ChemComm
www.rsc.org/chemcomm

Porphyrin ring contraction: a one-pot reaction leading to divalent corroles†

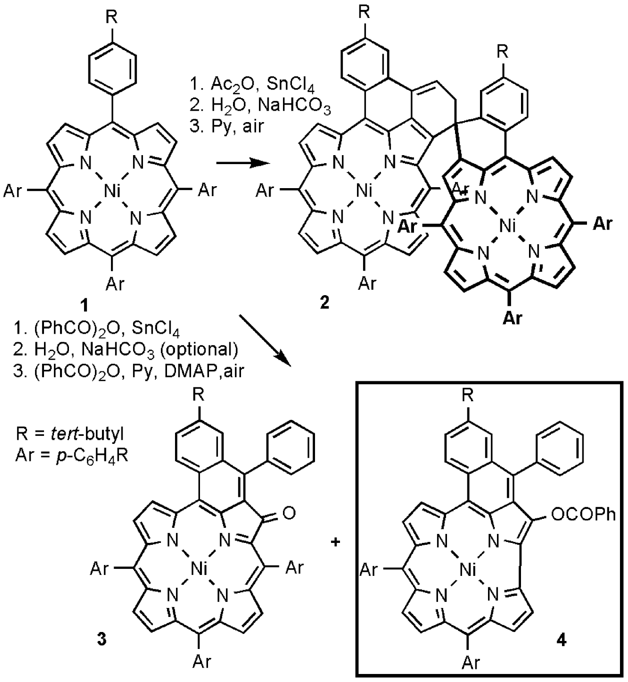
Christophe Jeandon, Romain Ruppert and Henry J. Callot*
Université Louis Pasteur, UMR CNRS 7123, Faculté de Chimie, 1 rue Blaise Pascal, 67000 Strasbourg, France. E-mail: callot@chimie.u-strasbg.fr

Received (in Cambridge, UK) 19th January 2004, Accepted 11th March 2004
First published as an Advance Article on the web 2nd April 2004

Reaction of nickel *meso*-tetraarylporphyrins with benzoic anhydride and tin tetrachloride, followed by air oxidation under basic conditions, results in ring contraction, yielding divalent corroles.

When we attempted the acylation of various *meso*-tetraarylporphyrins, as nickel complexes, under Friedel–Crafts conditions, we obtained a variety of products and also found that only highly hindered substrates and/or reagents produced the normal β-acyl derivatives.[1] As a rule, a cyclisation involving the neighbouring aryl group occurs, except when the *ortho* positions are already substituted or when sterically demanding substituents inhibit this reaction. In the case of acetylation, the initial product undergoes several additional reactions, ending in the formation of dimer **2** in good yield (Scheme 1).

In order to block this reaction sequence, we selected anhydrides that do not bear hydrogen(s) bound to the α carbon and ran the reaction using benzoic anhydride under similar conditions: (i) benzoylation catalysed by $SnCl_4$; (ii) hydrolysis (aqueous $NaHCO_3$). As was the case under acetylation conditions, the initial product proved to be unstable and the benzoylation of a hypothetical alcohol was attempted. We found that the use of benzoic anhydride induced a complete change in the course of the reaction and led to the formation of green **3** and dark blue **4**, in addition to several minor products. The initial yield of **4** was very low (*ca.* 3–6%) but increased to 24% (R = OEt) upon modification of the reaction conditions and substrate. This yield falls in the range of the best values published for corrole syntheses.[2] In addition, we found that the hydrolysis step could be skipped, thus realising one-pot conditions: vacuum evaporation followed by benzoylation under air gave **4** (R = OEt) in 15% yield. Ketone **3** was produced in all experiments in 15–35% yield and its structure was easily deduced from its NMR and UV-visible data, these being very similar to those of the analogue which is unsubstituted at the new six-membered ring.[3,4]



Scheme 1

The NMR data for **4** showed at first sight the absence of aromaticity in the compound. The pyrrole signals are located between 5.7 and 7.2 ppm, while the *meso*-aryl groups do not show the typical pattern for *meso*-arylporphyrins. In addition, one *meso*-aryl group was missing, but a phenyl and a benzoyl group had been added, as shown by MS and NMR data. The UV-visible spectrum (R = OEt) did not look like that of either a porphyrin or an aromatic corrole (bands at 394, 496, 602, 704 and 766 nm).

In the *para*-tolyl series (**4**, R = Me), the structure shown in Fig. 1 was determined by X-ray crystallography.‡ The product is a non-aromatic corrole, but the planarity of the tetrapyrrole unit is remarkable. While the β,β C–C bonds of pyrroles are usually short—and this is true for three of the pyrroles in **4**—the substituted pyrrole shows the opposite, with a long β,β C–C bond of 1.449 Å. The long pyrrole *meso*-C–C bond (1.447 Å) is likely to be the result of H···H interaction (see Fig. 1).

Although it is not aromatic, corrole **4** (R = alkyl or alkoxy groups) is very stable in the solid state as well as in solution. Unlike the classical corroles,[2] it is a divalent ligand and its nickel(II) complex is neutral.

For the mechanistic study, we started with **1** (R = OEt), the *para*-ethoxy series combining reasonably soluble starting material with excellent crystallinity of the products. The transformation can be divided in two sequences, an acylation and cyclisation sequence forming the six-membered ring, followed by an oxidation, coupled, in the case of **4**, to a ring contraction, the loss of the *meso*-bridge and an esterification.

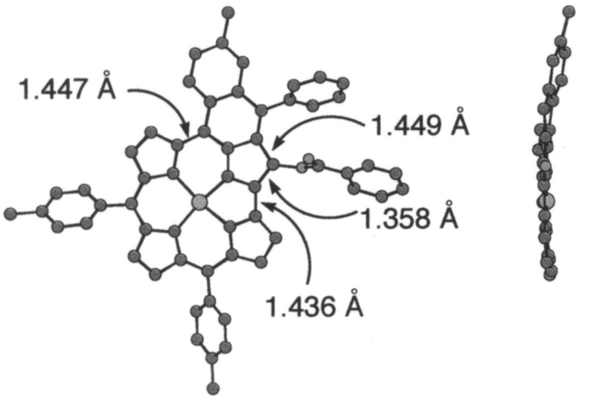


Fig. 1 X-Ray crystal structure of **4** (R = CH_3; one of the two independent molecules): (left) viewed perpendicularly to the corrole plane (H omitted for clarity); (right) rotated by 90° (aryl and benzoate substituents omitted).

---

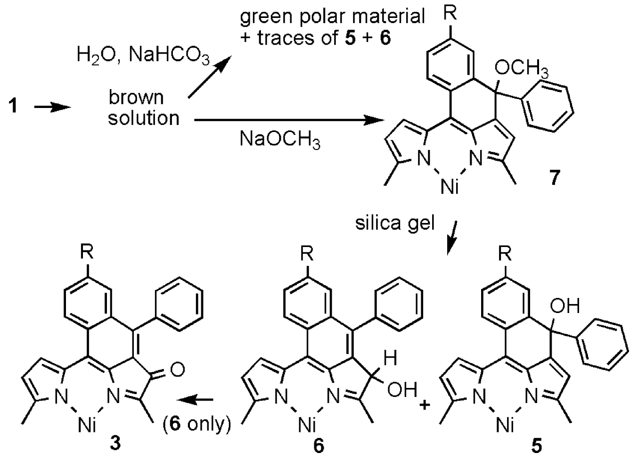
† Electronic supplementary information (ESI) available: experimental procedures for syntheses of corrole **4** and ketone **3** (R = OEt), and for preparing **4** from **11** (R = H). See http://www.rsc.org/suppdata/cc/b4/b400812j/

DOI: 10.1039/b400812j

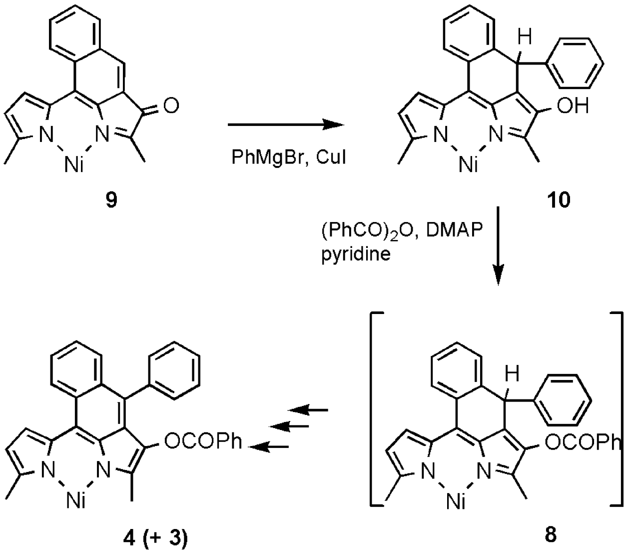
The first sequence (Scheme 2) has already been discussed in the literature[1] and should give one (or two) isomeric allylic alcohol(s), like **5** or **6**. However, the crude brown reaction mixture gave a green solution on hydrolysis, which had a chlorin-like UV-visible spectrum, but only traces of alcohols **5** and **6** were detected by TLC, in addition to a very polar green material. Quenching the brown solution with $NaOCH_3$ gave ether **7** in high yield. On standing on silica gel, this ether slowly hydrolysed to give both **5** and **6**. The sequence shown in Scheme 2 accounts for these observations.

The second sequence leading from the green hydrolysis mixture, or directly from the initial brown solution, to the **3** + **4** mixture is more difficult to account for. None of the products shown above (**3**, **5**, **6** or **7**), when treated with $(PhCO)_2O$ and DMAP in pyridine, proved to be a precursor of corrole **4**. Only **6** produced ketone **3**, but it was almost absent from the green hydrolysis mixture.

When considered retrosynthetically, the formation of corrole **4** could require (i) an oxygenated function at the pyrrolic β-position and (ii) two β-sp^2 carbons. This would realise the appropriate pyrrolic substitution, 'frozen' as an enol ester, as well as create on the new six-membered ring an oxidation-prone C–H bond of the triphenylmethyl type, as in **8** (Scheme 3). These requirements are in agreement with the observed beneficial effects of excess anhydride and the presence of an electron-donating group on the *meso*-phenyl moiety. Such a structure is accessible on reaction of the known ketone **9** (*meso*-tetraphenyl series)[3,4] with a phenyl cuprate to give enol **10**. This reaction proceeded in good yield and, indeed, **10**—a rather unstable compound that do not need to be purified—gave corrole **4** in 11% yield, in addition to ketone **3** (34%), upon treatment with $(PhCO)_2O$/DMAP in pyridine, demonstrating that, at some stage, an allylic alcohol to enol isomerisation operates.



Scheme 2



Scheme 3

The presence of the nickel ion proved to be crucial [and, indeed, the copper(II) complex did not produce corrole, but only the copper analogue of **3**]. We think that the ring contraction is triggered by the fact that this small ion fits much better in a corrole rather than in a porphyrin.

Porphyrin to corrole ring contraction is virtually unknown. The only known example operates under reductive conditions: when treated with $Re_2(CO)_{10}$, *meso*-tetratrifluoromethylporphyrin gave the corresponding corrole in 9% yield[5] and it was suggested that the product was formed from reduced intermediates. A few ring contractions with loss of a carbon bridge from an unsaturated tetrapyrrole are known: porphycene to isocorroles,[6] homoporphyrin to hemiporphycene[7] or porphyrin[8] and phthalocyanine to triazacorrole.[9] In addition, an octapyrrole to bis-corrole rearrangement with the loss of a bridge carbon was recently described.[10] Little is known of the mechanism, but in some cases, an intermediate cyclopropane has been suggested.

In conclusion, this porphyrin to corrole ring contraction gives access to a new series of divalent corroles. The reaction utilises the cheapest available synthetic porphyrins and its yield, although modest, is comparable to that of most corrole syntheses. The reactivity and the coordination chemistry of these divalent corroles are now being actively investigated.

We thank A. Decian and N. Kyritsakas for solving the structure of corrole **4**.

Notes and references

‡ *Crystal data* for **4** (R = Me): $C_{54}H_{36}N_4NiO_2$, M = 831.62, triclinic, space group $P\bar{1}$; a = 13.7819(2), b = 16.2114(2), c = 18.7744(3) Å, α = 71.381(5), β = 87.314(5), γ = 85.678(5)°, V = 3962.7(1) Å^3, Z = 4, D_c = 1.39 g cm^{-3}. A total of 34 497 $\pm h \pm k + l$ reflections were collected on a red prism of dimensions 0.20 × 0.16 × 0.04 mm^3 using a KappaCCD diffractometer utilising graphite-monochromated Mo-Kα radiation with $2.5 < \theta < 30.04$ and T = 173 K. 12 578 unique reflections having $I > 3\sigma(I)$ were used to determine and refine the structure. Final results: R = 0.046, Rw = 0.063, GOF = 1.071, largest peak in final difference = 0.529 e Å^{-3}. CCDC 229351. See http://www.rsc.org/suppdata/cc/b4/b400812j/ for crystallographic data in CIF or other electronic format.

1 C. Jeandon, R. Ruppert, S. Richeter and H. J. Callot, *Org. Lett.*, 2003, **5**, 1487.

2 R. Paolesse, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, 2000, **vol. 2**, p. 201; C. Erben, S. Will and K. M. Kadish, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, 2000, vol. 2, p. 233; J. Sessler and S. J. Weghorn, *Expanded, Contracted and Isomeric Porphyrins*, Pergamon, Oxford, 1997, p. 11; D. T. Gryko, *Eur. J. Org. Chem.*, 2002, 1735. For more recent articles, see, for example: L. Simkhovich, I. Goldberg and Z. Gross, *Org. Lett.*, 2003, **5**, 1241; D. Gryko, M. Tasior and B. Koszarna, *J. Porphyrins Phthalocyanines*, 2003, **7**, 239; M. Bröring, C. Hell, C. D. Brandt and E. Consul Tejero, *J. Porphyrins Phthalocyanines*, 2003, **7**, 214; E. Steene, A. Dey and A. Ghosh, *J. Am. Chem. Soc.*, 2003, **125**, 16 300.

3 Y. V. Ishkov, *Russ. J. Org. Chem.*, 2001, **37**, 288.

4 S. Richeter, C. Jeandon, J.-P. Gisselbrecht, R. Graff, R. Ruppert and H. J. Callot, *Inorg. Chem.*, 2004, **43**, 251.

5 M. K. Tse, Z. Zhang, T. C. W. Mak and K. S. Chan, *Chem. Commun.*, 1998, 1199.

6 S. Will, A. Rahbar, H. Schmickler, J. Lex and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1390; K. L. Neumann, PhD Dissertation, University of Cologne, Germany, 1994, p. 37.

7 H. J. Callot, A. Rohrer and T. Tschamber, *New J. Chem.*, 1995, **19**, 155.

8 H. J. Callot and E. Schaeffer, *J. Chem. Res.*, 1978, (*S*)51; (*M*)690.

9 N. Kobayashi, M. Yokoyama, A. Muranaka and A. Ceulemans, *Tetrahedron Lett.*, 2004, **45**, 1755.

10 E. Vogel, M. Michels, L. Zander, J. Lex, N. S. Tuzun and K. N. Houk, *Angew. Chem., Int. Ed.*, 2003, **42**, 2857.