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Unusual Formation of 21-Oxacorrole from 21-Oxaporphyrin Induced by Phosphoryl Chloride

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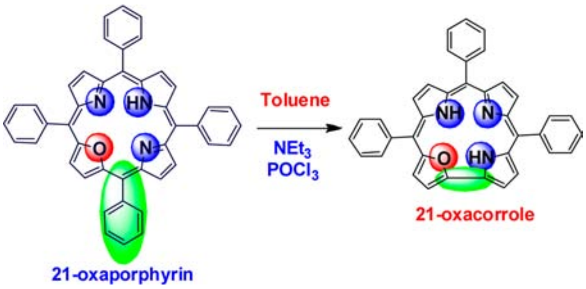
ABSTRACT



An unusual formation of 21-oxacorrole from 21-oxaporphyrin by concomitant elimination of a *meso*-aryl group and ring contraction is reported.

Corroles are tetrapyrrolic macrocycles containing three methine bridges and one direct pyrrole–pyrrole linkage.[1] Corroles contains one carbon atom less than porphyrins but possesses three inner NH protons instead of two inner NH protons present in porphyrin. Thus, corroles have a greater ability to stabilize higher central metal oxidation states than porphyrins. In addition to their very interesting metal coordination chemistry, corroles also exhibit novel spectral, electrochemical, and luminescent properties as evident from the extensive research on corrole chemistry in the past decade.[2] Although, now the chemistry of corroles with a regular N$_4$ core is relatively better understood, the chemistry of core-modified corroles[2b] largely remains unexplored. The core-modified corroles resulting from the replacement of one or two inner nitrogens with other heteroatoms such as sulfur, oxygen, selenium, phosphorus, tellurium, etc. are expected to possesses interesting physicochemical properties that differ from regular N$_4$ corroles. However, reports on *meso*-aryl heterocorroles are very few because of the lack of proper synthetic protocols and instability of these macrocycles. Recently we reported[3] the synthesis of stable *meso*-aryl 22-thiacorroles by condensing thiophene carbinol with aryl aldehyde and pyrrole under mild acid catalyzed conditions. Chandrashekar and coworkers[4] isolated the 22-oxacorrole containing a direct pyrrole–pyrrole linkage as a side product during their attempts toward the synthesis of stable *meso*-triaryl smaragdyrins by 3 + 2 condensation of 16-oxatripyrrane and *meso*-aryl dipyrromethane under acid catalyzed conditions. Lee and co-workers[5] developed a rational approach for the synthesis of both 21-oxa and 22-oxacorroles by using appropriate precursors. Thus, the possible two corroles that

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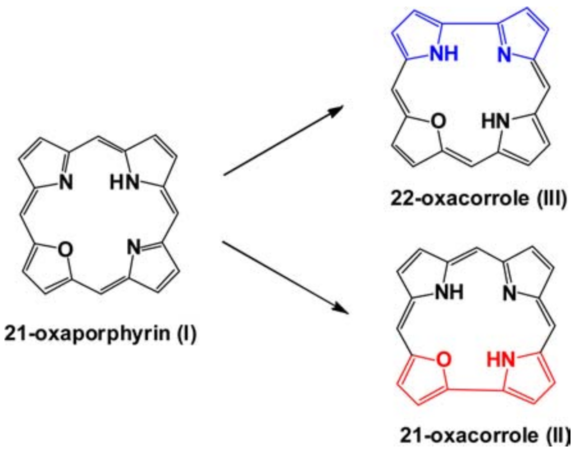
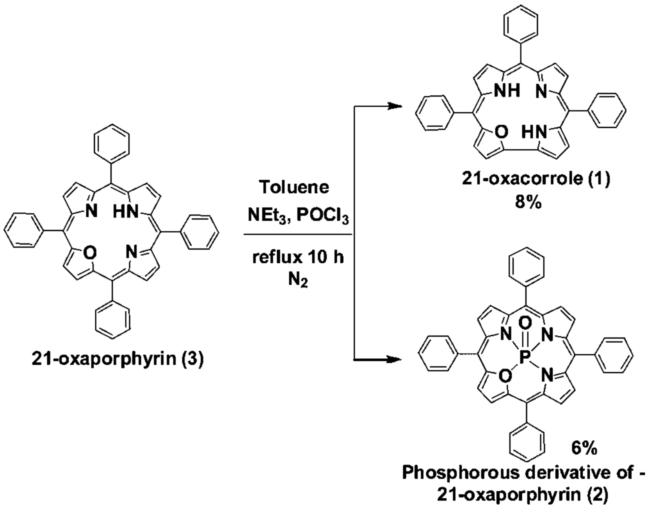
can be derived from 21-oxaporphyrin **I** macrocycle are (1) the 21-oxacorrole **II** that has a direct pyrrole–pyrrole link and (2) the 22-oxacorrole **III** that has a direct pyrrole–furan link (Scheme 1). Among these two corroles, the 22-oxocorrole was characterized crystallographically and spectral, electrochemical, photophysical, and metal complexation properties were explored reasonably well,[6] whereas the 21-oxacorrole containing a direct pyrrole–furan linkage has not been investigated in detail.[5] In this paper, we report the unusual formation of free base 5,10,15-triphenyl-21-oxacorrole **1** containing a pyrrole–furan direct linkage during our attempts to prepare a phosphorus derivative of 21-oxaporphyrin **2** by treating 5,10,15,20-tetraphenyl-21-oxaporphyrin **3** with $POCl_3$ in the presence of triethylamine in toluene under reflux conditions. Prior to our study, Chan et al.[7] reported the formation of oxorhenium(V) corrolate during their attempts to metalate the highly electron-deficient 5,10,15,20-tetrakis(trifluoromethyl)porphyrin in PhCN at refluxing temperature. Grazynski and co-workers[8] showed the unique formation of 3-pyranone dioxacorrole from 21,23-dioxaporphyrin by solid-supported Achmatowicz rearrangement in the porphyrin macrocycle. Our serendipitous observation of the formation of free base 21-oxacorrole **1** from free base 21-oxaporphyrin **3** by concomitant elimination of one *meso*-aryl group and ring contraction is one of the unusual rare reactions on the porphyrin macrocycle.[9]

Scheme 1. Possible 21- and 22-Oxacorroles from the Parent 21-Oxaporphyrin



Since our interest is to insert phosphorus into 21-oxaporphyrin **3** to prepare a phosphorus derivative of 21-oxaporphyrin **2**, we carried out the reaction by treating **3** with excess $POCl_3$ in toluene in the presence of triethylamine at reflux for 10 h (Scheme 2). TLC analysis showed a major bright pink spot followed by one clear minor green spot. The crude compound was subjected to silica gel column chromatography using petroleum-ether/dichloromethane, and the fast moving major pink fraction (8%) and the subsequent green fraction (6%) were collected separately. The mass spectral analysis showed a molecular ion peak at *m*/*z* 528.2069 (HR–MS) for the pink fraction and 661.35 (ES–MS) for the green fraction (Supporting Information pp S3–S4). Although we thought that the pink fraction could be our desired phosphorus derivative of 21-oxaporphyrin **2**, mass spectral analysis indicated that the minor green fraction is the phosphorus inserted 21-oxaporphyrin **2**. Even though we proposed the phosphorus derivative of 21-oxaporphyrin **2** formed in this reaction as a phosphorus(III) derivative, we do not rule out the possibility of formation of a phosphorus(V) derivative since we did not have any crystal structure evidence at present.[10] The absorption spectrum recorded for the pink fraction showed Q-type bands at 523, 488, 549, and 604 nm and a split Soret band at 402 and 416 nm indicating the formation of a corrole type of macrocycle. A perusal of literature revealed that the absorption spectrum of the pink fraction matched closely with the reported 21- oxacorrole by Lee et al.[5] indicating that the 21-oxaporphyrin underwent ring contraction by dearylation of the *meso*-aryl group which is present between furan and pyrrole to form 21-oxacorrole. The plausible mechanism for this unusual reaction is presented in Scheme 3.

Scheme 2. Formation of 21-Oxacorrole from 21-Oxaporphyrin along with the Formation of Phosphorous Derivative of 21-Oxaporphyrin[10]



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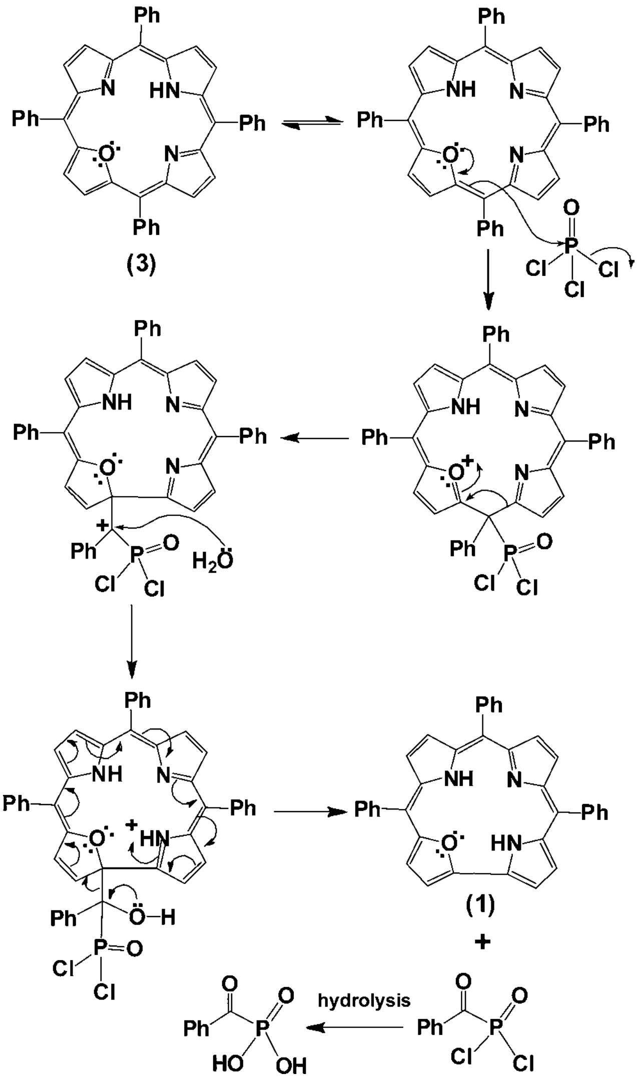
(10) The formation of the phosphorous derivative of 5,10,15,20-tetraphenyl-21-oxaporphyrin **2** was confirmed by a molecular ion peak in an ES–MS mass spectrum (Supporting Information p S4). The complete characterization and properties of **2** are under investigation in our laboratory (Supporting Information pp S11–S12, S14, and S22).

Scheme 3. Proposed Reaction and Ring Contraction Mechanism from **3** to **1**



We also prepared the other possible 22-oxacorrole such as 5,10,15-tritolyl-22-oxacorrole **4** by following the reported procedure[4] to compare its characteristic properties with the isolated 21-oxacorrole **1**. The absorption spectra of 21-oxacorrole **1** and 22-oxacorrole **4** are significantly different from each other, and 21-oxacorrole **1** bands experienced a blue shift compared to 22-oxacorrole **4** (Supporting Information p S13). The ^{1}H NMR showed furan signals as two doublets at 9.55 and 9.06 ppm in 21-oxacorrole **1** which are downfield shifted compared to furan signals in 22-oxacorrole **4** which appeared at 9.00 and 8.81 ppm (Supporting Information pp S5–S9). This supports the direct linkage between furan and pyrrole in 21-oxacorrole **1**.

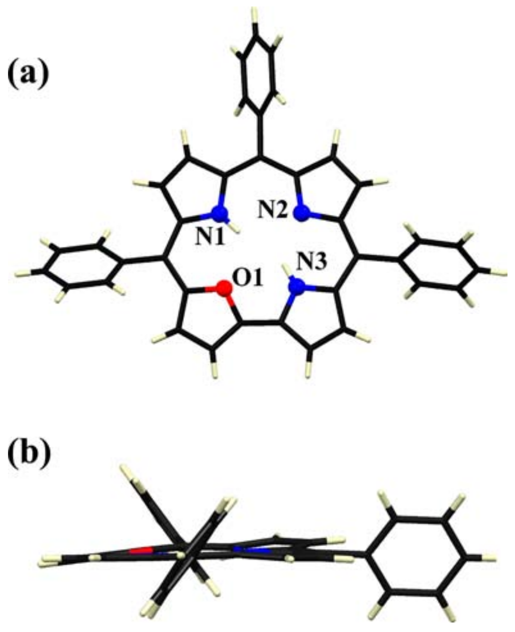


Figure 1. Single crystal X-ray structure of the compound **1**: (a) perspective view and (b) side view showing the nonplanarity of the macrocycle and the cross-orientation of the trans *meso*-aryl groups.

The proof for the formation of 21-oxacorrole **1** by the ring contraction of 21-oxaporphyrin **3** was unambiguously elucidated by single-crystal X-ray diffraction analysis.[11] Suitable crystals of compound **1** were obtained by slow diffusion of *n*-hexane into the dry dichloromethane/chloroform solution for over a period of one week. The crystal structure of **1** is shown in Figure 1. The single crystal X-ray structure of **1** obtained here is compared with the reported[6] analogous 5,10,15-triphenyl-22-oxacorrole[4] **5** and 5,20-bis(*p*-tolyl)-10,15-diphenyl-21-oxaporphyrin[12] **6**. The compound **1** was found to be crystallized in the monoclinic space group *P*21/*c* unlike compound **5** which crystallized in an orthorhombic space group *P*212121. The macrocycle **1** adopts a near-planar conformation like compound **5** as evident from Figure 1. This is in contrast to 21-oxaporphyrin **6** which is significantly distorted. Thus, the direct furan–pyrrole bond in compound **1** and the direct pyrrole–pyrrole bond in compound **5** assisted these contracted macrocycles to be more planar compared to the distorted porphyrin macrocycle **6**. The close inspection of crystal structures of compounds **1**, **5**, and **6** indicated that the deviation of the furan ring from the mean plane of the macrocycle in compounds **1** (5.69°) and **5** (5.50°) are much less compared to compound **6** (11.35°). Similarly, the deviation of three pyrrole rings from the mean plane of the macrocycle are much more pronounced in **6** (16.93°, 11.64°, 11.03°) than in compounds **1** (1.98°, 4.46°, 5.50°) and **5** (7.40°, 6.08°, 7.72°). Due to the ring contraction in compounds **1** and **5**, the O1–N2 and N2–N3 distances are

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(11) Selected crystal data for compound **1**: Formula = [$C_{37}H_{25}N_3O$; M = 527.60; monoclinic; $P21/c$; a = 17.131(3) Å, b = 10.7442(18) Å, c = 14.687(2) Å; α = 90.00°, β = 93.702(6)°, γ = 90.00°; V = 2697.7(8) Å^3; T = 200(2) K; Z = 4; μ = 0.079 mm^{-1}; F(000) = 1104; reflections collected = 17 633; independent reflections = 3359 (R_{int} = 0.047); final R values [$I > 2\sigma(I)$] R_1 = 0.0476, wR_2 = 0.1261; R values (all data) R_1 = 0.0787, wR_2 = 0.1548.

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much shorter (by ~0.2−0.3 Å) compared to 21-oxaporphyrin **6**. Furthermore, in compound **1**, the O1−N2 distance (3.81 Å) is little longer than the N2−N3 (3.77 Å) distance. But these distances are in reverse order in compound **5** where the O1−N2 distance (3.76 Å) is a little shorter than the N2−N3 (3.86 Å) distance. Interestingly, the direct distance between the pyrrole and furan rings in compound **1** (1.40 Å) is little shorter than the direct pyrrole−pyrrole distance in compound **5** (1.43 Å). In compound **1**, the *meso*-phenyl groups which are trans to each other are oriented in opposite directions with respect to each other by crossing the mean macrocycle plane (Figure 1b), where, as in compound **5**, the trans *meso*-phenyl groups are oriented in the same direction. The more coplanar nature of the *meso*-phenyl groups with the corrole rings in compounds **1** and **5** compared to porphyrin **6** is revealed from the average dihedral angles between the *meso*-phenyl groups and the mean macrocycle plane which are quite less in compounds **1** and **5**. In crystal packing, the two adjacent molecules are arranged in a parallel direction by the π−π stacking between the directly linked pyrrole−furan moieties of both macrocycles with an average plane-to-plane separation of 3.328 Å (Supporting Information p S19). Thus, the crystal structure analysis revealed that the oxacorrole macrocycles **1** and **5** are more planar compared to 21-oxaporphyrin macrocycle **6**.

The electrochemical and photophysical properties of corroles **1** and **4** were investigated and compared with 21-oxaporphyrin **3**. The 21-oxacorrole **1** is redox active and exhibited one reversible and one irreversible oxidation and one reversible and one irreversible reduction (Supporting Information p S16). Compared to 21-oxaporphyrin **3**, the 21-oxacorrole **1** was found to be difficult to oxidize and reduce (Supporting Information pp S16−S18). Both 21-oxacorrole **1** and 22-oxacorrole **4** are brightly fluorescent with emission maxima at 611 and 643 nm respectively (Supporting Information p S15), and the quantum yield is in the range of 0.3−0.4.

In conclusion, we report the unusual formation of 21-oxacorrole in 8% yield by treating 21-oxaporphyrin with $POCl_3$ in toluene in the presence of base under reflux conditions. The corrole formation was not observed when we treated 21-oxaporphyrin with different phosphorylating reagents such as PCl_3, PCl_5, and $POBr_3$. Furthermore, the corrole formation was not observed with other porphyrin macrocycles containing N_4, N_3S, N_2SO cores under similar reaction conditions.

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Supporting Information Available. General experimental procedures and characterization data and crystal packing diagram. This information is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.