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A Survey of Acid Catalysis and Oxidation Conditions in the Two-Step, One-Flask Synthesis of Meso-Substituted Corroles via Dipyrromethanedicarbinols and Pyrrole

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The reaction of dipyrromethanedicarbinols with pyrrole leading to meso-substituted corroles was investigated to determine whether mild acid catalysts [$Dy(OTf)_3$, $Yb(OTf)_3$, $Sc(OTf)_3$, and $InCl_3$] known to provide porphyrins from dipyrromethanecarbinol species while suppressing undesired reversibility (resulting in scrambling) are applicable to reactions affording corrole, and to explore the requirements of the oxidation step. We examined a model reaction leading to *meso*-triphenylcorrole (TPC) to survey the effect of acid catalyst, acid concentration, ratio of pyrrole to dipyrromethanedicarbinol, oxidant, oxidant quantity, and reaction time on the yield of TPC (by UV−vis) in reactions performed at room temperature in CH_2Cl_2. Key to this survey was a modification of the well-known spectrophotometric method for monitoring reactions leading to porphyrin. The survey revealed that TPC could be prepared via a subset of the mild acid catalysts [$Dy(OTf)_3$ and $Yb(OTf)_3$], and a preparative-scale reaction afforded an isolated yield of TPC of 49%, devoid of porphyrin. Suppression of reversible processes was further demonstrated by the synthesis of three corroles bearing different meso substituents in defined locations in isolated yields ranging from 50% to 80%. The reaction conditions were applicable to a dipyrromethanedicarbinol bearing electron-withdrawing pentafluorophenyl substituents—provided that the reaction time of the condensation step was increased. We identified circumstances under which DDQ can cause severe interference with the detection and isolation of some corroles, we found that the yield and purity of the corrole depend on judicious selection of oxidation conditions, and we assessed the sensitivity toward light of dilute solutions of the corroles prepared in this study.

Introduction

In recent years, studies of porphyrinic macrocycles with expanded, contracted, isomeric, and heteroatom modified core structures have intensified.[1] New molecules have been discovered such as N-confused porphyrin,[2] and well-known molecules have enjoyed a resurgence in interest. Corrole is an important example of the latter category. The relationship of corrole to the corrin macrocycle of vitamin B12 led to past interest,[3] and recent progress in synthetic methodology has helped to fuel the current interest in corrole's unique properties. The core structure of corrole is distinguished from that of porphyrin by the absence of one of the four meso-positions, resulting in a direct bipyrrole linkage. This deviation leads to an overall contraction of the macrocycle core, and results in a free base structure containing three "pyrrole-type" hydrogens. These structural differences endow corrole with unique properties (e.g., stabilization of metal ions in unusually high oxidation states relative to porphyrin[4]). The interesting core structure of corrole also presents a synthetic challenge. While the syntheses of β-substituted corroles date back to the historic efforts to prepare vitamin B12,[3] such syntheses involved inconvenient stepwise procedures. Unlike the case with porphyrin, syntheses of meso-substituted corroles from readily available starting materials did not exist prior to the late 1990s.[5,6]

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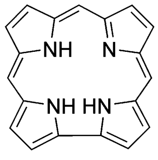
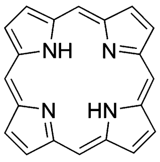


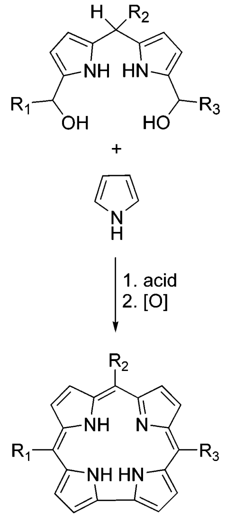
corrole



porphyrin

The recent progress in the preparation of meso-substituted corroles has largely mirrored the major developments in the syntheses of meso-substituted porphyrins—albeit with a sharply compressed time frame.[7] The initial independent reports by Gross[5] and Paolesse[6] of the syntheses of meso-substituted corroles bearing three identical meso substituents (A_3-corroles) from reaction of pyrrole with an arylaldehyde parallel the Rothemund[8] and Adler[9] syntheses of tetraarylporphyrins. More recently, Paolesse and co-workers[10] and Gryko and co-worker[11] have reported two-step, one-flask conditions that are similar to the Lindsey method.[12] Successful syntheses of A_3-corroles were closely followed by syntheses of corroles bearing two different substituents in an alternating pattern (ABA-corroles) from a dipyrromethane precursor.[11,13−15] This approach is akin to the stepwise preparation of *trans*-A_2B_2-porphyrins.[16] Close on the heels of those studies were reports from Guilard, Gryko, and co-workers[17a] and Gryko and co-workers[17b] describing the synthesis of corroles bearing up to three different meso substituents in defined locations via the reaction of a dipyrromethanedicarbinol with excess pyrrole, and a report from Collman and co-worker involving reaction of a dipyrromethanedicarbinol with 2,2′-bipyrrole.[18] Both approaches are similar to the preparation of porphyrins bearing up to four different substituents in defined locations.[19]

SCHEME 1. Dipyrromethanedicarbinol + Pyrrole Route to Meso-Substituted Corrole



Given our involvement in previous studies of reactions of dipyrromethanecarbinols leading to meso-substituted porphyrins[20]—especially the identification of mild acid catalysts that suppress undesired reversibility leading to scrambling[21]—a dipyrromethanedicarbinol + pyrrole route to meso-substituted corroles was attractive to us (Scheme 1). In a practical sense, this route could allow the tuning of macrocycle properties by the incorporation of a broad range of meso substituents in defined locations, and it would avoid the formation of porphyrin byproduct thereby simplifying the purification of the corrole. In a fundamental sense, we were interested in comparing the requirements of dipyrromethanedicarbinol reactions leading to corroles to those of similar reactions leading to porphyrins. It is that latter point that is a primary focus of this paper.

Since the initiation of our study, Guilard, Gryko, and co-workers have published the results of their related work.[17] The study reported herein is complementary to their reports. Our study was aimed at examining reaction conditions with close analogy to those developed for the preparation of porphyrins from dipyrromethanecarbinol species.[21] A model reaction of a dipyrromethanedicarbinol with pyrrole leading to *meso*-triphenylcorrole (TPC) was investigated so that our results could be compared to the rich data available from studies of the synthesis of *meso*-tetraphenylporphyrin (TPP).[20,22] In complementary fashion, Guilard, Gryko, and co-workers primarily investigated reactions in neat pyrrole with TFA catalysis, and their model reaction utilized a dipyrromethanedicarbinol

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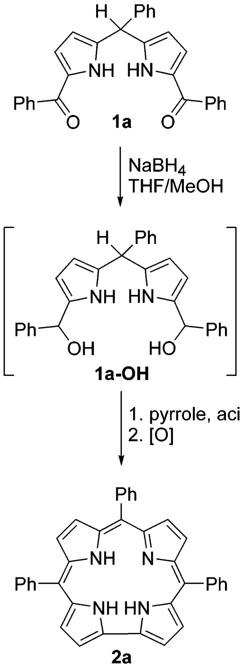
bearing a strongly electron-withdrawing pentafluorophenyl substituent.[17a] They do report an attempt to employ the mild acid $Yb(OTf)_3$ in CH_2Cl_2, but they obtained a poor yield of corrole (2%) and they did not report investigating such conditions further.

In this paper we describe studies of the dipyrromethanedicarbinol + pyrrole route to meso-substituted corroles. A primary aim was to determine whether mild conditions [$Yb(OTf)_3$, $Dy(OTf)_3$, $Sc(OTf)_3$, or $InCl_3$ catalysis in CH_2Cl_2] of proven success in reactions of dipyrromethanecarbinol species leading to porphyrin are amenable to syntheses of corroles. Toward that end, we systematically investigated the effects of key reaction parameters (acid catalyst, acid catalyst concentration, ratio of pyrrole to dipyrromethanedicarbinol, and reaction time) on a model reaction leading to TPC formation. The yield of TPC in analytical-scale reactions was assessed by a modification of the UV–vis spectrophotometric method commonly employed in porphyrin syntheses.[12] We also examined the effects of important reaction parameters in the oxidation step (oxidant and quantity of oxidant) as it has been proposed that macrocycle formation occurs during this step,[6b,10,11,14,17,23] and the literature has accumulated a variety of oxidation methods without systematic comparison. Results from analytical-scale experiments were confirmed by representative preparative-scale syntheses. Undesired reversibility (leading to scrambling or formation of porphyrin) was assessed by UV–vis and TLC analysis for the presence of TPP.[24] The suppression of scrambling was further confirmed by laser desorption mass spectrometry (LD-MS) and TLC analysis of three corroles bearing different substituents in defined locations prepared under one of the best reaction conditions identified. The applicability of this condition to the preparation of corroles bearing electron-withdrawing substituents was investigated via a reaction leading to 5,10,15-tris(pentafluorophenyl)corrole (TpFPC). Finally, the sensitivity toward light of the corroles prepared in this study was qualitatively compared by monitoring changes in UV–vis spectra as a function of time.

Results and Discussion

Investigation of the Model Reaction Leading to *meso*-Triphenylcorrole (2a). The studies of the model reaction of dipyrromethanedicarbinol **1a-OH** (prepared freshly via $NaBH_4$ reduction of 1,9-bis-benzoyl-5-phenyldipyrromethane **1a**) with pyrrole leading to TPC **2a** (Scheme 2) involved the development of a spectrophotometric method to quantify TPC in analytical-scale reactions, acid screening experiments, an examination of the ratio of pyrrole to dipyrromethanedicarbinol, reaction time course experiments, oxidant screening experiments, and a preparative-scale synthesis of TPC. Key to these studies was our observation that **1a** could be purified without chromatography—affording the gram quantities required for systematic, analytical-scale reactions (Supporting Information).

SCHEME 2. The Model Reaction Leading to TPC



1. Determination of the Yield of Corrole in Analytical-Scale Reactions. UV–vis spectrophotometric analysis was investigated for the rapid determination of the yield of TPC from an aliquot of a crude reaction mixture due to the success of UV–vis monitoring of reactions leading to porphyrin,[12] and reports of spectrophotometric monitoring of reactions affording corrole[6,10,18] (although no details of the methodology as applied to corrole have been published to the best of our knowledge). Despite the encouragement, we expected that UV–vis monitoring of TPC would be challenging. The molar extinction coefficient of the Soret band of TPC is about one fifth that of TPP,[6] so there is heightened potential for interference from other absorbing species.[25] TPC is known to be both basic and acidic, and the UV–vis spectra of the various species differ.[5a,6a] Reaction aliquots containing residual acid catalyst or excess weak base used to neutralize the acid could give rise to inconsistent spectra.

To address these concerns, a series of experiments were performed that utilized solutions of authentic TPC[6] doped with individual and combinations of species that would be present in crude, oxidized reaction mixtures (acid catalyst, DDQ, pyrrole, triethylamine, and oligopyrrylmethenes). DDQ was found to severely interfere with the detection of TPC by causing a near total loss of the Soret band (Figure 1b) and strong retention of TPC on silica TLC. The latter observation is consistent with a report of TPC retention by a silica pad employed prior to HPLC analysis of DDQ oxidized reaction mixtures of pyrrole +

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[25] The porphyrin byproduct produced in some reported reactions leading to corrole would interfere with spectral monitoring of corrole given the similar λ_{max} of the Soret bands of porphyrin and corrole and the greater molar extinction coefficient of the porphyrin. In our reaction route, porphyrin can only arise as the result of undesired reversibility. Thus, spectral monitoring of corrole generated from reactions devoid of scrambling will not suffer from interference due to porphyrin.

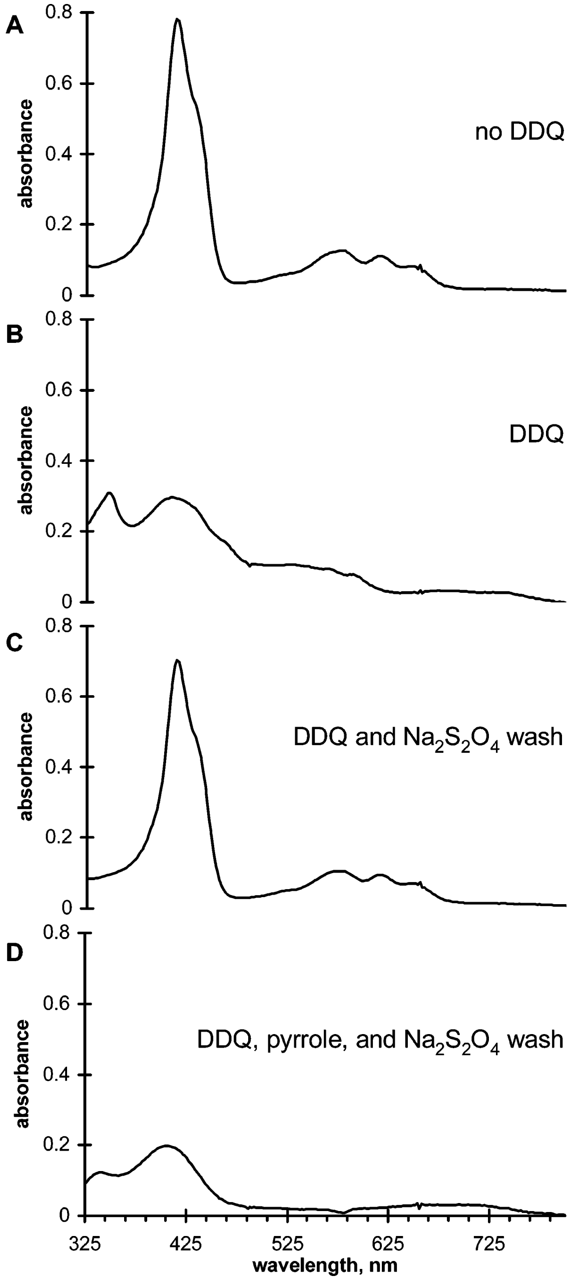

FIGURE 1. Comparison of UV−vis spectra of TPC under conditions that mimic aspects of the spectrophotometric analysis of crude reaction mixtures. An aliquot (200 μL) of a solution of TPC in CH_2Cl_2 (0.625 mM) was treated as follows: (A) diluted in toluene (300 μL), (B) diluted in a DDQ solution (10 mM) in toluene (300 μL), (C) diluted in a DDQ solution (10 mM) in toluene (300 μL) followed by washing with an aq solution of 5% $Na_2S_2O_4$ and 5% NaOH, and (D) addition of pyrrole (100 equiv relative to TPC), followed by dilution with a DDQ solution (10 mM) in toluene (300 μL) and washing with an aq solution of 5% $Na_2S_2O_4$ and 5% NaOH. A portion (50 μL) of each solution was then diluted in CH_2Cl_2/EtOH (3:1, 3 mL) and UV−vis spectra were recorded.

benzaldehyde.[26] DDQ interference was reversible, as vigorous shaking of the mixture in an aq basic solution of sodium dithionite led to the reappearance of the Soret band (Figure 1c), and the typical retention on silica TLC. It has been reported that DDQ produces an adduct with tetraphenylporphyrin upon 3−5 days of exposure.[27] A DDQ/TPP (2:1) adduct was identified, and the spectral evidence was consistent with the interaction of a lone pair of a pyrrolenine nitrogen of the TPP with an empty π^* orbital of a −CN group of DDQ.[27] Nevertheless, the rapid and severe interference of DDQ in the detection of triphenylcorrole is interesting given that DDQ has been employed in syntheses of a variety of corroles.[5,11,13,14,15,17,18,23,28,29] The presence of other absorbing species in the sample matrix (e.g., oligopyrrylmethenes) interfered with detection of TPC. We found that passing an aliquot of the oxidized reaction mixture through a Pasteur pipet filled with silica followed by elution with CH_2Cl_2 removed interfering species.[30] Excess pyrrole (>50-fold relative to TPC) partly disrupted the interaction of TPC with DDQ according to analysis by TLC, but the UV−vis spectrum was still sharply altered. The Soret band of TPC was broadened and its intensity was attenuated by the combined presence of pyrrole and DDQ, and the interference persisted after dithionite wash (Figure 1d) and filtration through a silica pipet. Although we were unable to identify a suitable additive that could counteract the interference brought on by pyrrole + DDQ, we found that the effect was constant at >6-fold excess pyrrole relative to TPC, and that the absorbance of the broadened Soret band (~420 nm) varied linearly with the concentration of TPC. Thus, the level of TPC in the reaction mixtures could be reproducibly quantified despite the altered appearance of the spectra. The optimum methodology to emerge from these studies is as follows: oxidation of an aliquot of a reaction mixture with a solution of DDQ, washing the oxidized mixture with aq dithionite, passing an aliquot of the washed mixture through a Pasteur pipet containing silica gel, and recording the UV−vis spectrum of the eluent. This protocol provided spectra with the appearance of that shown in Figure 1d.

2. Acid-Screening Experiments. Acid-screening experiments were performed to identify suitable reaction conditions for the condensation step. These experiments utilized **1a-OH** (2.5 mM) in CH_2Cl_2 at room temperature in keeping with conditions previously identified for the analogous reaction providing porphyrin.[21] 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.[31] TFA catalysis was also investigated as a control for reversible processes, as previous studies of analogous reactions leading to porphyrin detected scrambling under elevated concentration of TFA in CH_2Cl_2.[20,21] Pyrrole was employed at concentrations of 125, 250, and 500 mM, corresponding to a ratio of pyrrole to carbinol unit of 25, 50, and 100, respectively. The yield of TPC was determined spectrophotometrically at reaction times of 15 min

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[31] 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 in CH_2Cl_2 and the reaction mixtures were heterogeneous as reported previously.[21,26]

TABLE 1. Condensation Conditions Providing Good Yields of TPC Devoid of TPP Byproduct for Each Concentration of Pyrrole Investigated under Catalysis by $Dy(OTf)_3$, $Yb(OTf)_3$, or TFA[a]

entry	acid	[acid], mM[b]	[pyrrole], mM	% yield of TPC[c]
1	$Dy(OTf)_3$	1.0	125	54
2	$Dy(OTf)_3$	1.0	250	63
3	$Dy(OTf)_3$	3.2	500	65
4	$Yb(OTf)_3$	0.32	125	40
5	$Yb(OTf)_3$	0.32	250	58
6	$Yb(OTf)_3$	0.32	500	60
7	TFA	0.32	125	43
8	TFA	0.32	250	56
9	TFA	0.32	500	66

[a] The reactions were performed with **1a-OH** (2.5 mM) on a 5−10 mL scale in CH_2Cl_2 at room temperature. The reactions were monitored at 15 min and 1 h. [b] The lowest acid concentration for each concentration of pyrrole that provided a near-maximal yield of TPC. Higher quantities of $Dy(OTf)_3$ and $Yb(OTf)_3$ commonly provided yields of corrole similar to those reported here. [c] The highest yield (UV−vis) at either of the two time points is reported.

and 1 h. The presence of TPP (indicating undesired reversible processes) was assessed by TLC and by UV−vis.

The best reaction conditions identified from the acid-screening experiments are summarized in Table 1 (see the Supporting Information for plots of the yield of TPC as a function of acid concentration). The highest yield of TPC with no detected TPP was provided by $Dy(OTf)_3$, $Yb(OTf)_3$, and low concentrations of TFA (≤1.0 mM). TFA concentrations of >3.2 mM provided no detectable TPC and instead gave low levels of TPP (1−3%) indicative of undesired reversible processes. This observation is consistent with previous reports pertaining to dipyrromethanecarbinol reactions leading to porphyrin.[20] $InCl_3$ and $Sc(OTf)_3$ provided detectable tetraphenylporphyrin (3−10%) at all acid quantities investigated. The level of detected TPP declined with an increasing ratio of pyrrole to carbinol units; nevertheless, it was surprising to obtain any TPP from these reactions given the mild nature of the catalysts and the large excess of pyrrole. The origin of this result is not clear, but the observation suggests that each acid should be investigated when adapting reaction conditions devised for porphyrin syntheses to the synthesis of other macrocycles. The highest spectral yields of TPC obtained under the best conditions (~65%) are in line with the 65% yield of TPC obtained by Lee and co-workers upon DDQ oxidation of a linear triaryltetrapyrrane.[23] The yield of TPC generally increased upon an increase in ratio of pyrrole to carbinol units from 25:1 to 50:1 (45−55% and 55−65%, respectively) whereas little additional improvement was observed at the 100:1 ratio. The yield of TPC was fairly insensitive to the quantity of $Dy(OTf)_3$ and $Yb(OTf)_3$. This observation is consistent with a report pertaining to dipyrromethanecarbinol reactions leading to porphyrin.[21] Catalysis by TFA in acetonitrile solvent[19] was also investigated, and found to provide poorer results in terms of the yield and purity of the isolated TPC (Supporting Information).

3. Ratio of Pyrrole to Dipyrromethanedicarbinol. Analytical-scale reactions employing ratios of pyrrole to **1a-OH** ranging from 2:1 to 5760:1 were performed in CH_2Cl_2 at room temperature under catalysis by $Dy(OTf)_3$ (1.0 mM). The yield of TPC was monitored spectrophotometrically at 15 min and 1 h. The maximum yield of TPC (~65%) was obtained at a ratio of pyrrole to carbinol units ranging from 50:1 to 244:1 (Figure 2). This result suggests that optimal formation of the tetrapyrrane intermediate requires a fairly large excess of pyrrole, and that our initial selection of conditions for the acid-screening experiments was appropriate. The decline in the yield of TPC at the highest quantities of pyrrole could stem from interference with the acid catalyst by the weakly basic pyrrole or by the formation of oligomers containing multiple bipyrrole units.[17b] Low levels of TPP (<3%) were detected at the lowest ratios of pyrrole to carbinol units investigated (≤2.5:1). This observation suggests that even with this mild acid, reversible processes can occur if there is insufficient pyrrole to rapidly react with the free carbinol units. Such reversibility is not observed in the stoichiometric reaction of a dipyrromethanedicarbinol and a dipyrromethane leading to porphyrins bearing similar substituents.[21]

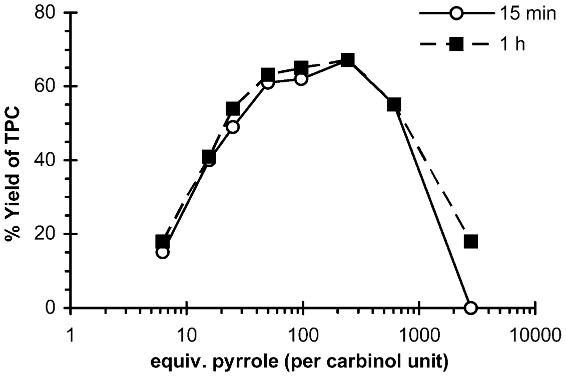

FIGURE 2. Yield of TPC as a function of the ratio of pyrrole to dipyrromethanedicarbinol for reactions of **1a-OH** (2.5 mM) with $Dy(OTf)_3$ (1.0 mM) in CH_2Cl_2 at room temperature. Reactions were monitored spectrophotometrically for the yield of TPC.

4. Reaction Time Course Experiments. Reactions were performed under three of the best reaction conditions identified from the acid-screening experiments (Table 1, entries 2, 5, and 9), and the yield of TPC was monitored spectrophotometrically from 1 min to 24 h (Figure 3). The maximum yields of TPC (~65%) were in good agreement with the earlier results of the screening experiments. The reaction under TFA catalysis reached a maximum yield of TPC within 1 min of the addition of the TFA. The yield of TPC increased more gradually under catalysis by $Dy(OTf)_3$ and $Yb(OTf)_3$, reaching a maximum yield by 30 and 15 min, respectively. In all cases, the yield of TPC remained fairly constant throughout the reaction until reaction times >7 h. Trace levels of TPP (<1%) were generally detected at only the longest time point—after the yield of TPC was observed to decline. Thus, a trace level of undesired reversibility can occur at long reaction times, but it can be readily avoided. In general, the reaction time course of the model reaction was similar to analogous reactions leading to porphyrins.[21]

5. Oxidant Screening Experiments. In the synthesis of porphyrin it is common to assume that the porphyrinogen produced during the condensation step is rapidly and quantitatively oxidized to porphyrin upon

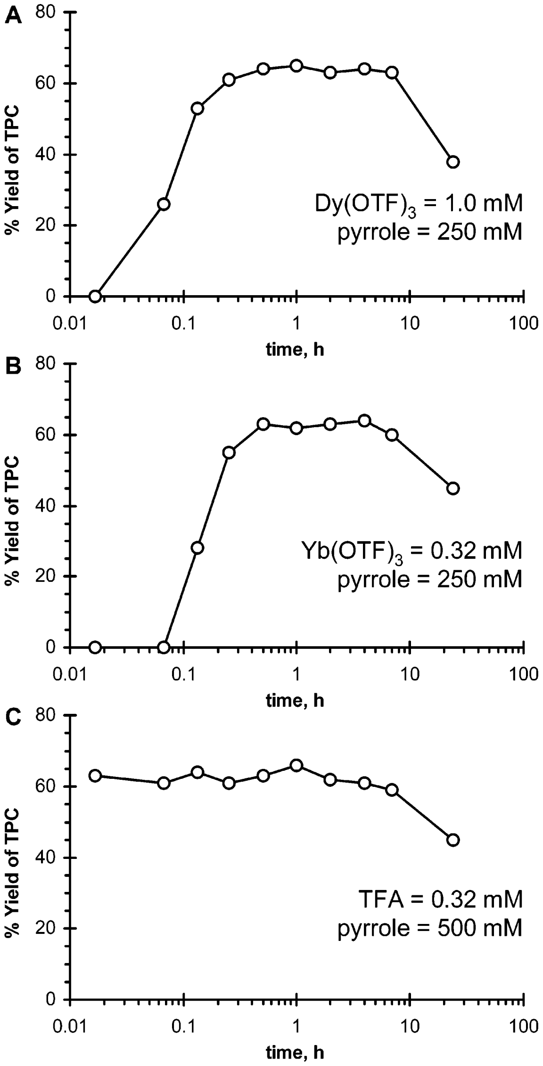

FIGURE 3. Yield of TPC as a function of condensation time for reactions of dipyrromethanedicarbinol **1a-OH** (2.5 mM) with excess pyrrole in CH_2Cl_2 at room temperature under the following conditions: (A) pyrrole (250 mM) and $Dy(OTf)_3$ (1.0 mM), (B) pyrrole (250 mM) and $Yb(OTf)_3$ (0.32 mM), and (C) pyrrole (500 mM) and TFA (0.32 mM). Reactions were monitored spectrophotometrically. Note the log scale for time.

addition of DDQ. As a result, studies of porphyrin syntheses have largely focused on the condensation step. In the case of corrole synthesis, the conditions of the oxidation step might be more exacting. For example, Lee and co-workers found that the yield of TPC obtained upon the oxidation of a purified triaryltetrapyrrane was impacted by the choice of solvent, oxidant, and inorganic additive.[23] The ease of corrole isolation might also depend on the choice of oxidation conditions in light of our observation that DDQ can interfere with the detection and TLC retention of TPC. Control experiments involving *p*-chloranil showed no interference with TPC.[32] However, it was not clear whether the weaker oxidant would provide a yield of corrole comparable to DDQ oxidation.[23] Thus, we investigated the impact of oxidant and oxidant quantity on the yield and ease of isolation of TPC.

i. DDQ Oxidation. Aliquots from the condensation of **1a-OH** (2.5 mM) with pyrrole (250 mM) catalyzed by $Dy(OTf)_3$ (1.0 mM) in CH_2Cl_2 were treated with 0.5 to 80 equiv of DDQ relative to **1a-OH**. The yield of TPC was determined spectrophotometrically after washing with aq dithionite, and the complexity of the mixtures was assessed by TLC. TPC was observed in all cases, and the optimal quantity (~60%) was obtained from 3 to 4 equiv of DDQ. A gradual decline in yield of TPC was observed with higher equivalents of DDQ (e.g., 52% yield of corrole with 8 equiv of DDQ compared to 43% yield with 80 equiv). The oxidation conditions employed in our protocol for spectrophotometric monitoring of the yield of TPC (6 equiv of DDQ) compare favorably to this result.

ii. *p*-Chloranil Oxidation. Aliquots from the condensation of **1a-OH** (2.5 mM) with pyrrole (250 mM) catalyzed by $Dy(OTf)_3$ (1.0 mM) in CH_2Cl_2 and quenched by the addition of triethylamine (5 equiv relative to the acid) were treated with 0.25 to 16 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. Oxidation with 2 equiv of *p*-chloranil for 45−60 min was found to provide the best result. [Note that this quantity of oxidant is lower than the stoichiometric quantity of 3 equiv.] Reactions employing >2 equiv of *p*-chloranil provided a brown pigment (R_f 0.50) in addition to the desired green TPC pigment (R_f 0.40) [TLC analysis, silica, CH_2Cl_2/hexanes (1:1)]. Lee and co-workers reported observing a similar pigment that they provisionally assigned as a bilatriene derivative.[23] The intensity of the brown pigment increased with the quantity of *p*-chloranil and with the time of oxidation (e.g., treatment with ≥4 equiv of *p*-chloranil for 1.5 h provided almost exclusively the brown pigment at the expense of TPC). The brown pigment fell below the limits of detection by TLC in reactions employing ≤2 equiv of *p*-chloranil. However, the yield of TPC was also impacted by the use of low quantities of *p*-chloranil (e.g., the yield of TPC from 0.25, 0.50, 1.0, and 2.0 equiv of *p*-chloranil was 2%, 7%, 18%, and 50%, respectively). None of the reactions produced detectable TPP, indicating that the oxidation was rapid relative to reversible processes.

iii. Comparison of DDQ and *p*-Chloranil Oxidations in Semipreparative-Scale Reactions. Aliquots (50−100 mL) from the condensation of **1a-OH** (2.5 mM) with pyrrole (250 mM) catalyzed by $Dy(OTf)_3$ (1.0 mM) in CH_2Cl_2 were treated with DDQ or *p*-chloranil to compare isolated yields of TPC and ease of isolation in the absence of a dithionite wash (Table 2).[33] The low isolated yield of TPC from the DDQ oxidation is consistent with interference by DDQ. The *p*-chloranil reactions provided TPC that was readily isolated in yields that were similar to the spectral yields obtained from the analytical-scale reactions involving *p*-chloranil oxidation. TLC analysis [silica, CH_2Cl_2/hexanes (1:1)] under overloaded conditions revealed a faint tan band consistent with the previously observed brown pigment under all conditions—including DDQ oxidation and conditions in-

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[32] *p*-Chloranil lacks the cyano groups that are reportedly important in the interaction between DDQ and porphyrin,[27] and are potentially important in the corresponding interaction of DDQ with corrole.

[33] The aq dithionite wash of crude reaction mixtures on a semipreparative scale is irksome as the mixtures are prone to formation of an emulsion and the organic/aqueous interface is challenging to locate.

TABLE 2. Isolated Yields of TPC Obtained from Semipreparative-Scale Reactions Comparing Oxidation Conditions Involving DDQ and *p*-Chloranil[a]

entry	oxidant	equiv[b]	% yield of TPC[c]
1	DDQ	3	2[d]
2	*p*-chloranil	1.5	18
3	*p*-chloranil	1.75	26
4	*p*-chloranil	1.9	54
5	*p*-chloranil	2.0	53

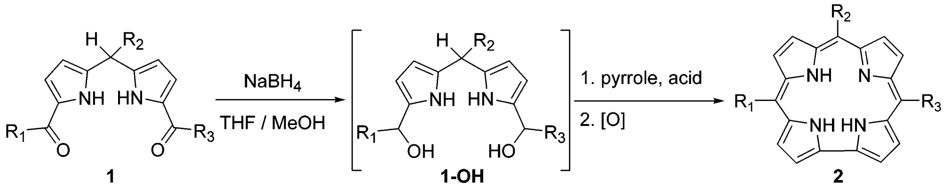
[a] The condensation of **1a-OH** (2.5 mM) + pyrrole (250 mM) was catalyzed by Dy(OTf)$_3$ (1.0 mM) in CH_2Cl_2 at room temperature. Aliquots (50−100 mL) of the reaction mixture were treated with oxidant at room temperature (DDQ) or at reflux (*p*-chloranil) for 45 min. TPC was isolated by filtration through a silica pad (CH_2Cl_2) followed by silica gel chromatography [CH_2Cl_2/hexanes (1:1)]. [b] Equivalents of oxidant relative to **1a-OH** originally present in the aliquot. [c] Isolated yield of TPC after drying under vacuum. [d] Retention of TPC in the presence of DDQ was observed during the initial filtration through a silica pad.

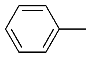
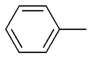
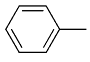
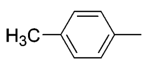
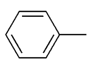
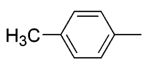
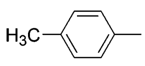
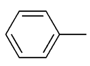
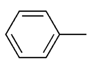
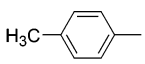
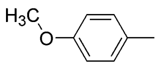
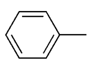
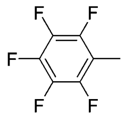
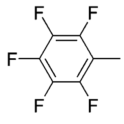
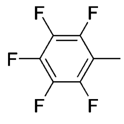
volving lower quantities of *p*-chloranil. Together, these observations suggest that ~2 equiv of *p*-chloranil for 30 min to 1 h of reflux provides the best balance of yield of TPC, ease of isolation, and minimization of impurities.

6. Preparative-Scale Synthesis of TPC. Dipyrromethanedicarbinol **1a-OH** (0.50 mmol, 2.5 mM) and pyrrole (250 mM) were treated with Dy(OTf)$_3$ (1.0 mM) in CH_2Cl_2 at room temperature (Table 3). The reaction was monitored spectrophotometrically at 15-min intervals. Consistent with analytical-scale reactions, a spectral yield of ~65% was obtained by 45 min. Triethylamine (5 equiv. relative to acid) was added followed by *p*-chloranil (1.0 mmol, 2 equiv relative to **1a-OH**) and the mixture was heated to reflux for 45 min. The TPC was isolated from polar byproducts upon passage through a pad of silica gel to afford TPC contaminated with a low level of the less polar brown pigment. The TPC was further purified via a short silica column, eluting with CH_2Cl_2/hexanes (1:1) to obtain 128 mg, 49% yield. The discrepancy between the isolated yield of TPC (~50%) and the spectral yield (~65%) could reflect the differences in the oxidation conditions, losses of TPC incurred during isolation, and/or a degree of systematic overestimation of the yield of TPC by spectral monitoring. The isolated yield of TPC compared favorably to the ~50% yield of TPC obtained from the semipreparative-scale experiment.

Preparation of Corroles 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 corroles bearing two or three different substituents in defined locations (Table 3). Analytical-scale reactions leading to **2b** and **2d** were followed for yield of corrole (UV−vis) as a function of time under the three best conditions identified from studies of the model reaction (Table 1, entries 2, 5, and 9). These studies provided results very similar to those obtained from the model reaction (Supporting Information). Preparative-scale reactions were performed in identical fashion to the model reaction. In each case, a trace level of a brown pigment was produced in addition to the corrole. The exceptionally high yield of **2b** (~80%) was reproducible, but the origin of the high yield for that particular corrole is unclear. The corroles were produced devoid of porphyrin and without detectable scrambling as evidenced by TLC and LD-MS analysis. Thus, the reaction conditions identified from the model reaction are suitable for the

TABLE 3. Preparative Synthesis of Meso-Substituted Corroles



Diacyl DPM	R_1	R_2	R_3	Corrole	Yield	Mass
1a				**2a**	49%	128 mg
1b				**2b**	80%	222 mg
1c				**2c**	50%	135 mg
1d				**2d**	59%	169 mg
1e				**2e**	18-24%	28-39 mg

efficient preparation of corroles bearing meso substituents in defined locations.

Preparation of 5,10,15-Tris(pentafluorophenyl)-corrole. Given general interest in corroles bearing electron-withdrawing substituents, we examined the reaction of **1e-OH** with pyrrole leading to TpFPC **2e** (Table 3). Authentic TpFPC was prepared by the method of Gross and co-workers,[5] and was used to confirm the applicability of our spectrophotometric analysis for this corrole, and to investigate potential interference of the isolation of TpFPC by DDQ. This latter point was of interest as DDQ has been widely used in the preparation of corroles bearing electronegative substituents.[5,11,13,15,29] DDQ interference with the isolation of TpFPC was observed, but to a much lesser extent than was the case with TPC (e.g., isolation of authentic TpFPC after treatment with DDQ resulted in a 15% loss of TpFPC compared to a 53% loss of TPC in side-by-side experiments).

Analytical-scale reactions leading to TpFPC were followed for yield of corrole (UV−vis) as a function of time under the three best conditions identified from studies of the model reaction (Table 1, entries 2, 5, and 9). The reactions differed sharply from those leading to the other corroles in that the condensation reactions were much slower and the maximum yields of TpFPC were lower. Catalysis by Dy(OTf)$_3$ provided a 36% yield of TpFPC by 8 h, Yb(OTf)$_3$ provided a 40% yield by 8 h, and TFA provided a 25% yield by 8 h (Supporting Information). This result demonstrates the importance of monitoring the reaction—had the condensation step of these reactions been performed for 1 h (as was determined appropriate for the other corroles) we would have erroneously concluded that the reactions had failed.

Preparative-scale experiments were performed under reaction conditions identical to the other corroles (with the exception that 0.20 mmol of **1e** was used due to limited quantities). The reaction was allowed to proceed for 10 h providing a spectral yield of TpFPC of 30% prior to oxidation with *p*-chloranil (2 equiv relative to **1e-OH**). After 45 min of reflux, little corrole was detected by TLC or UV−vis. DDQ (3 equiv) was then added at room temperature over 30 min, followed by stirring for 30 min at room temperature. An isolated yield of 24% (39 mg) was obtained. The reaction was repeated under identical condensation conditions (the reaction required 8 h to reach a spectral yield of 34%) followed by oxidation with 3 equiv of DDQ. After the solution was stirred at room temperature for 1 h, the quantity of TpFPC appeared to be low based on TLC and UV−vis analysis. Additional DDQ (3 equiv) was added over 30 min, and an isolated yield of corrole of 18% (28 mg) was obtained. Although additional work is required to optimize the oxidation step of this reaction, it is clear from these results that mild catalysis conditions can promote the condensation reaction leading to corroles that bear electron-withdrawing substituents.

On the Choice of Oxidant. The observation of interference of detection and isolation of TPC by DDQ and the poor result of *p*-chloranil in the synthesis of TpFPC prompted a reexamination of oxidation conditions reported in the literature. Consistent with our findings, DDQ oxidation has been generally applied with best success in the preparation of corroles bearing electron-withdrawing groups and/or facially encumbering groups.[5,11,13,15,29] Success in these cases is understandable if the mechanism by which DDQ interacts with corrole proves to be similar to that of porphyrin.[27] An electron-poor corrole would not be expected to readily donate electron density to a −CN group of DDQ, and it has been shown that a facially encumbered porphyrin, tetramesitylporphyrin, does not readily form an adduct with DDQ for presumably steric reasons.[27] Recently, reports have appeared that describe exacting conditions involving DDQ oxidation. The authors proposed that excess DDQ can result in overoxidation of corrole,[13c,18] or in the formation of a corrole−DDQ complex[11,13c] leading to poor isolated yields of corrole. Corroles that lack electron-withdrawing groups and/or facially encumbering substituents were initially prepared by air oxidation in an “Adler-like” procedure.[6] Reports of the use of *p*-chloranil with a diverse range of substituents have appeared more recently, but without explanation for the choice of oxidant or without direct comparison to the use of DDQ.[10,14,15]

Interestingly, there are a handful of reports that are at apparent odds with the general trends in the literature. (1) Lee and co-workers reported the synthesis of TPC in a yield of up to 65% via DDQ oxidation of a triaryltetrapyrrane species.[23] (2) Brückner and co-workers reported the synthesis of TPC in a yield of 40% via condensation of an aldehyde with excess 5-phenyldipyrromethane followed by DDQ oxidation.[14] (3) Guilard, Gryko, and co-workers and Gryko and co-workers reported the preparation of TPC in a yield of 22−25% via condensation of a dipyrromethanedicarbinol **1a-OH** in neat pyrrole (25 equiv per carbinol unit) followed by dilution in CH$_2$Cl$_2$ and treatment with DDQ (3 equiv per **1a-OH**).[17] (4) Ghosh and co-workers reported the synthesis of TPC in a yield of ∼6% from pyrrole and benzaldehyde[28] using the Gross method involving DDQ oxidation.[5] We investigated each of these reports to reconcile them with our observations and with the general trends found in the literature.

We suspected that the results of Lee and co-workers could be understood, in part, by their choice of solvent. They obtained their best results using propionitrile, and only a trace quantity of TPC was obtained from a reaction performed in CH$_2$Cl$_2$ in the absence of other additives.[23] We treated propionitrile solutions of authentic TPC with 0−10 equiv of DDQ relative to TPC, and then attempted to pass aliquots through a silica pipet with elution with CH$_2$Cl$_2$. In all cases, a band of TPC was observed to elute rapidly through the silica pipet, although the intensity of Soret and Q-bands were diminished in samples of TPC treated with >3 equiv of DDQ. Thus, it appears that propionitrile assists with the isolation of TPC in the presence of modest levels of DDQ. In the work reported by Brückner and co-workers, the presence of excess 5-phenyldipyrromethane attracted our attention. Control experiments involving solutions of TPC doped with DDQ and varying quantities of 5-phenyldipyrromethane revealed that the addition of the dipyrromethane allowed improved recovery of TPC. Interestingly, 6 equiv of dipyrromethane relative to DDQ were required to completely nullify the interference of DDQ with the TPC—close to the quantity of excess of dipyrromethane employed in Brückner's conditions. Thus, the requirement for excess dipyrromethane in this particular reaction may be related to counteracting interference from DDQ in addition to providing an optimal oligomer composition for corrole formation. (Note that *p*-chloranil was used to prepare the other corroles in their study.) Our investigation of the procedure of Guilard, Gryko, and co-workers provided findings that were consistent with interference of the isolation of TPC by DDQ. The condensation of **1a-OH** with pyrrole mediated by TFA was performed in accordance with the published procedure[17a] (Supporting Information). After dilution in CH_2Cl_2, the mixture was divided evenly between two flasks and subjected to oxidation by DDQ (3 equiv) at room temperature or *p*-chloranil (2 equiv) at reflux. While spectral monitoring of the two oxidation reactions provided similar results, DDQ oxidation afforded an isolated yield of TPC of 11% (11.2 mg) whereas *p*-chloranil oxidation provided an isolated yield of 50% (50.0 mg). The difference between our isolated yield of TPC under DDQ oxidation (11%) and the yield reported by Guilard, Gryko, and co-workers (22−25%) could reflect variability in the extent to which DDQ interfered with the initial filtration through a silica pad. Regardless, it is clear that oxidation with *p*-chloranil provided a higher isolated yield. Oxidation with *p*-chloranil also provided a cleaner reaction mixture and final product as assessed by TLC analysis. Both oxidants provided the characteristic green spot of TPC along with a low level of the brown pigment. Additionally, DDQ oxidation provided an olive green band that eluted slightly ahead of the TPC—consistent with published observations pertaining to the preparation of A_3-corroles from pyrrole + aldehyde,[10] and ABA-corroles via dipyrromethane + aldehyde,[13b] but not reported in corrole syntheses via dipyrromethanedicarbinols.[17] Finally, our attempts to replicate the report[28] of the preparation of TPC via the Gross method were not successful even upon attempted dithionite wash of the crude reaction mixture prior to isolation of the TPC. The origin of our lack of success is not clear, but this observation is consistent with the original report of Gross and co-workers.[5]

On the basis of our observations and reports from the literature, the choice of oxidant appears to be critical to the success of the reaction and/or to the ease of corrole isolation. While we make no claims that the generally superior yield of corroles bearing electron-withdrawing and/or facially-encumbering groups in reactions involving DDQ stem solely from differential interactions between various corroles and DDQ, we suggest that it may be a factor in at least some situations. *p*-Chloranil appears to be best suited for corroles that tend to interact strongly with DDQ, and DDQ appears to be best suited for reactions leading to corrole that require stronger oxidizing conditions. Corroles lacking electron-withdrawing or facially-encumbering substituents appear to fall in the former group, and corroles with strongly electron-withdrawing substituents appear to fall in the latter group. For intermediate cases, the best oxidation conditions are not presently clear. A comparison of *p*-chloranil (2 equiv. at reflux for 45 min) and DDQ (3 equiv at room temperature for 1 h) would seem to provide a good starting point.

Stability of Corroles. While determining molar extinction coefficients for the corroles prepared in this study, we noted a gradual decrease in the absorbance of the Soret band over time. The instability of solutions of some corroles toward light and air has been reported in the literature,[34] but we were unable to find detailed information on the scope and magnitude of corrole instability. Thus, we performed a simple side-by-side comparison of the solution stabilities of the corroles prepared in this study. Solutions of each corrole were prepared in toluene and UV−vis spectra were recorded upon exposure to ambient light. Changes in the absorbance of the Soret band for TPC and TpFPC as a function of time are summarized in Figure 4. Consistent with literature reports,[11,17a] the corrole bearing electron-withdrawing substituents was found to be fairly stable. In contrast, TPC underwent substantial decomposition over a short period of time (e.g., ~50% of the intensity of the Soret band was lost by 2 h of exposure to light). Light is required for the decomposition as an identical solution of TPC stored in the dark did not undergo decomposition. Corroles **2b**−**d** showed rates of decomposition similar to or even a little faster than that of TPC (Supporting Information). We have not identified the products of the decomposition, but others have identified an open chain tetrapyrrole (biliverdin) structure in the decomposition of a corrole bearing a combination of β and meso substituents.[34] As corroles become candidates for a variety of applications, their stability in solution will need to be delineated. Key questions include the following: How many electron-withdrawing groups are necessary to impart stability? How strong of an electron-withdrawing group is required? Does the placement of the electron-withdrawing group (5 or 10 position) matter? Can electron-donating groups be tolerated if other substituents are present?

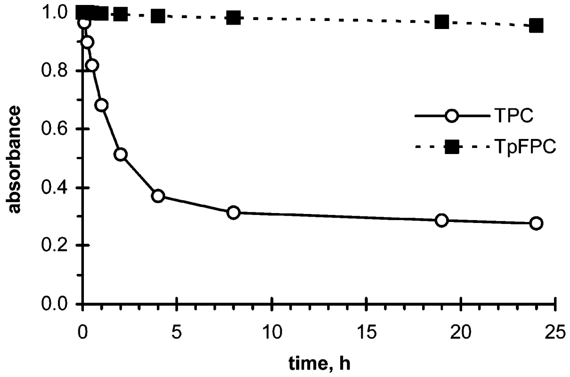


FIGURE 4. Absorbance of the Soret band as a function of time for dilute solutions of TPC **2a** and TpFPC **2e** in toluene in the presence of ambient light. The λ_{max} of the Soret band of TPC shifted from 420 to 401 nm during the experiment. The λ_{max} of the Soret band of TpFPC was 414 nm.

Conclusions

We have found that mild acids [$Dy(OTf)_3$ or $Yb(OTf)_3$] or a low concentration of TFA can be applied to the synthesis of meso-substituted corroles devoid of scrambling. The effect of $Dy(OTf)_3$ or $Yb(OTf)_3$ concentration on the yield of TPC and the reaction time course under the best reaction conditions was similar to that of previous studies of analogous reactions leading to por-

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[34] Tardieux, C.; Gros, C. P.; Guilard, R. *J. Heterocycl. Chem.* **1998**, *35*, 965−970.

phyrin. The behavior of $InCl_3$ and $Sc(OTf)_3$ deviated from our expectations in that TPP (indicative of reversible processes) was observed under all conditions investigated. A dipyrromethanedicarbinol species bearing electron-withdrawing pentafluorophenyl substituents treated similarly to the model reaction also underwent reaction leading to corrole—albeit more slowly. Together, these results suggest that sharp deviations from the catalytic conditions used to prepare porphyrins from dipyrromethanedicarbinols are not required to obtain good yields of corrole devoid of scrambling—although not all of the mild acid catalysts work equally well. The critical role of the choice and quantity of oxidant was identified—including a direct comparison of DDQ and *p*-chloranil. An examination of dilute corrole solutions provided a comparison of their instability toward light and air. As a whole, this study adds to the growing understanding of reaction conditions affording corrole, it demonstrates similarity between dipyrromethanedicarbinol routes to corroles and to porphyrins, and it provides methodology complementary to that previously reported for the preparation of corroles bearing substituents in defined locations.

Experimental Section

UV–Vis Spectrophotometric Determination of the Yield of Corrole. Corrole-forming reactions were monitored by transferring an aliquot (200 μL) of the condensation reaction mixture by syringe to a 1.8-mL microcentrifuge tube containing a DDQ solution (300 μL, 10 mM in toluene). The mixture was vortex mixed for 2–5 s. To the oxidized reaction mixtures was added an aq solution of 5% $Na_2S_2O_4$, 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 μL) was transferred by syringe to a Pasteur pipet filled two-thirds full with silica gel (~1.5 g).[30] The sample was eluted with three, 1-mL portions of CH_2Cl_2. Solvent was driven off the column by using a handheld pipet tool. The eluent was transferred to a cuvette and the UV–vis spectrum was recorded. The yield of corrole was determined by comparing the absorbance at 420 nm with the theoretical absorbance calculated from the following equation:

$$A_{\text{theoretical}} = (110\,000\ \text{cm}^{-1}\ \text{M}^{-1})(1.0\ \text{cm})(0.0025\ \text{M}) \times \left(\frac{200\ \mu\text{L}}{500\ \mu\text{L}}\right)\left(\frac{50\ \mu\text{L}}{3050\ \mu\text{L}}\right)(1.30)(0.306) = 0.716$$

where $110\,000\ \text{cm}^{-1}\ \text{M}^{-1}$ is the reported molar extinction coefficient for TPC,[6b] 1.0 cm is the path length of the cuvette, 0.0025 M is the theoretical concentration of corrole given the initial concentration of dipyrromethanedicarbinol (2.5 mM), (200 μL/500 μL) ,and (50 μL/3050 μL) account for the dilution of the corrole upon oxidation of an aliquot in the DDQ solution and passage through the silica pipet, respectively, 1.30 is an empirically derived correction factor for the volume of CH_2Cl_2 eluent that is retained on the silica pipet,[30] and 0.306 is an empirically derived correction factor for the attenuation of the absorbance of the Soret band of corrole in the presence of pyrrole and DDQ. See the Supporting Information for a discussion of the determination of the two correction factors.

Acid-Screening Experiments. Immediately prior to the condensation reactions, **1a** (215 mg, 0.500 mmol) was reduced to the corresponding dipyrromethanedicarbinol **1a-OH** with $NaBH_4$ (1.3 g, 36 mmol) in THF/methanol (40 mL, 3:1) following a literature procedure.[19] After being dried under vacuum for 30 min, the dicarbinol was dissolved in CH_2Cl_2 and transferred to a 100-mL volumetric flask. A solution of pyrrole (0.25, 0.50, or 1.0 M) was prepared in CH_2Cl_2 in a second 100-mL volumetric flask. The contents of the two volumetric flasks were mixed in an amber bottle equipped with a solvent pump, thereby providing a stock solution of **1a-OH** (2.5 mM) and pyrrole (125, 250, or 500 mM). Reactions were performed at room temperature in tightly capped 20-mL vials that were stirred with a micro stir bar. Solid acids were weighed into all reaction vials prior to beginning the reaction sequence for the day, and each reaction was started by the addition of 5–10 mL of the reactant solution from the solvent pump. Reactions involving TFA were initiated by the addition of TFA to reaction vials already containing 5 mL of the reactant stock solution. The reactions were monitored spectrophotometrically for yield of TPC at 15 min and 1 h as described above. TLC was performed on the crude, oxidized mixture [silica, CH_2Cl_2/hexanes (2:1)] after washing with the aq dithionite solution.

Ratio of Pyrrole to Dipyrromethanedicarbinol Experiments. Portions (5 mL) of a freshly prepared solution of dipyrromethanedicarbinol **1a-OH** (2.5 mM) in CH_2Cl_2 were transferred to 20-mL vials. Pyrrole was added by syringe to afford concentrations of pyrrole ranging from 5.0 to 488 mM. Solutions containing pyrrole in concentrations ranging from 1.22 to 14 M were prepared by concentrating the 5-mL portion of the solution of **1a-OH**, transferring the concentrated solution to a volumetric flask (5 mL), adding pyrrole, and filling to the mark with CH_2Cl_2. The contents of the volumetric flasks were returned to 20-mL vials. Reactions were initiated by pouring each solution of **1a-OH** and pyrrole into a 20-mL vial containing $Dy(OTf)_3$ (3.0 mg, 0.0050 mmol, 1.0 mM). The reactions were monitored spectrophotometrically for yield of TPC at 15 min and 1 h as described above. TLC was performed on the crude, oxidized mixture [silica, CH_2Cl_2/hexanes (2:1)] after washing with the aq dithionite solution.

Reaction Time Course Experiments. Reaction monitoring as a function of time was performed as described above for the acid-screening experiments with the exception of using a 10-mL reaction volume. Each reaction was initiated by the addition of the appropriate acid at room temperature (Table 1, entries 2, 5, and 9). The reactions were monitored for yield of corrole as described above at 1 min, 4 min, 8 min, 15 min, 30 min, 1 h, 2 h , 4 h, 7 h, and 24 h. TLC was performed on the crude, oxidized mixtures [silica, CH_2Cl_2/hexanes (2:1)] after washing with the aq dithionite solution.

Determination of the Stability of Corroles. Solutions of corroles **2a–e** were prepared in toluene in the dark. The concentration of each solution was adjusted to provide an absorbance of ~1.0. UV–vis spectra were recorded in the dark, and again from 5 min to 24 h after the room lights were turned on. Decomposition of corrole was inferred from changes in the intensity of the Soret band. A control experiment involving corrole solutions maintained in the dark was performed similarly.

General Procedure for the Preparative-Scale Syntheses of Corroles, Given for 5,10,15-Triphenylcorrole (2a). 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**. The carbinol was dried under vacuum for 30 min and then immediately subjected to condensation with pyrrole (3.47 mL, 50.0 mmol) in the presence of $Dy(OTf)_3$ (122 mg, 0.200 mmol) in CH_2Cl_2 (200 mL) for 1.3 h at room temperature followed by the addition of triethylamine (0.139 mL, 1.00 mmol) and oxidation with *p*-chloranil (246 mg, 1.00 mmol) at reflux for 45 min. The entire reaction mixture was filtered through a pad of silica gel and eluted with CH_2Cl_2. The filtrate was concentrated to dryness. The corrole sample was dissolved in CH_2Cl_2 (75 mL), adsorbed onto silica gel (15 g), concentrated, and purified by chromatography [silica, CH_2Cl_2/hexanes (1:1)]. The green band containing TPC was collected, concentrated, and dried under vacuum affording TPC (128 mg, 49%) that was subsequently crystallized from

CH_2Cl_2/hexanes providing analytical data consistent with published values.[6]

5,15-Bis(4-methylphenyl)-10-phenylcorrole (2b). The reduction of **1b** (229 mg, 0.500 mmol) followed by condensation with pyrrole (3.47 mL, 50.0 mmol) in the presence of $Dy(OTf)_3$ (122 mg, 0.200 mmol) in CH_2Cl_2 (200 mL) for 1 h at room temperature, addition of triethylamine (0.139 mL, 1.00 mmol), oxidation with *p*-chloranil (246 mg, 1.00 mmol) at reflux for 45 min, and purification identical to the general procedure afforded 2**b** (222 mg, 80%) that was subsequently crystallized from CH_2Cl_2/hexanes. λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 421 (130), 564 (16.4), 617 (13.4), 651 (13.7); ^1H NMR [CD_3OD (0.6%) in $CDCl_3$][35] δ 2.67 (s, 6H), 7.62 (d, $J = 7.7$ Hz, 4H), 7.73 (m, 3H), 8.16 (d, $J = 5.7$ Hz, 2H), 8.24 (d, $J = 7.7$ Hz, 4H), 8.52 (d, $J = 4.6$ Hz, 2H), 8.57 (d, $J = 3.5$ Hz, 2H), 8.87 (d, $J = 4.6$ Hz, 2H), 8.91 (d, $J = 4.0$ Hz, 2H); LD-MS obsd 554.1 (M^+); HRMS (FAB) obsd 555.2583 (MH^+), calcd 555.2549 (MH^+) ($C_{39}H_{30}N_4$).

5,10-Diphenyl-15-(4-methylphenyl)corrole (2c). The reduction of **1c** (222 mg, 0.500 mmol) followed by condensation with pyrrole (3.47 mL, 50.0 mmol) in the presence of $Dy(OTf)_3$ (122 mg, 0.200 mmol) in CH_2Cl_2 (200 mL) for 1.25 h at room temperature, addition of triethylamine (0.139 mL, 1.00 mmol), oxidation with *p*-chloranil (246 mg, 1.00 mmol) at reflux for 45 min, and purification identical to the general procedure afforded **2c** (135 mg, 50%) that was subsequently crystallized from CH_2Cl_2/hexanes. λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 421 (133), 564 (16.9), 617 (13.1), 651 (13.3); ^1H NMR [CD_3OD (0.6%) in $CDCl_3$] δ 2.68 (s, 3H), 7.62 (d, $J = 7.7$ Hz, 2H), 7.73 (m, 4H), 7.81 (m, 2H), 8.16 (d, $J = 5.7$ Hz, 2H), 8.25 (d, $J = 7.7$ Hz, 2H), 8.35 (d, $J = 7.2$ Hz, 2H), 8.53−8.57 (m, 4H), 8.87 (m, 2H), 8.92 (m, 2H); LD-MS obsd 540.2 (M^+); HRMS (FAB) obsd 541.2366 (MH^+), calcd 541.2392 (MH^+) ($C_{38}H_{28}N_4$).

5-Phenyl-10-(4-methoxyphenyl)-15-(4-methylphenyl)-corrole (2d). The reduction of **1d** (237 mg, 0.500 mmol) followed by condensation with pyrrole (3.47 mL, 50.0 mmol) in the presence of $Dy(OTf)_3$ (122 mg, 0.200 mmol) in CH_2Cl_2 (200 mL) for 1 h at room temperature, addition of triethylamine (0.139 mL, 1.00 mmol), oxidation with *p*-chloranil (246 mg, 1.00 mmol) at reflux for 45 min, and purification identical to the general procedure with the exception that CH_2Cl_2/hexanes (3:2) was used during chromatography afforded **2d** (169 mg, 59%) that was subsequently crystallized from CH_2Cl_2/hexanes. λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 421 (121), 563 (15.8), 619 (12.4), 652 (13.4); ^1H NMR [CD_3OD (0.6%) in $CDCl_3$] δ 2.68 (s, 3H), 4.08 (s, 3H), 7.28 (d, $J = 8.2$ Hz, 2H), 7.62 (d, $J = 7.4$ Hz, 2H), 7.71 (t, $J = 7.3$ Hz, 1H), 7.81 (t, $J = 7.3$ Hz, 2H), 8.07 (d, $J = 8.2$ Hz, 2H), 8.25 (d, $J = 7.4$ Hz, 2H), 8.34 (d, $J = 7.2$ Hz, 2H), 8.56 (m, 4H), 8.85−8.91 (m, 4H); LD-MS obsd 570.1 (M^+); HRMS (FAB) obsd 571.2515 (MH^+), calcd 571.2498 (MH^+) ($C_{39}H_{30}N_4O$).

5,10,15-Tris(pentafluorophenyl)corrole (2e). The reduction of **1e** (140 mg, 0.200 mmol) followed by condensation with pyrrole (1.39 mL, 20.0 mmol) in the presence of $Dy(OTf)_3$ (48.8 mg, 0.0800 mmol) in CH_2Cl_2 (80 mL) for 10 h at room temperature, addition of triethylamine (056 μL, 0.40 mmol), oxidation with DDQ (136 mg, 0.600 mmol) at room temperature for 1 h, addition of a further quantity of DDQ (136 mg, 0.600 mmol) over 30 min, and purification identical to the general procedure afforded **2e** (28 mg, 18%) that was subsequently crystallized from CH_2Cl_2/hexanes providing analytical data consistent with published values.[5]

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Supporting Information Available: General experimental methods, synthesis of diacyldipyrromethanes **1a** and **1c**, description of oxidant screening experiments, discussion of correction factors for spectrophotometric analysis of corroles, plots of the yield of TPC as a function of acid concentration, investigation of TFA/acetonitrile condensation conditions, time course experiments for reactions leading to corroles **2b**,**d**,**e**, data pertaining to the stability of corroles **2a**−**e**, ^1H NMR spectra of diacyl dipyrromethanes **1a** and **1c**, ^1H NMR spectra of corroles **2a**−**e**, and COSY spectra of corroles **2b**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[35] The ^1H NMR spectral results that we obtained differ slightly from those previously reported for **2b**.[14] This likely stems from differences in resolution between the spectra.