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Modified Corroles with One Meso-Free Carbon: Synthesis and Characterization

Jeyaraman Sankar, Venkatramanarao G. Anand, Sundararaman Venkatraman, Harapriya Rath, and Tavarekere K. Chandrashekar*

Department of Chemistry, Indian Institute of Technology, Kanpur-208 016, India

tkc@iitk.ac.in

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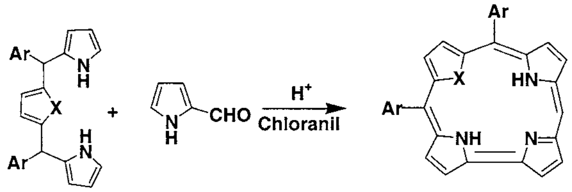
ABSTRACT



Synthesis of mono meso-free modified corroles by a [3+1] methodology is reported.

Even though the chemistry of corroles had its genesis with the work of Johnson and Kay in the early 1960s,[1] research on the development of corrole chemistry has gained momentum only recently after the landmark discovery of one-pot synthesis of meso aryl corroles independently by Gross,[2] Smith and Paolesse,[3] and their co-workers in 1999. Later on several groups optimized the syntheses of meso aryl corroles by reaction of various substituted and unsubstituted dipyrromethanes with normal and sterically hindered aldehydes using either TFA or BF_3-OEt_2 as catalyst.[4] In some cases, even the intermediate, bilane, was isolated, which further undergoes oxidative radical cyclization to afford meso aryl corroles in about 5−40% yield.[5]

Further functionalization of corroles can be achieved by the syntheses of meso free corroles taking advantage of the high reactivity of the meso carbon bridge. Such meso-free corroles are useful building blocks to construct large delocalized π-conjugated systems, which are useful electronic materials.[6] In this context meso-free porphyrins have been recently exploited to synthesize meso−meso linked dimeric, trimeric, and oligomeric arrays which exhibit useful electronic properties that result from strong π-conjugation.[7] A perusal of literature reveals only two reports on the synthesis of meso-free corroles. Specifically, Guilard, Kadish, and co-workers[8] reported synthesis of meso-free corroles by the reaction of diphenyl pyrrole aldehyde with dipyrromethane to afford a, c biladiene, which on subsequent cyclization gave the desired corrole. On the other hand, Bröring et al.[9] achieved the synthesis of β-substituted meso-free corrole by treatment of the bis(dipyrrin) with manganese acetate in the presence of molecular oxygen. The Mn(III) corrole formed was demetalated to the respective free base with use of HBr in acetic acid. In this letter, we wish to report a one-pot synthesis of meso-free corroles by a [3+1] methodology of the appropriate precursors (Scheme 1). It has been shown that the method works for both all aza corroles and mono oxa corroles with the normal and sterically hindered meso substituents.

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(1) Johnson, A. W.; Kay, I. T. *J. Chem. Soc.* **1965**, 1620−1629.

(2) Gross, Z.; Galili, N.; Saltsman, I. *Angew. Chem., Int. Ed.* **1999**, *38*, 1427−1429.

(3) Paolesse, R.; Jaquinod, L.; Nurco, D. J.; Mini, S.; Sagone, F.; Boschi, T.; Smith, K. M. *Chem. Commun.* **1999**, 1037−1308.

(4) Gryko, D. T. *Eur. J. Org. Chem.* **2002**, 1735−1743.

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

(6) (a) Paolesse, R. In *Porphyrin Handbook*; Kadish, K. M., Smith K. M., Guilard R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 2, pp 201−232. (b) Chou, J.-H.; Kosal, M. E.; Nalwa, H. S.; Rakow, N. A.; Suslick, K. S. In *Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 6, pp 43−131.

(7) (a) Osuka, A.; Shimidzu, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 135. (b) Aratani, N.; Osuka, A.; Kim, Y. H.; Jeong, D. H.; Kim, D. *Angew. Chem., Int. Ed.* **2000**, *39*, 1458. (c) Tsuda, A.; Osuka, A. *Science* **2001**, *293*, 79.

(8) Guilard, R.; Gros, C. P.; Bolze, F.; Jerome, F.; Ou, Z.; Shao, J.; Fischer, J.; Weiss, R.; Kadish, K. M. *Inorg.Chem.* **2001**, *40*, 4845−4855.

(9) Bröring, M.; Hell, C. *Chem. Commun.* **2001**, 2336−2337.

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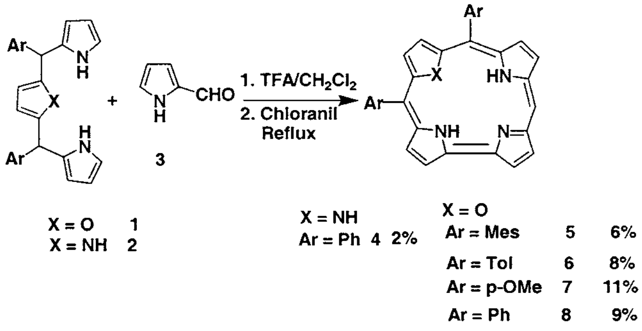
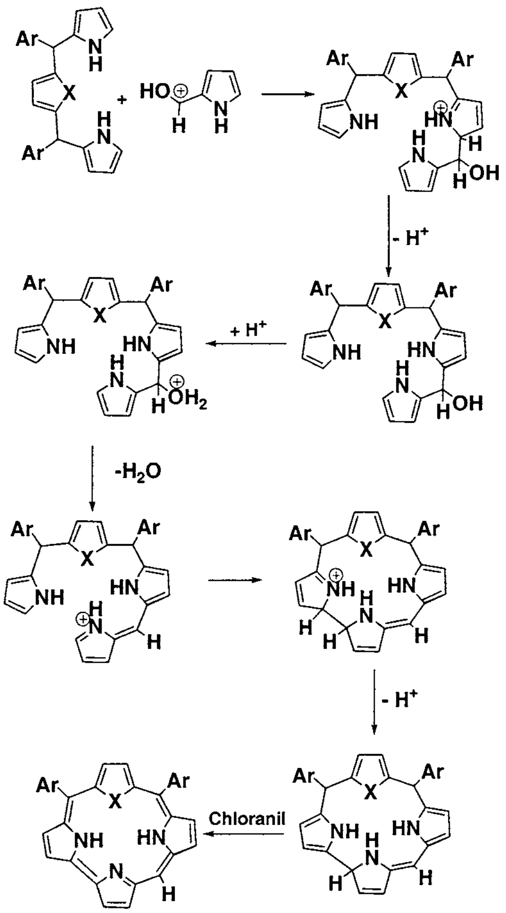
Scheme 1. [3+1] Condensation and Coupling



Acid-catalyzed MacDonald-type condensation and oxidative coupling reactions have been recently used by several research groups to synthesize various porphyrins and expanded porphyrins.[10] We have recently used [3+2][11] and [4+4][12] acid-catalyzed oxidative coupling reactions of appropriate precursors to synthesize meso aryl smaragdyrins and meso aryl octaphyrins, respectively, where direct pyrrole−pyrrole links were generated in the final step of the reaction. On the other hand, [4+3][13] and [3+1][14] acid catalyzed condensation reactions of appropriate precursors afforded heptaphyrins and modified porphyrins. In the present synthesis, we have followed a [3+1] methodology. The synthesis of corroles using [3+1] methodology can be achieved only when both condensation and oxidative coupling reactions take place simultaneously where the required direct pyrrole−pyrrole link and the third meso carbon bridge can be generated. Taking advantage of the reactivity of pyrrole for the selective electrophilic substitution at the α-positions, we speculated that the use of pyrrole carboxaldehyde as one of the precursors with tripyrrane should form the required corrole macrocycle. Thus the reaction of tripyrranes **1** or **2** with pyrrole carboxaldehyde **3** in the presence of 1 equiv of TFA catalyst followed by oxidation with chloranil undergoes a simultaneous oxidative coupling and condensation to generate a direct pyrrole−pyrrole link on one side and a meso carbon bridge on the other side to give the desired meso-free corroles[18] in 5−11% yield. However, the reaction of **2** with **3** was found to be sensitive to the TFA concentration as well as the volume of the solvent. Under dilute conditions and at low acid concentration the desired corrole was formed in 1−2% yield while the major product was mono meso-free triphenyl porphyrin. An increase in the concentration of TFA resulted in exclusive formation of porphyrin rather than corrole. To optimize the reaction, two different concentrations of TFA were tried. At 0.1 equiv of TFA, the reaction did work but the yield of the final corrole was only 2−5% depending on the nature of the aldehyde. Tripyrranes containing sterically hindered substituents gave slightly lower yield relative to tripyrranes containing simple meso aryl substituents. At 1 equiv of TFA concentration, the yields were almost doubled. No attempt was made to further increase the acid concentration as at concentrations above 1 equiv, the tripyrranes are not stable and undergo acidolysis. The possible reaction mechanism is depicted in Scheme 2.

Scheme 2. Mechanism for the Formation of the Corroles



The structures of the corroles were confirmed by a variety of spectroscopic techniques (see Supporting Information for

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[10] (a) Sessler, J. L.; Gebauer, A.; Weghorn, S. J. In *Porphyrin Hand Book*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 2, pp 55−124. (b) Lash, T. D. In *Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 2, pp 125−199.

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[12] Anand, V. G.; Pushpan, S. K.; Venkatraman, S.; Dey, A.; Chandrashekar, T. K.; Joshi, B. S.; Roy, R.; Teng, W.; Ruhlandt-Senge, K. *J. Am. Chem. Soc.* **2001**, *123*, 8620−8621.

[13] (a) Anand, V. G.; Pushpan, S. K.; Srinivasan, A.; Narayanan, S. J. P.; Sridevi, B.; Chandrashekar, T. K.; Roy, R.; Joshi, B. S. *Org. Lett.* **2000**, *2*, 3829−3832. (b) Anand, V. G.; Pushpan, S. K.; Venkatraman, S.; Narayanan, S. J. P.; Dey, A.; Chandrashekar, T. K.; Roy, R.; Joshi, B. S.; Deepa, S.; Sastry, G. N. *J. Org. Chem.* **2002**, *67*, 6309−6319.

[14] (a) Venkatraman, S.; Anand, V. G.; Pushpan, S. K.; Sankar, J.; Chandrashekar, T. K. *Chem. Commun.* **2002**, 462−463. (b) Venkatraman, S.; Anand, V. G.; Prabhuraja, V.; Rath, H.; Sankar, J.; Chandrashekar, T. K.; Teng, W.; Ruhlandt-Senge, K. *Chem. Commun.* **2002**, 1660−1661.

[15] Isocorrole also exhibits a similar kind of tautomerism. For details see: (a) Will, S.; Rahbar, A.; Schmickler, H.; Lex, J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1390−1393. (b) Vogel, E.; Binsack, B.; Hellwig, Y.; Erben, C.; Heger, A.; Lex, J.; Wu, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2612−2615.

details). The FAB mass spectrum confirmed the composition and the solution structures were assigned by detailed ^{1}H and 2D NMR experiments. Briefly, for **6**, the outer meso hydrogen resonates as a sharp singlet at 9.6 ppm and the two β-CH protons of the furan ring appear as a singlet at 8.9 ppm. The four bipyrrolic β-CH protons are not equal and hence appear as two AB patterns in the region 8.5−9.1 ppm.

The β-CH protons of the pyrrole ring adjacent to the furan ring appear as two quartets at 8.5 and 9.0 ppm. The appearance of quartets indicates the four-bond coupling of the NH protons with the β-CH protons. Of the two inner NH protons, one of them, the NH proton on the pyrrole ring, is localized and resonates at −2.5 ppm and the other proton on the bipyrrole ring undergoes a rapid tautomerism, exchanging sites on the two nitrogens of the bipyrrolic ring,[15] and hence could not be detected up to 233 K. However, upon protonation, this tautomerism is arrested and three distinct signals for the three NH protons are seen at −4.9, −2.6, and −2.3 ppm at 233 K.

The electronic absorption spectra (Figure 1) show an intense Soret band and weak Q-bands in the visible region and the effect of core modification is seen in the blue shift of absorption bands[16] for **5**−**8** relative to all aza corrole **4**. Upon protonation, the Soret band of the modified corrole split into two bands suggesting the lowering of the symmetry in solution due to the steric crowding. Overall, the spectroscopic properties suggest that the corroles are aromatic and are consistent with the presence of $(4n+2)$ π-electrons. The aromatic nature is also evident from the chemical shift difference ($\Delta\delta$) between the most shielded and the most deshielded protons in the ^{1}H NMR spectrum. The $\Delta\delta$ value varies in the range 11−12 ppm for free bases and 13−15 ppm for the protonated derivatives.

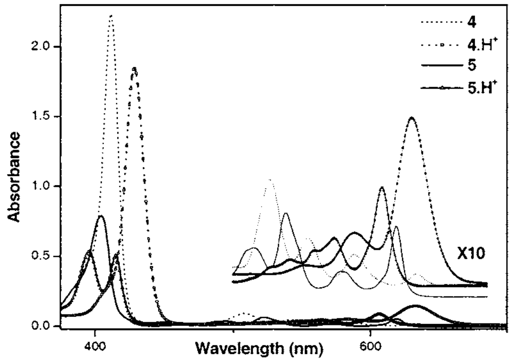
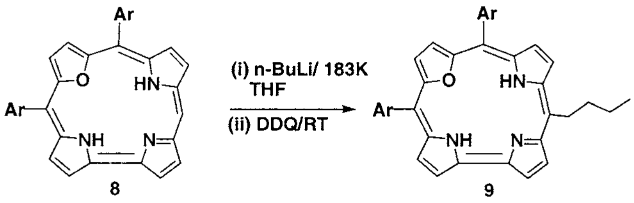


Figure 1. Electronic absorption spectra of **4** and **5** [$\sim 10^{-6}$ M] and their protonated derivatives in CH_2Cl_2. The protonation is achieved by addition of a dilute solution of TFA in CH_2Cl_2.

The reactivity of the meso free corroles was tested by the reaction with organo lithium reagents (Scheme 3). Reaction of **8** with n-butyllithium at 183 K followed by oxidation with DDQ at room temperature afforded the meso-substituted derivative **9** in 10% yield and no evidence was found for the reaction of n-BuLi on the β-pyrrole positions. Senge and co-workers[17] have recently reported the reaction of organo lithium reagents with meso free porphyrins. They have observed the formation of meso-substituted products as well as meso−meso linked dimer depending on the reaction conditions. In the present study the meso−meso linked corrole was not formed since there is only one free meso position in the corroles as opposed to two free meso positions in the porphyrins used by Senge and co-workers.

Scheme 3. Reaction of **8** with n-BuLi and DDQ



In conclusion, a rational method is described for the synthesis of meso-free corroles and modified oxa corroles using easily available, stable precursors. Since the meso substituent is a part of all the precursors, the methodology works for both sterically crowded and normal meso substituents. Furthermore, the availability of all aza corroles and the modified corroles by a single method would allow synthesis of authentic metal complexes of corroles in +3 and +2 oxidation states. For example, all aza corrole stabilizes the +3 oxidation state while the oxa corrole stabilizes the +2 oxidation state of the metals. Studies on the metal complexes and further functionalization are in progress.

Acknowledgment. We thank CSIR, New Delhi, India for the research grant provided.

Supporting Information Available: Characterization data including FAB mass, UV−vis data, ^{1}H NMR, and 2D NMR of selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org..

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(16) The replacement of pyrrole nitrogen by furan oxygen in the tetraphenyl porphyrins results in the blue shift of the absorption bands and the magnitude of the shift depending on the number of oxygens present in the core. For details see: Sridevi, B.; Narayanan, S. J.; Srinivasan, A.; Reddy, M. V.; Chandrashekar, T. K. *J. Porphyrins Phthalocyanins* **1998**, *2*, 69−78.

(17) Senge, M. O.; Feng, X. *Tetrahedron Lett.* **1999**, 4165−4168.

(18) In a typical reaction, for example, **1** (386 mg, 1.02 mmol) was reacted with **3** (97 mg, 1.02 mmol) in dichloromethane (200 mL) containing TFA (0.07 mL, 1.02 mmol) under nitrogen atmosphere with stirring for about 90 min. The reaction was monitored with TLC. After the reaction was completed, the mixture was opened to air and chloranil (251 mg, 1.02 mmol) was added and the mixture was heated at reflux for a further period of 90 min. After the usual workup, the purification by column chromatography with alumina (basic, grade III) the first pink band eluted with 2:8 dichloromethane/petroleum ether gave **6,** as a purple solid.