_2$ | Octaphyrin | Yield | Mass |
|---|---|---|---|---|---|
| 1a |  |  | 4a | 25% | 64 mg |
| 1b |  |  | 4b | 23% | 65 mg |
| 1c |  |  | 4c | 16% | 25 mg |

column [$CH_2Cl_2$, then $CH_2Cl_2$/ethyl acetate (25:1)] to afford 64 mg, 25% yield. The isolated yield was very close to the spectral yield obtained while the reaction was monitored.

**Preparation of an Octaphyrin Bearing Different Substituents in Defined Locations.** To rigorously confirm the absence of scrambling under reaction conditions identified for the model reaction, we investigated the preparation of an octaphyrin bearing two different substituents in defined locations (Scheme 3). A preparative-scale reaction was performed in identical fashion to the model reaction. The octaphyrin **4b** (65 mg, 23%) was produced devoid of corrole and without detectable scrambling as evidenced by LD-MS analysis.

**Preparation of 5,10,19,24,29,38-Hexakis(pentafluorophenyl)[34]octaphyrin(1.1.1.0.1.1.1.0) (4c).** Analytical-scale reactions were followed for yield of HpFPO (UV−vis) as a function of time under the three best conditions identified from studies of the model reaction (Table 2, entries 2, 4, and 5).[25] The rate of reaction of **1c-OH** with **3** was found to vary widely under the three conditions investigated, and all were more sluggish than the model reaction. HpFPO was first detected at 24 h [$Dy(OTf)_3$ catalysis], 6 h [$Yb(OTf)_3$ catalysis], or 2 h [$Sc(OTf)_3$ catalysis], and the time of maximum yield was 24, 10, or 4 h, respectively, for the three catalysts (see the Supporting Information for plots of yield of HpFPO as a function of time). The maximum yields of HpFPO were also lower than those observed from the model reaction [17%, 12%, and 9%, respectively, for $Dy(OTf)_3$, $Yb(OTf)_3$, and $Sc(OTf)_3$]. TpFPC was not detected under any of the reaction conditions. The observation of a slower, less efficient reaction is consistent with our previous study of the reaction of a dipyrromethanedicarbinol with excess pyrrole leading to TpFPC.[11]

A preparative-scale reaction was performed under reaction conditions similar to those for **4a,b**, with the exceptions that 0.20 mmol of **1c-OH** and **3** was used due to limited quantities of **1c**, and $Dy(OTf)_3$ (10 mM) was employed. The reaction was allowed to proceed for 25 h, providing a spectral yield of 16% prior to oxidation with DDQ (5 equiv relative to **1c-OH**).[26] HpFPO was purified by passing the reaction mixture through a silica pad and eluting with $CH_2Cl_2$, followed by crystallization from $CH_2Cl_2$/methanol. An isolated yield, after crystallization, of 16% (25 mg) was obtained. TpFPC was not observed.

**Characterization of Meso-Substituted [34]Octaphyrin(1.1.1.0.1.1.1.0) Species (4a−c).** The characterization of HpFPO **4c** was the most straightforward of the three octaphyrins. HpFPO is dark green in solution and a maroon powder in the solid state. The characteristic UV−vis spectrum was observed, and satisfactory LD-MS, high-resolution FAB-MS, and elemental analysis data were obtained. The $^1H$ NMR spectrum recorded in $CDCl_3$ was in accordance with expectations (Supporting Information). The N−H resonance appeared as a broad singlet at 12.9 ppm, and three doublets arising from the $\beta$-pyr-

(25) Our initial attempt was aborted after it became clear that the methodology for spectrophotometric monitoring required modification for this particular reaction. The aqueous basic dithionite wash was not helpful, and the $CH_2Cl_2$/ethyl acetate (25:1) solvent used to elute the HpFPO from the silica pad was too polar, allowing impurities with significant absorbance to also elute. Thus, the dithionite wash was omitted and $CH_2Cl_2$ was used to elute HpFPO from the silica pad.

(26) We did not attempt to use *p*-chloranil because DDQ did not appear to interfere with the isolation of HpFPO, and we had previously encountered difficulties when attempting to use *p*-chloranil in the synthesis of TpFPC.

role protons were observed at 6.36, 6.25, and 5.28 ppm with integrated peak areas of 4, 8, and 4, respectively. The downfield chemical shift of the N−H protons and the upfield chemical shift of the $\beta$-pyrrole protons suggest that the overall macrocycle is nonaromatic despite a main conjugation path of 34 $\pi$-electrons. It is probable that HpFPO adopts a chiral figure-eight structure akin to that reported for the $\beta$-ethyl-substituted octaphyrin[5] as the two molecules share very similar spectral properties.

Like HpFPO, octaphyrins **4a** and **4b** afford green solutions. In the solid state the two species were obtained as rust-red crystals with a metallic luster consistent with the reported appearance of the analogous $\beta$-ethyl-substituted octaphyrin.[5] Characteristic UV−vis spectra were observed from both **4a** and **4b**, and satisfactory LD-MS and high-resolution FAB-MS data were obtained. Neither species afforded satisfactory elemental analysis, even after extended drying under vacuum. LD-MS and TLC analysis of **4a,b** did not detect significant impurity (Supporting Information). $^1$H NMR spectra recorded at room temperature in $CDCl_3$ provided very broad, poorly resolved signals at 5.9−6.7 and 6.7−8.0 ppm, reminiscent of a paramagnetic species (Supporting Information). The addition of methanol, commonly employed to sharpen signals for meso-substituted corrole,[27] had no effect. Vogel and co-workers reported adding thiophenol as a radical trapping agent when recording the $^1$H NMR spectrum of their octaphyrin.[5] Titration of both **4a** and **4b** with a solution of thiophenol in $CDCl_3$ resulted in substantial but incomplete improvement. HPO provided a broad singlet at ∼13 ppm (N−H), and doublets corresponding to the $\beta$-pyrrole protons appeared at 6.27, 6.24, and 5.32 ppm. However, the aromatic region still displayed a complex combination of broad and sharp signals. The octaphyrin **4b** provided a similar spectrum with the exception that $\beta$-pyrrole protons were observed at 6.26 and 5.31 ppm, and a singlet appeared at 2.34 ppm due to the *p*-tolyl methyl groups. Sprutta and Latos-Grazynski have reported dramatic sharpening of resonances upon cooling for a figure-eight tetrathiaoctaphyrin.[28] In the case of **4a,b**, cooling to 240 K had no effect in the absence of thiophenol and only a modest effect in the presence of thiophenol. The chemical shifts of the N−H and $\beta$-pyrrole protons along with the UV−vis spectra suggest that **4a,b** are also nonaromatic. The source of the difficulty in obtaining well-resolved NMR spectra for **4a** and **4b** remains to be definitively established.

**Stability of Meso-Substituted [34]Octaphyrin(1.1.1.0.1.1.1.0) Species (4a−c).** Dilute solutions of octaphyrins **4a**−**c** were prepared in $CH_2Cl_2$ in cuvettes in the dark, and UV−vis spectra were recorded over time upon exposure to ambient light. The UV−vis spectra for each octaphyrin were unchanged for at least 24 h of exposure. Thus, the meso-substituted [34]octaphyrin(1.1.1.0.1.1.1.0) species appear to be quite stable in comparison to some meso-substituted corroles.[11]

## Conclusions

We have found that the reaction of dipyrromethanedicarbinols with 2,2′-bipyrrole carried out under a variety of reaction conditions generally provides [34]octaphyrin(1.1.1.0.1.1.1.0) rather than corrole. Thus, preferential formation of the octaphyrin species extends beyond reactions involving 2,2′-bipyrroles bearing $\beta$-substituents. It is attractive to attribute the preference, in part, to the conformational energetics of 2,2′-bipyrrole that favor the anti form appropriate for octaphyrin formation. It would be interesting to examine reactions of 2,2′-bipyrrole known to afford expanded porphyrinic macrocycles bearing bipyrrole linkage(s) in the syn orientation for evidence of competing reaction pathways that involve species derived from the anti form of 2,2′-bipyrrole. Our refinement of the synthesis of 2,2′-bipyrrole should assist work in this area. Although a majority of the conditions in our survey led to exclusive formation of HPO, a subset of conditions (TFA in THF) afforded modest levels of TPC (10%) in addition to HPO. The observation of a relatively good yield of HPO from a subset of the reactions performed in $CH_2Cl_2$ facilitated the isolation of meso-substituted [34]octaphyrin(1.1.1.0.1.1.1.0) species for the first time. In addition to HPO, an octaphyrin bearing two different meso substituents in defined locations and an octaphyrin possessing electron-withdrawing pentafluorophenyl substituents were prepared. One can envision the incorporation of a wide variety of meso substituents for tuning macrocycle properties and/or for creating elegant architectures—as has been done with great success with meso-substituted porphyrins. Preliminary examination of the properties of the [34]octaphyrin(1.1.1.0.1.1.1.0) species revealed features consistent with the absence of overall aromaticity. The structures of the meso-substituted octaphyrins are probably similar to the known chiral figure-eight $\beta$-substituted [34]octaphyrin(1.1.1.0.1.1.1.0). All of the octaphyrins displayed excellent stability in dilute solution. The interference with the detection of HPO by DDQ akin to that already observed with TPC further raises the possibility that DDQ might mask the presence of other interesting species in some instances. This study extends the application of dipyrromethanedicarbinol species and mild acid catalysts in the synthesis of porphyrinic macrocycles.

## Experimental Section

**UV−Vis Spectrophotometric Determination of the Yield of [34]Octaphyrin(1.1.1.0.1.1.1.0) Species and Corrole.** Reactions of **1-OH** with **3** were monitored by transferring an aliquot (200 $\mu$L) of the condensation reaction mixture by syringe to a 1.8 mL microcentrifuge tube containing a DDQ solution (300 $\mu$L, 10 mM in toluene). The mixture was vortex mixed for 2−5 s. To the oxidized reaction mixture was added an aqueous solution of 5% $Na_2S_2O_4$ and 5% NaOH (0.5 mL), followed by vigorous shaking for 10 s. Samples were spun in a microcentrifuge at 1000*g* for 1−3 min to hasten the separation of the aqueous and organic layers. A portion of the upper organic layer (50 $\mu$L) was transferred by syringe to a Pasteur pipet filled two-thirds full with silica gel (∼1.5 g).[29] The sample was eluted with three 1-mL portions of $CH_2Cl_2$/ethyl acetate (25:1). Solvent was driven off the column with a handheld pipet tool. The eluent was transferred to a cuvette and the UV−vis spectrum was recorded (see Supporting Information for a discussion of the calculations). For monitoring reactions leading to **4c**, the aqueous dithionite wash was omitted, and $CH_2Cl_2$ was used to elute **4c** from the silica pad.

(27) Ka, J.-W.; Cho, W.-S.; Lee, C.-H. *Tetrahedron Lett.* **2000**, *41*, 8121−8125.

(28) Sprutta, N.; Latos-Grazynski, L. *Chem. Eur. J.* **2001**, *7*, 5099−5112.

(29) Geier, G. R., III; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1596−1603.

**Refined Synthesis of 2,2′-Bipyrrole (3).**[14] To a 500 mL flask were added **2** (1.72 g, 12.8 mmol) and diglyme (200 mL). Argon was continuously bubbled through the solution, and the mixture was heated to ~60 °C to dissolve **2**. To the solution was added 10% palladium on carbon (1.70 g, 1.60 mmol of palladium). The mixture was heated to reflux, and monitored by GC/MS at 15 min intervals (Supporting Information). After 1 h of reflux, the hot reaction mixture was passed through a fluted filter. The collected palladium on carbon was washed with ~100 mL of hot ethyl acetate. The lavender solution was evaporated to dryness, and the gray residue was gently rinsed with three portions of hexanes (10 mL) to wash away residual diglyme. The crude **3** was purified by sublimation (90 °C, 200 mTorr) to afford an off-white powder (1.28 g), followed by crystallization from diethyl ether/hexanes to afford a white crystalline solid [1.2 g, 71%, mp 189−190 °C (lit mp 189−190 °C)[14]]. Anal. Calcd for $C_8H_8N_2$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.76; H, 6.16; N, 21.27. Analytical data are consistent with literature values.[16] The 2,2′-bipyrrole was stored in the dark at −15 °C to avoid decomposition.

**General Procedure for the Preparative-Scale Syntheses of [34]Octaphyrin(1.1.1.0.1.1.1.0), Given for 5,10,19,-24,29,38-Hexaphenyl[34]Octaphyrin(1.1.1.0.1.1.1.0) (4a).** The reduction of **1a** (215 mg, 0.500 mmol) with $NaBH_4$ (946 mg, 25.0 mmol) in THF/methanol (40 mL, 3:1) afforded the corresponding carbinol **1a-OH**.[19] The carbinol was dried under vacuum for 30 min and then immediately subjected to condensation with **3** (66.0 mg, 0.500 mmol) in the presence of Yb(OTf)$_3$ (1.24 g, 2.00 mmol) in $CH_2Cl_2$ (200 mL) at room temperature. The reaction was monitored spectrophotometrically at 15 min intervals. At a reaction time of 50 min, triethylamine (1.39 mL, 10.0 mmol) was added, followed by oxidation with *p*-chloranil (615 mg, 2.50 mmol) at reflux open to air for 45 min. The entire reaction mixture was filtered through a pad of silica gel and eluted with $CH_2Cl_2$. A fast-moving blue pigment was allowed to elute, and then the solvent was changed to $CH_2Cl_2$/ethyl acetate (25:2). The dark green band of HPO eluted quickly. The fractions containing HPO were concentrated to dryness. The HPO sample was redissolved in $CH_2Cl_2$ (50 mL), adsorbed onto silica gel (6 g), concentrated, and purified by chromatography [silica, $CH_2Cl_2$, and then $CH_2Cl_2$/ethyl acetate (25:1)]. The green band containing HPO was collected, concentrated, and dried under vacuum, affording HPO (64 mg, 25%) that was subsequently crystallized from $CH_2Cl_2$/methanol to afford rust-red crystals with a metallic luster. $\lambda_{abs}$ ($CH_2Cl_2$, $\epsilon \times 10^{-3}$) 340 (38.9), 397 (81.9), 518 (18.9), 661 (133), 810 (12.8), 1083 (12.4); $^1$H NMR (Supporting Information); LD-MS obsd 1050.1 ($M^+$); HRMS (FAB) obsd 1051.4299 ($MH^+$), calcd 1051.4237 ($MH^+$) ($C_{74}H_{50}N_8$).

**5,24-Diphenyl-10,19,29,38-tetrakis-(4-methylphenyl)-[34]octaphyrin(1.1.1.0.1.1.1.0) (4b).** The reduction of **1b** (229 0.500 mmol) followed by condensation with **3** (66.0 mg, 0.500 mmol) in the presence of Yb(OTf)$_3$ (1.24 g, 2.00 mmol) in $CH_2Cl_2$ (200 mL) for 40 min at room temperature, addition of triethylamine (1.39 mL, 10.0 mmol), oxidation with *p*-chloranil (615 mg, 2.50 mmol) at reflux for 45 min, and purification identical to the general procedure afforded 4**b** (65 mg, 23%) that was subsequently crystallized from $CH_2Cl_2$/ methanol to afford rust-red crystals with a metallic luster. $\lambda_{abs}$ ($CH_2Cl_2$, $\epsilon \times 10^{-3}$) 343 (39.3), 404 (91.0), 519 (21.7), 662 (137), 812 (14.9), 1083 (13.1);$^1$H NMR (Supporting Information); LD-MS obsd 1106.3 ($M^+$); HRMS (FAB) obsd 1107.5021 ($MH^+$), calcd 1107.4863 ($MH^+$) ($C_{78}H_{58}N_8$).

**5,10,19,24,29,38-Hexakis(pentafluorophenyl)[34]-octaphyrin(1.1.1.0.1.1.1.0) (4c).** The reduction of **1c** (140 mg, 0.200 mmol) was followed by condensation with **3** (26.4 mg, 0.200 mmol) in the presence of Dy(OTf)$_3$ (0.488 g, 0.800 mmol) in $CH_2Cl_2$ (80 mL) for 25 h at room temperature, addition of triethylamine (0.56 mL, 4.0 mmol), and oxidation with DDQ [227 mg, 1.00 mmol dissolved in toluene (5 mL)] at room temperature for 1 h. The entire reaction mixture was filtered through a pad of silica gel and eluted with $CH_2Cl_2$. The dark green band of HpFPO eluted quickly. The fractions containing HpFPO were concentrated to dryness. Without further purification, HpFPO was crystallized from $CH_2Cl_2$/methanol to afford a maroon powder (25 mg, 16%). $\lambda_{abs}$ ($CH_2Cl_2$, $\epsilon \times 10^{-3}$) 343 (39.3), 404 (91.0), 519 (21.7), 662 (137), 812 (14.9), 1083 (13.1);$^1$H NMR [$CDCl_3$] $\delta$ 5.28 (d, $J$ = 3.8 Hz, 4H), 6.25 (d, $J$ = 4.8 Hz, 8H), 6.36 (d, $J$ = 4.8 Hz, 4H), 12.9 (br s, 4H); LD-MS obsd 1589.7 ($M^+$); HRMS (FAB) obsd 1591.1400 ($MH^+$), calcd 1591.1410 ($MH^+$) ($C_{74}H_{20}F_{30}N_8$). Anal. Calcd for $C_{74}H_{20}F_{30}N_8$: C, 55.87; H, 1.27; N, 7.04. Found: C, 56.23; H, 1.58; N, 7.30.

**Acknowledgment.** This research was supported by an award from Research Corporation. Partial support for this work was provided by the National Science Foundation's Course, Curriculum, and Laboratory Improvement Program under Grant DUE-0088227. We thank Tim LeSaulnier for the preparation of **1c** and the Research Council of Colgate University for a publication grant. High-resolution FAB mass spectra were obtained at the Mass Spectrometry Laboratory for Biotechnology at North Carolina State University. Partial funding for the facility was obtained from the North Carolina Biotechnology Center and the NSF.

**Supporting Information Available:** General experimental methods; synthesis of 2,2′-(1′-pyrrolinyl)pyrrole **2**, description of analytical-scale reactions of **2** leading to 2,2′-bipyrrole **3**, and GC/MS monitoring of reactions of **2** leading to **3**; discussion of the calculations for the spectrophotometric determination of the yield of octaphyrin and corrole; experimental details pertaining to the survey of catalyst conditions, reaction time course experiments, examination of oxidation conditions leading to HPO, and stability experiments; GC data from the refinement of the synthesis of **3**; plots of the yield of HPO as a function of acid concentration and of oxidant quantity and plots of the yield of HPO or HpFPO as a function of time; discussion of TLC analysis of **4a,b**; and UV−vis, LD-MS, and $^1$H NMR spectra of octaphyrins **4a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO049131Z