ORGANIC LETTERS

2001
Vol. 3, No. 15
2281−2284

MacDonald [2 + 2]-Type Condensation with Vicinal Diketones: Synthesis and Properties of Novel *Spiro*-Tricyclic Porphodimethenes

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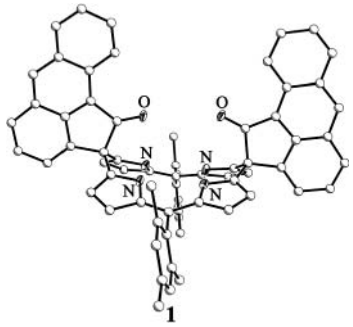
Received April 30, 2001

ABSTRACT



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Acid-catalyzed [2 + 2] condensation reactions of polycyclic aromatic vicinal diketones including aceanthrenequinone, phenathrenequinone, and pyrene-4,5-dione with 5-mesityldipyrromethanes are outlined, and this methodology provides a flexible entry to *spiro*-tricyclic porphodimethenes. The porphodimethene products have been fully characterized, including X-ray structure analyses and fluorescence spectroscopy. In the case of the phenanthrenone-substituted macrocycle, the two *spiro*-locks can be ring-opened to form a *trans*-bis(2′-hydroxymethylbiphenyl)-substituted porphyrin.

The development of methodologies for the preparation of porphodimethenes has attracted considerable interest in recent years, since these tetrapyrrolic macrocycles exhibit chemical and physical properties noticeably divergent from the related porphyrins. While porphyrins are fully aromatic, planar macrocycles, porphodimethenes contain two saturated *meso*-carbon atoms within the ring system that disrupt the aromaticity and induce a roof-like fold. Consequently, the molecular orbitals of metals coordinated by these ligands are often distinct from analogous porphyrin species,[1] and this disparity should bring about divergent reactivity. Unfortunately, although several synthetic pathways can be used to generate porphodimethenes,[1,2] convenient quantities of *meso*-aryl-substituted macrocycles are currently only isolated via acid-catalyzed [2 + 2] condensation reactions of 5-aryldipyrromethanes with ketones.[3,4] In contrast to *meso*-alkyl porphodimethenes, the electronic properties of the *meso*-aryl-substituted macrocycles can be easily modified through simple substitutions of electron-withdrawing or -donating groups onto the aryl rings, and methods for their preparation warrant continued refinement.

(1) Da Silva, C.; Bonomo, L.; Solari, E.; Scopelliti, R.; Floriani, C.; Re, N. *Chem. Eur. J.* **2000**, *6*, 4518−4531 and references therein.

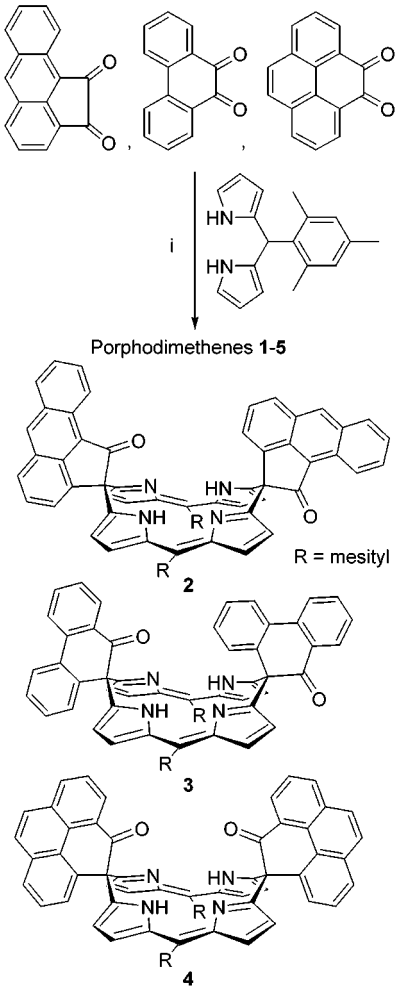
(2) (a) Senge, M. O.; Runge, S.; Speck, M.; Ruhlandt-Senge, K. *Tetrahedron* **2000**, *56*, 8927−8932. (b) Botulinski, A.; Buchler, J. W.; Lay, K.-L.; Stoppa, H. *Liebigs Ann. Chem.* **1984**, 1259−1269 and references therein.

(3) (a) Harmjanz, M.; Scott, M. J. *Chem. Commun.* **2000**, 397−398. (b) Harmjanz, M.; Gill, H. S.; Scott, M. J. *J. Org. Chem*. In press.

(4) Král, V.; Sessler, J. L.; Zimmerman, R. S.; Seidel, D.; Lynch, V.; Andrioletti, B. *Angew. Chem., Int. Ed.* **2000**, *39*, 1055−1058.

10.1021/ol016046u CCC: $20.00
Published on Web 06/27/2001

Scheme 1. Synthesis of Porphodimethene Macrocycles from Vicinal Diketones and 5-Mesityldipyrromethane[a]



[a] Reagents and conditions: (i) 1. TFA, CH_2Cl_2, rt, 1−2.5 h, 2. DDQ, rt.

Recently, we described a simple procedure for the preparation of porphyrins bearing two 8-functionalized naphthalene spacers, and unlike conventional strategies for the preparation of porphyrins, our methodology involved the isolation of *spiro*-tricyclic porphodimethenes prior to the ring opening of the *spiro*-lock and formation of the desired porphyrin derivatives.[3] With reactive groups poised above the plane of the macrocycle, the porphyrins exhibited rather unusual electrochemical properties,[5] and they were also found to be excellent building blocks for the generation of heterometallic, one-dimensional porphyrin arrays.[6] The procedure for the preparation of the porphodimethene precursors was initially restricted to the reaction of acenaphthenequinone and 5-aryldipyrromethanes,[3b] and with the intent to expand the diversity of the resultant macrocycles, efforts to prepare porphodimethenes utilizing other vicinal diketones were undertaken.

Under Lindsey conditions,[7] most aliphatic vicinal diketones (e.g., 2,3-butanedione) do not appear to react with dipyrromethanes to form porphodimethenes, but polycyclic aromatic vicinal diketones such as aceanthrenequinone, phenanthrenequinone, and pyrene-4,5-dione[8] readily produce the desired, orange *spiro*-tricyclic macrocycles (Scheme 1). Using 5-mesityldipyrromethane and TFA as the acid catalyst, the ratios of the *syn* and *anti* isomers vary depending on the diketone used, and the overall isolated yields of the macrocyles range between 5 (**4**, **5**) and 22% (**1**, **2**) (Table 1).

Table 1. Selected Diketones and Yields for the Formation of Porphodimethenes **1**−**5**

diketone	*syn* yield (%) UV−vis, λ_{max} (log ϵ)	*anti* yield (%) UV−vis, λ_{max} (log ϵ)
aceanthrenequinone	**1** (4), 452 nm (4.92)[a]	**2** (18), 448 nm (4.94)[a]
phenanthrenequinone		**3** (11), 432 nm (4.89)[a]
pyrene-4,5-dione	**4** (1), 442 nm (4.97)[b]	**5** (4), 440 nm (4.94)[b]

[a] $CHCl_3$. [b] *o*-Dichlorobenzene.

Interestingly, the reaction between the dipyrromethane and phenanthrenequinone yields only the *anti* isomer while the structurally related pyrene-4,5-dione produces both the *syn* and *anti* isomers.

As previously observed with acenaphthenequinone,[3] aceanthrenequinone or pyrene-4,5-dione will react with dipyrromethanes to afford significantly reduced amounts of the *syn* isomer relative to the *anti*, possibly due to a sterically less favored porphyrinogen intermediate for these isomers. Six different isomers can be envisioned as products of the condensation reaction with aceanthrenequinone, but as confirmed by X-ray structural analysis[9] of **1** and **2** and by ^{1}H NMR spectroscopy, only two major products were formed. A third, minor (<1%) byproduct has also been identified, but it has not been fully characterized. The aceanthrenone moieties in both **1** and **2** are bound at the 2-position to the porphodimethene macrocycle, and this product distribution is likely a result of the differences in the electronic as well as steric properties of the two carbonyl groups. In a related reaction of 9-anthraldehyde with pyrrole, steric congestion between the anthracene group and the *meso* hydrogens on the desired porphyrinogen intermediate has been suggested to impede the formation of porphyrin products.[7]

Although the extinction coefficients of the main absorption band in the UV−vis spectra of **1**−**5** are quite large and comparable to those of the acenaphthenequinone derivatives,[2]

(5) Harmjanz, M.; Gill, H. S.; Scott, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 10476−10477.
(6) Harmjanz, M.; Scott, M. J. *Inorg. Chem.* **2000**, *39*, 5428−5429.
(7) Lindsey, J. S.; Wagner, R. W. *J. Org. Chem.* **1989**, *54*, 828−836.
(8) Young, E. R. R.; Funk, R. L. *J. Org. Chem.* **1998**, *63*, 9995−9996.
(9) The crystal structures of both **1** and **2** were solved to confirm the orientation of the aceanthrenone groups. Only **1** was fully refined, and the structure is presented in the Supporting Information.

the position of the absorption maxima varies among the respective isomers (*syn* and *anti*) and the anchored polyaromatic residues from 432 (**3**) to 452 (**1**) nm (Figure 1).

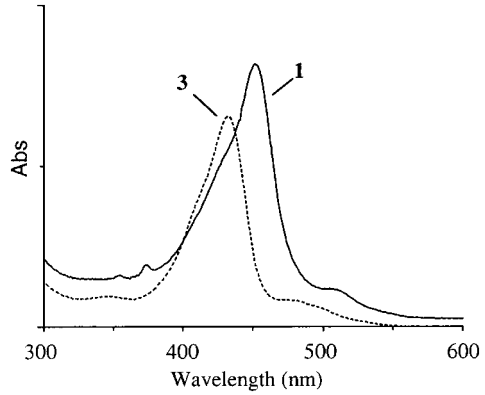


Figure 1. UV−vis spectra of porphodimethenes **1** and **3** in $CHCl_3$ within the region of 300 to 600 nm.

The fluorescence spectra of compounds **1**−**5** were measured via excitation at the absorption wavelengths corresponding to their UV−vis λ_{max}. All the compounds exhibit weak emission maxima between 592 and 688 nm. Quantum yields are low in comparison to those of porphyrins[10] and range between 1.02×10^{-4} and 8.70×10^{-3}, depending on the substituent and the isomer (*syn* or *anti*). In regard to the quantum yields and emission maxima, no trend could be identified among the different macrocycles, although the quantum yields of the isomer pairs were comparable.

Figure 2 displays the X-ray structure of **5**.[11] Bound to the 4-position of the pyrenones, the porphodimethene skeleton shares a *meso*-carbon atom with each of the polyaromatic ring systems, and they are aligned *trans* to each other. The two saturated carbon atoms force the macrocycle to adopt a strong roof-like folded structure with an interplanar roof angle of 139.1° with one carbonyl oxygen pointing toward and the other away from the macrocycle.

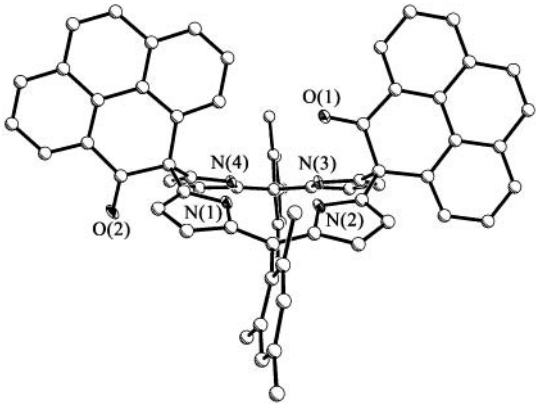


Figure 2. ORTEP diagram of the solid-state structure of **5** (30% probability; carbons atoms depicted with arbitrary radii). Hydrogen atoms omitted for clarity.

Regardless of whether the *spiro*-carbons are part of a five (**1**, **2**) or six (**3**−**5**) membered ring, all *anti* isomers exhibit a single set of signals for both the *meso*-bound polyaromatic ring systems and the mesityl substituents in the ^1H NMR, suggesting a fast flexing of the porphodimethene roof-like folded macrocycle as described for the related acenaphthenone derivatives.[2]

Even though the pyrenone derivatives **4** and **5** and the phenanthrenone-substituted porphodimethene **3** all contain a rigid six-membered ring at the *spiro*-lock of the *meso*-carbon, the reactivity of the pyrenone-substituted porphodimethenes **4** and **5** differs notably from that of the phenanthrenone derivative **3**. For instance, **4** and **5** were found to be stable under harsh reaction conditions (30% $KOH_{(aq)}$ in refluxing THF or H_2SO_4 in refluxing *o*-dichlorobenzene), and even in the presence of reagents such as $NaBH_4$, the macrocycle was resistant to ring opening and porphyrin formation. The rigidity of the pyrene backbone may prevent the opening of the six-membered ring since it would be converted to a 10-functionalized phenanthrene group upon porphyrin formation, and in this scenario, the functional group would be forced to point directly at the macrocyclic ring. In light of the inability to ring-open **4** and **5**, these compounds should be amenable to further functionalization of the carbonyl groups (e.g., Schiff base reactions) without altering the porphodimethene backbone, and attempts to derivatize the carbonyl groups in these compounds as well as related acenaphthenone porphodimethenes are underway.

In sharp contrast to the macrocycle containing the two pyrenone arms, the opening of the ring at the *spiro*-carbons in the phenanthrenone derivative **3** should yield a *trans* 2′ functionalized biphenyl substituted porphyrin, with the biphenyls being flexible enough to direct the functional groups away from the plane of the macrocycle. In an initial attempt to ring-open this compound, compound **3** was reacted with excess $NaBH_4$ in a THF/MeOH mixture at room temperature. After standard acidic workup, the desired *trans*-bis(2′-hydroxymethylbiphenyl)-substituted porphyrin (**3a**) was isolated in very high yield, although the product was sometimes contaminated with trace amounts of the *cis* isomer. To the best of our knowledge, methods for the preparation of 2′-functionalized biphenyl substituted porphyrins have not been reported. Figure 3 outlines the structure of the α,β-isomer **3a**.[11,12] In the solid state, the biphenyl moieties exhibit a twist of 75.7° relative to the macrocyclic ring, and in addition, the two phenyl groups of the biphenyl substituents are twisted by approximately 75° around the connecting C−C axis. As a result, the two hydroxymethyl carbons are situated 3.11 Å from the plane of the porphyrin, and this arrangement allows for minimal interactions of the

(10) Takahashi, K.; Goda, T.; Yamaguchi, T.; Komura, T.; Murata, K. *J. Phys. Chem. B* **1999**, *103*, 4868−4875.

(11) **5**: Crystals were grown by slow evaporation of a solution of **5** in dichlorobenzene. **3a**: Diffusion of pentane into a solution of **3a** in $CHCl_3$ produced crystals suitable for X-ray crystallography.

(12) The hydroxymethyl groups were disordered in the solid state, and the groups were refined in two distinct orientations (60 and 40% site occupancy respectively). For clarity, only one position is shown.

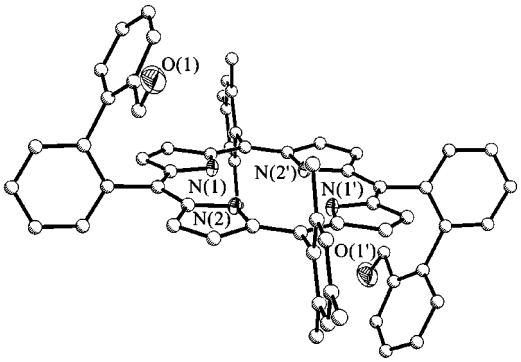


Figure 3. ORTEP diagram of the solid-state structure of **3a** (30% probability; carbons atoms depicted with arbitrary radii). Hydrogen atoms omitted for clarity. Primed and unprimed atoms are related by a center of inversion.

hydroxy group with the electron rich macrocycle. Upon heating, solutions of **3a** will equilibrate to a mixture of the α,α and α,*β* isomers.[13]

In summary, we have successfully demonstrated the utility of polyaromatic vicinal diketones for the preparation of *spiro*-tricycylic porphodimethenes. Depending on the nature of the diketone used in the synthetic scheme, porphodimethenes capable of or resistant to ring-opening reactions at the *spiro*-lock can be prepared. Following these promising results, the utility of other polycyclic diketones for porphodimethene formation is under investigation with the intent to further develop the chemistry of these unusual macrocycles.

Acknowledgment. We are very grateful to Prof. Kirk Schanze and Benjamin Harrison from the University of Florida for their assistance in performing the fluorescence measurements, and we thank the Research Corporation (RI0162), the Deutsche Forschungsgemeinschaft (post-doctoral fellowship for M.H.), and the University of Florida for financial support. Support from the National Science Foundation (CAREER Award 9874966) is also gratefully acknowledged.

Supporting Information Available: Synthetic and characterization details including NMR data for all porphodimethenes; X-ray crystallographic details for **1**, **5**, and **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) After 24 h of reflux, toluene solutions of the α,*β* isomer of **3a** convert to a 53:47 mixture of the α,α and α,*β* isomers of the porphyrin.