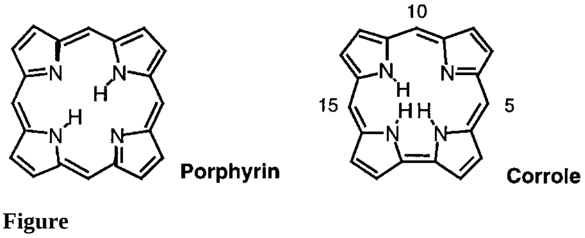
Triarylcorroles by Oxidative Coupling of Triaryltetrapyrranes

Raymond P. Briñas, Christian Brückner*
Department of Chemistry, University of Connecticut, Storrs, CT 06269, USA
Fax +1 (860) 486-2981; E-mail: bruckner@nucleus.chem.uconn.edu

Received 20 December 2000

Abstract: A general two-step, one-pot synthesis of *meso*-triphenylcorrole from 5-phenyldipyrrane is presented. A number of *p*-phenyl-substituted 5-phenyldipyrranes were condensed with substituted benzaldehydes under acid catalyzed conditions to produce a mixture highly enriched in the corresponding tetrapyrranes. The crude mixtures were oxidized with DDQ or chloranil to produce the corresponding *meso*-triarylcorroles in good to excellent yield. The method is applicable to the synthesis of *meso*-triarylcorroles containing two differently substituted phenyl groups in the 5-,15- and 10-positions, respectively.

Key words: corrole synthesis, tetrapyrrane, oxidative coupling, "2+2" condensation

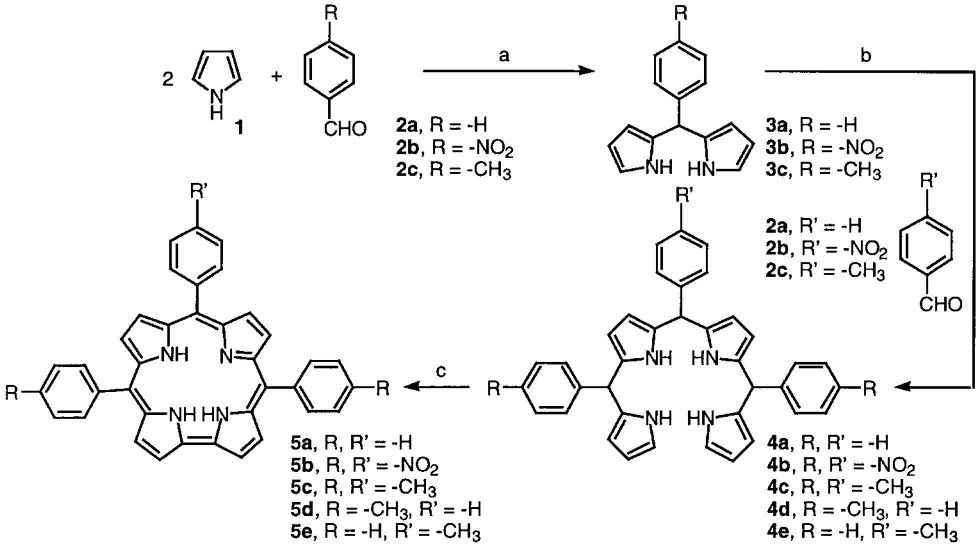


Figure

Corroles, the parent compound of the hydrocorrole (corrin) macrocycle found in coenzyme B_{12}, are tetrapyrrolic fully conjugated macrocycles containing three methine bridges and one direct pyrrole-pyrrole linkage.[1] Thus, their macrocycle skeleton is contracted by one carbon atom as compared to that of porphyrins. This difference results inter alia in altered metal coordination properties of the smaller trianionic tetradentate corrole ligand when compared to those of the tetradentate dianionic porphyrin ligand.[2] Corroles are particularly able to stabilize high metal oxidation states.[3,4]

One of the most studied porphyrins is *meso*-tetraphenylporphyrin (TPP) for which optimized syntheses have been available for some time.[5] Surprisingly, the analogous *meso*-triphenylcorrole did not become known until 1999, although synthetic corroles have also had a long history.[2,6-9] Iron complexes of *meso*-tri(pentafluorophenyl)corrole have been pioneered by Gross as catalysts for epoxidation, hydroxylation and cyclopropanation reactions.[10] His group also described chiral N-substituted corroles.[11] However, the convenient and simple one-step syntheses described by Gross and Goldberg for *meso*-tri(pentafluorophenyl)corrole are not general since they are restricted to the use of highly reactive pentafluorobenzaldehyde as reactant.[7,12] The parent unsubstituted *meso*-triphenylcorrole was isolated in (unoptimized) 6% yield as one of several macrocyclic products from a modified Rothemund reaction.[8] Clearly, this method is limited with respect to the amounts of corrole accessible.

The aforementioned syntheses of triarylcorrole hint at the mechanism operating in its formation. Particularly, Gross's and Goldberg's paper, describing linear oligo-



Scheme Reagents and conditions: (a)[17] TFA, 25 °C (b) solvent (see Table), 1 equiv TFA; no isolation of **4a-e** (c) neutralization with Et_3N; 5 equiv oxidant (see Table) in toluene, 12 h, 25 °C; chromatography CH_2Cl_2:pet ether 1:1.

Synlett 2001, No. 3, 442–444 ISSN 0936-5214 © Thieme Stuttgart · New York

Table Triarylcorrole derivatives **5a-e** produced as shown in the Scheme

Entry	Aldehyde	Dipyrrane	Product	Yield [%]	^{1}H NMR Spectroscopic Data[d] (400 MHz, CDCl$_3$/5% CD$_3$OD) [ppm]
1[a,b]	**2a**	**3a**	**5a**	40	δ 8.83 (br s, 4H), 8.50 (br s, 4H), 8.33 (d, *J*=5 Hz, 4H), 8.15 (d, *J*=5 Hz, 2H), 7.85-7.70 (m, 9H)[c]
2[a,c]	**2a**	**3a**	**5a**	34[g]	
3[f,c]	**2b**	**3b**	**5b**	18	δ 9.04 (d, *J*=4.5 Hz, 2H), 8.75-8.65 (m, 12H), 8.55 (d, *J*=8.5 Hz, 2H), 8.48 (d, *J*=4.5 Hz, 2H), 8.40 (d, *J*=4.5 Hz, 2H)
4[f,c]	**2c**	**3c**	**5c**	20	δ 8.88-8.80 (m, 4H), 8.50 (br s, 4H), 8.23 (br s, 4H), 8.05 (d, *J*=5 Hz, 2H), 7.65-7.50 (m, 6H), 2.67 (s, overlapping, 3H), 2.65 (s, overlapping, 6H)
5[a,c]	**2a**	**3c**	**5d**	20	δ 8.90 (br s, 2H), 8.80 (br s, 2H), 8.55-8.45 (m, 4H), 8.40-7.95 (m, 6H), 7.80-7.45 (m, 7H), 2.64 (s, 6H)
6[a,c]	**2c**	**3a**	**5e**	30	δ 8.92 (br s, 2H), 8.83 (br s, 2H), 8.60-8.40 (m, 4H), 8.40-8.30 (m, 4H), 8.0 (m, 2H), 7.80-7.60 (m, 6H), 7.50 (m, 2H), 2.66 (s, 3H)

[a] CH$_3$CN, 1 equiv TFA, 25 °C (ref. 23) [b] oxidant DDQ [c] oxidant chloranil [d] **5a-e** were characterised by ^{13}C NMR, UV-VIS and MS; analytical purity of **5a** was proven by elemental analysis [e] in DMSO-d_6 additional signal at δ -2.7 (br s, 3H) [f] CH$_2$Cl$_2$ distilled over CaH$_2$; 1 equiv TFA, 0 °C (ref. 23) [g] 9 mmol scale, yield of 1.9g **2a**.

pyrrolic pigments isolated as side products of their corrole synthesis,[12] indicated to us that it was likely that a tetrapyrrane[13] was formed as a primary condensation product and that, upon oxidation, the pyrrole-pyrrole linkage was established. The macrocycle subsequently formed oxidizes to the final corrole oxidation state. Similar oxidatively induced formations of direct pyrrole-pyrrole linkages are known reactions in pyrrole and pyrrolic macrocycle chemistry, including the formation of heterocorroles.[14,15] Some ß-alkylcorrole syntheses also rely on the formation of the pyrrole-pyrrole linkage as the penultimate step (before oxidation), although their mechanisms are diverse.[2,6,16]

Hence, the task became the directed synthesis of 5,10,15-triphenyltetrapyrrane and its oxidative ring closure. The chemistry of 5-phenyldipyrranes, 5,10-diphenyltripyrranes and their higher homologues has seen rapid development in past years.[17,18] One- and multi-step syntheses of 5,10,15-triaryltetrapyrranes were recently described by Lindsey and co-workers,[18] Lee and co-workers[18,19] and Liebeskind and Nickel,[20] respectively. We opted for an alternative two-step one-pot route towards the required tetrapyrranes, illustrated in the Scheme. Pyrrole (**1**) and benzaldehydes **2a-c** were reacted in known fashion to produce 5-aryldipyrranes **3a-3c**.[16] They were condensed with benzaldehydes **2a-c** under mild acid catalysis (molar ratio of **2**:**3** 1:6). Upon the disappearance of benzaldehyde, as monitored by TLC, the crude reaction mixture containing the tetrapyrranes **4a-c** was treated with a 5-fold molar excess (based on the amount of benzaldehyde used) of DDQ or chloranil.[21] Flash column chromatography, followed by recrystallization, was used to isolate and purify the dark green non-polar corroles **5a-c** in moderate to high yields. Importantly, only traces of other pyrrolic macrocycles and no TPP could be detected in these corrole syntheses. The excess dipyrranes were oxidized to form the basic and polar *meso*-aryldipyrrins, visible as bright yellow spot on TLC plates developed with polar solvents, and do not interfere with the isolation of the corroles.[22] The table provides detailed information about the reactions.

The above described syntheses of corroles have the advantage that the isolation of the intermediate triaryltetrapyrranes, while possible,[19] is not required. In fact, isolation of the triaryltetrapyrranes and subsequent oxidation lowered the overall yield as the chromatographic isolation of the tetrapyrranes is difficult and the products obtained are only moderately stable. Secondly, the conditions for preparing the tetrapyrranes **4** were selected by Lindsey to be sufficiently mild to prevent acid-catalyzed scrambling of the aryl groups.[23] This presented us with the option of choosing a substituted benzaldehyde with substituents differing from those of the 5-aryldipyrromethane. The resulting tetrapyrrane and the derived triarylcorrole (**5d-e**) contain, regiospecifically, two differently substituted phenyl groups. Our synthesis parallels the strengths of 2+2 syntheses of TPP. Recent work by Lee and co-workers describing the oxidative ring closure of tetrapyrranes and oxidative fusion of tri- with dipyrranes to form corroles and expanded corroles corroborates our conclusions with complementary findings. However, their method is not applicable to the synthesis of triarylcorroles containing regiospecifically two types of phenyl substituents in the 5-, 15-, and 10-positions, respectively.[19] After the submission of our manuscript, a paper by Gryko describing the synthesis of A$_2$B-corroles using a number of (sterically encumbered) 2,6- and 2,4,6-phenyl-substituted phenyldipyrromethanes and benzaldehydes was published.[24] While the exclusive use of benzaldehydes with electron-withdrawing substituents, the dipyrrane:benzaldehyde ratio, the details of the procedure and the resulting products differ from those described here, Gryko's paper further highlights the synthetic utility of the triarylcorrole synthesis by oxidative coupling of tetrapyrranes.

In summary, we present herein a general method for the synthesis of triarylcorroles, and a method of making triarylcorroles containing regiospecifically two types of aryl substituents. We present further evidence for the stepwise mechanism of the corrole formation in Rothemund-type condensations.[8]

Acknowledgement

This work was supported by a grant from the University of Connecticut Research Foundation. We thank Professor Chan-Hee Lee, Kangwon National University, South Korea, for providing us with a pre-print of his article (reference 19).

References and Notes

(1) *B12*; Dolphin, D., Ed.; John Wiley & Sons: New York, 1982; Vol. 1-2.

(2) Licoccia, S.; Paolesse, R. *Struct. Bonding (Berlin)* **1995**, *84*, 71-133.

(3) (a) Vogel, E.; Will, S.; Tilling, A. S.; Neumann, L.; Lex, J.; Bill, E.; Trautwein, A. X.; Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 731-735. (b) Will, S.; Lex, J.; Vogel, E.; Adamian, V. A.; Van Caemelbecke, E.; Kadish, K. M. *Inorg. Chem.* **1996**, *35*, 5577-5583. (c) Ghosh, A.; Wondimagegn, T.; Parusel, A. B. J. *J. Am. Chem. Soc.* **2000**, *122*, 5100-5104.

(4) Meier-Callahan, A. E.; Bray, H. B.; Gross, Z. *Inorg. Chem.* **2000**, *39*, 3605-3607.

(5) (a) Rothemund, P. *J. Am. Chem. Soc.* **1936**, *58*, 625. (a) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476. (b) Lindsey, J. S.; MacCrum, K. A.; Tyhonas, J. S.; Chuang, Y.-Y. *J. Org. Chem.* **1994**, *59*, 579-587.

(6) Grigg, R. In *The Porphyrins*; D. Dolphin, Ed.; Academic Press: New York, 1978; Vol. 2, 327.

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

(8) Paolesse, R.; Mini, S.; Sagone, F.; Boschi, T.; Jaquinod, L.; Nurco, D. J.; Smith, K. M. *Chem. Commun.* **1999**, 1307-1308.

(9) Paolesse, R.; Licoccia, S.; Bandoli, G.; Dolmella, A.; Boschi, T. *Inorg. Chem.* **1994**, *33*, 1171-1176.

(10) Gross, Z.; Simkhovich, L.; Galili, N. *Chem. Commun.* **1999**, 599-600.

(11) Gross, Z.; Galili, N. *Angew. Chem., Int. Ed.* **1999**, *38*, 2366-2369.

(12) Gross, Z.; Galili, N.; Simkhovich, L.; Saltsman, I.; Botoshansky, M.; Bläser, D.; Boese, R.; Goldberg, I. *Org. Lett.* **1999**, *1*, 599-602.

(13) The naming of tetrapyrranes follows suggestions of H. Falk In *The Chemistry of Oligopyrroles and Bile Pigments*, Springer: Wien, 1989, and is preferred over the more common but misleading names tetrapyrromethane or bilane.

(14) (a) Sessler, J. L.; Seidel, D.; Lynch, V. *J. Am. Chem. Soc.* **1999**, *121*, 11257-11258. (b) Narayanan, S. J.; Sridevi, B.; Chandrashekar, T. K.; Englich, U.; Ruhland-Senge, K. *Org. Lett.* **1999**, *1*, 587-590.

(15) Cho, W.-S.; Lee, C.-H. *Tetrahedron Lett.* **2000**, *41*, 697-701.

(16) Licoccia, S.; Di Vona, M. L.; Paolesse, R. *J. Org. Chem.* **1998**, *63*, 3190-3195.

(17) (a) Lee, C.-H.; Lindsey, J. S. *Tetrahedron* **1994**, *50*, 11427-11440. (b) Brückner, C.; Sternberg, E. D.; Boyle, R. W.; Dolphin, D. *Chem. Commun.* **1997**, 1689-1690. (c) Brückner, C.; Posakony, J. J.; Johnson, C.; Boyle, R. W.; James, B. R.; Dolphin, D. *J. Porphyrins Phtalocyanines* **1998**, *2*, 455-465.

(18) (a) Lee, C.-H.; Li, F.; Iwamoto, K.; Dadok, J.; Bothner-By, A. A.; Lindsey, J. S. *Tetrahedron* **1995**, *51*, 11645-11672. (b) Ka, J.-W.; Lee, C.-H. *Tetrahedron Lett.* **2000**, *41*, 4609-4613.

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

(20) Nickel, E.G.; Liebeskind, L.S. Poster Presentation at the 1st International Conference on Porphyrins and Phtalocyanines (ICCP-1), Dijon, France, June 25-30, 2000.

(21) Fumigation of the developed TLC plates with bromine vapor (CAUTION − fume hood) stains the dipyrranes bright red, the tripyrrane purple and the tetrapyrrane brown.

(22) Brückner, C.; Rettig, S. J.; Dolphin, D. *Can. J. Chem.* **1996**, *27*, 2182-2193.

(23) (a) Littler, B. J.; Cirgingh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864-2872. (b) Rao, P. D.; Littler, B. J.; Geier, G. R., III; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 1084-1092.

(24) Gryko, D.T. *Chem. Commun.* **2000**, 2243-2244.

Article Identifier:
1437-2096,E;2001,0,03,0442,0444,ftx,en;S09900ST.pdf