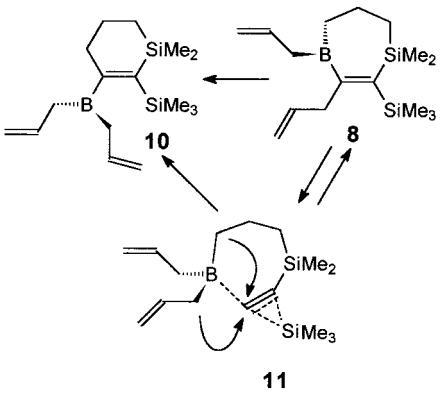
contrast, **8** undergoes further rearrangement to give the six-membered heterocycle **10**. This can be explained as the result of 1,1-deorganoboration[3c] followed by 1,1-organoboration after which both allyl groups remain at the boron atom (Scheme 2). Intermediates of the type **11** are rather short-lived, whereas comparable derivatives with tin[9] or lead[10] instead of silicon have been isolated and fully characterized.



Scheme 2. Proposed mechanism for the 1,1-deorganoboration and 1,1-organoboration of **8** to **10** via the short-lived intermediate **11**.

In summary, firm evidence for the presence of the Si-H-B bridge in **5** and **6** has been found. This kind of interaction will explain in particular intramolecular reactions of boron compounds which contain silyl groups with Si-H functionalities, and it will stimulate investigations in this field. First examples of novel routes to heterocycles have already been observed here in the attempt to combine 1,1-allylboration and hydrosilylation.

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Synthesis of Mono- and Di(oxopyri)porphyrins: A New Approach through Ring Enlargement with Diazomethane**

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The past decade has seen increasing attention being paid to the synthesis of novel porphyrinoid aromatic compounds. A large number of these macrocyclic structures, including "expanded porphyrins", has been reported recently.[1] The interest in cyclic polypyrrole systems and their heteroanalogues is based on their potential application as photosensitizers in the treatment of cancer by photodynamic therapy, and as highly selective catalysts and organic electrical conductors.[1]

The simplest expanded porphyrins known are homoporphyrins containing an extra carbon atom in their structure. This class of porphyrins was first reported by Callot and coworkers.[2] Homoporphyrins that are expanded at *meso* positions are nonaromatic and unstable, although the related metal complexes were found to be quite stable.[3] The insertion of a carbonyl group between the α- and β-pyrrole

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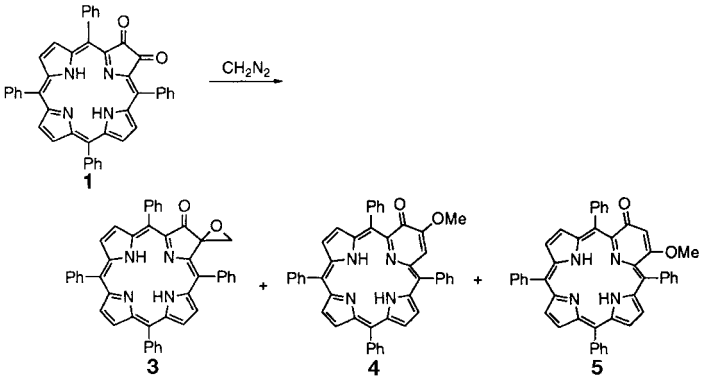
carbon atoms produced stable and fully aromatic homoporphyrinones containing a pyridine unit. The first synthesis of this type of porphyrin was presented by Bonnett and co-workers in 1993.[4] More recently, Lash reported[5] the synthesis of a similar semiquinone "oxobenziporphyrin" structure by a [3+1] approach,[6] and subsequently extended these studies to the pyridone system, which he termed "oxypyriporphyrin".[7] These novel 18-π-electron aromatic porphyrinoids exhibit spectroscopic properties similar to porphyrin-type systems, notably a significantly red shifted Soret band. Sessler and co-workers[8] have also shown that nonaromatic calix[4]pyrroles can also be converted into nonaromatic calix[4]pyridines by the insertion of dichlorocarbene into the pyrrole fragment.

The successful synthesis of verdinochlorins[9] by the reaction of 13^2-oxopyropheophorbide *a* with diazomethane prompted us to explore the utility of this methodology for porphyrin derivatives with one or more dioxopyrrole rings. We anticipated that a similar reaction with dioxo- and tetraoxo-TPP derivatives (TPP = *meso*-tetraphenylporphyrin) as substrates would yield the corresponding mono- and di(oxopyri)porphyrins, which are otherwise difficult to synthesize.

In our attempts to prepare these compounds, 2,3-dioxo-*meso*-tetraphenylchlorin (TPC, **1**; see Scheme 1) was prepared from the corresponding *vic*-dihydroxy analogue with the procedures reported by Dolphin and Bruckner[10] and Crossley et al.[11] A similar approach was followed to convert 2,3,17,18-tetrahydroxy-tetraphenyl-bacteriochlorin (TTPBC) into the tetraone **2** (see Scheme 3). These compounds have been previously synthesized by Crossley and co-workers,[12, 13] and have been used successfully as building blocks for the construction of linear polyporphyrin arrays and photosynthetic models.[14]

The reaction of **1** with a large excess of diazomethane gave a mixture of three compounds (Scheme 1), which were separated by chromatography on silica gel and identified by



Scheme 1. Synthesis of epoxychlorin **3** and mono(oxopyri)porphyrins **4** and **5**.

mass spectrometry and ^{1}H NMR spectroscopy. The fastest moving, green band (7%) was identified as 2-oxo-3-epoxymethylene-TPC (**3**; low-resolution mass spectrometry (LRMS): m/z 658). The NMR spectrum showed a characteristic pair of AB doublets at $\delta = 3.78$ for the nonequivalent protons of the epoxymethylene group. Because of the asymmetry of the molecule, each β-pyrrole proton appeared as an individual doublet in the low-field region.[15]

Analysis by LR-MS of the two polar, red-brown bands gave identical molecular ion peaks at m/z 672, which indicates the insertion of two CH_2 units into the molecule. The NMR spectra of these compounds showed a distinctive singlet for the protons of the methoxy groups at $\delta = 3.85$ (minor product) and $\delta = 3.39$ (major product) along with a singlet which integrated for one proton. This is strong evidence for the presence of a methoxypyridinone ring in each isomer. The minor isomer (12%), with the methoxy group signal shifted down field by the deshielding effect of neighboring carbonyl functionality, was identified as 2-oxo-2^a-methoxy-*meso*-tetraphenylpyriporphyrin (**4**; Scheme 1). This assignment was unambiguously confirmed by ^{1}H NMR 2D ROESY experiments, which showed a strong through-space interaction of the 2^a-methoxy protons and the hydrogen atom at position 3. The latter also showed clear interactions with the *ortho* and *meta* protons of the neighboring 5-phenyl substituent. Again, owing to asymmetry in the molecule, each pyrrole β-proton appeared as a well-resolved doublet in the region of $\delta = 8.4$–8.6. The resonances of the *ortho* and most of the *meta* hydrogen atoms of the phenyl group were also surprisingly well resolved, which provided the opportunity for a complete assignment of all the resonances.[16]

On the basis of the 2D ROESY NMR data, the structure of the major isomer, which is obtained from the most polar band (78% yield), was identified as 3-methoxy-2-oxo-*meso*-tetraphenylpyriporphyrin (**5**; Scheme 1). The spectrum exhibited a strong through-space interaction between the 3-methoxy group and the *ortho* and *meta* protons of the neighboring 5-phenyl ring, and gave a classic example of a nearest neighbor stepwise assignment of all NMR signals.[17] Selected NOE connectivities are shown in Figure 1. The UV/Vis spectra of oxopyriporphyrins **4** and **5** exhibited red-shifted, Soret-type absorptions at 450 and 444 nm, respectively.

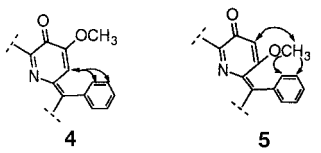


Figure 1. Selected NOE connectivities for oxopyriporphyrins **4** and **5**.

The mechanism of the formation of compounds **3**–**5** is consistent with that reported for reactions of diazoalkanes with electron-deficient cyclic ketones.[18] Nucleophilic attack of diazomethane on **1** produces the reactive species **7,** which can either generate the epoxide **3** or rearrange into ring-expanded products **8** and **9** (Scheme 2). The remarkable difference in the respective yields of these ring-expanded compounds (ca. 1:7) can be explained by the higher polarization of the 2-oxo group. Enolization of the activated methylene groups in **8** and **9** leads to the formation of the hydroxypyridinones **10** and **11**, which on reaction with a second molecule of diazomethane afford methoxy derivatives **4** and **5**, respectively.

The ring-enlargement reaction was extended to tetraoxobacteriochlorin (**2**). Owing to its highly electron deficient nature, it reacted immediately with diazomethane to give a mixture of three orange-brown products (Scheme 3), which

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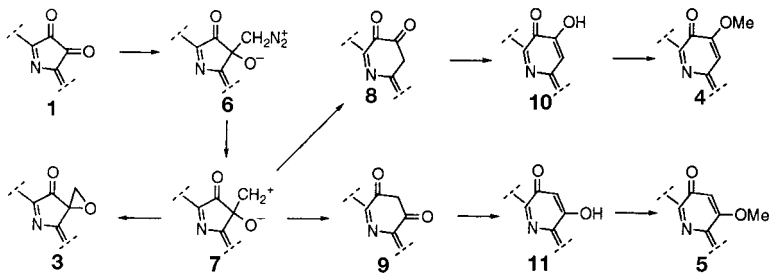
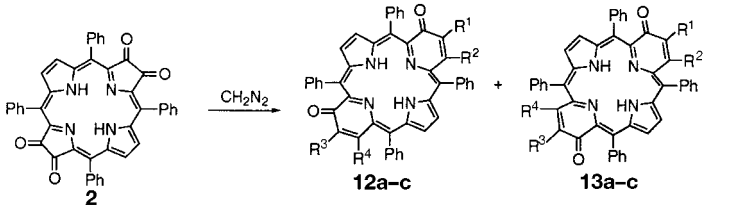


Scheme 2. A possible mechanism for the formation of epoxy- and oxopyriporphyrins.



Scheme 3. Synthesis of di(oxopyri)porphyrins **12** and **13**.

were separated by chromatography on silica gel and purified by preparative thin-layer chromatography (TLC). Each component gave the molecular ion peak $[M+1]^+$ at m/z 732, which indicated the formation of two opposed methoxypyridinone units. The ^{1}H NMR spectrum of the least polar band (18%) exhibited a singlet for the methoxy groups at $\delta = 3.9$, and on the basis of our assignments for **4**, it was identified as a mixture of the isomeric di(oxopyri)porphyrins **12a** and **13a,** with methoxy substituents at the 2^a- and 17^a-positions. The second band (31%), whose ^{1}H NMR spectrum showed two well-separated methoxy group singlets at $\delta = 3.9$ and 3.4, was found to be a mixture of isomers **12b** and **13b**. Similarly, the most polar band (47%), with a distinctive methoxy group singlet at $\delta = 3.3$ in the ^{1}H NMR spectrum, was identified as a mixture of **12c** and **13c**. All di(oxopyri)porphyrins showed resonances for β-pyrrole protons in the low-field region ($\delta =$ 8.5–8.7), which indicated that in spite of the presence of two pyridinone units, the molecule still retains aromaticity and a strong ring current. The tendency of these compounds to aggregate[7] and their existence as isomeric mixtures made it difficult to assign the individual low-field resonances, which were observed as several groups of multiplets. Attempts to separate the individual isomers by column chromatography were unsuccessful. The UV/Vis spectra of these novel oxopyriporphyrins showed a significant shift of the Soret-type band centered at 490 nm and weak absorptions at 560 and 660 nm. Currently, these novel homoporphyrins are being evaluated for their photophysical properties and photosensitizing efficacy, and these results will be published elsewhere.

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[15] Selected spectroscopic data for **8**: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ −0.8 (br s, 1H, NH), −0.2 (br s, 1H, NH), 3.78 (AB, 2H, 3-OCH_2), 7.72–7.78 (m, 18H), 7.82 (d, $J = 6.8$ Hz, 1H), 8.40 (d, $J = 6.8$ Hz, 1H), 8.46 (d, $J = 4.9$ Hz, 2H), 8.52 (d, $J = 4.8$ Hz, 1H), 8.64 (d, $J = 4.8$ Hz, 1H), 8.79 (d, $J = 4.8$ Hz, 1H), 9.21 (d, $J = 4.8$ Hz, 1H); UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [$M^{-1}cm^{-1}$]) = 429 (118000), 588 (13900), 588 (9500); LR-MS: m/z (%): 669.2 (100,$[M+1]^+$), 569 (9), 433 (23), 419 (34).
[16] Spectroscopic data for **9**: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -1.5$ (br s, 2H, NH), 3.85 (s, 3H, 2^a-OMe), 7.60 (dt, $J = 6.7$, 5.4 Hz, 2H, *meta* H of 20-Ph), 7.71 (t, $J = 6.9$ Hz, 2H, *meta* H of 5-Ph), 7.72 (t, $J = 6.8$ Hz, 2H, *meta* H of 10-Ph), 7.72–7.76 (m, 6H, *para* H of Ph and *meta* H of 15-Ph), 7.88 (s, 1H, 3-H), 8.05 (d, $J = 6.8$, 2.6 Hz, 2H, *ortho* H of 5-Ph), 8.12 (dd, $J = 6.9$, 1.8 Hz, 2H, *ortho* H of 10-Ph), 8.16 (dd, $J = 6.1$, 2.6 Hz, 2H, *ortho* H of 15-Ph), 8.24 (d, $J = 6.7$ Hz, 2H, *ortho* H of 20-Ph), 8.39 (d, $J = 5.4$ Hz, 1H, 7-H), 8.49 (s, 2H, 12-H and 13-H,), 8.52 (d, $J = 1.8$ Hz, 2H, 17-H and 18-H), 8.56 (d, $J = 5.4$ Hz, 1H, 8-H); UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [$M^{-1}cm^{-1}$]) = 450 (126000), 549 (14000), 588 (9500); LR-MS (%): $m/z = 673.3$ (100, $[M+1]^+$), 595 (8), 433 (43).
[17] Spectroscopic data for **10**: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -1.5$ (br s, 2H, NH), 3.39 (s, 3H, 3-OMe), 6.83 (s, 1H, 2^a-H), 7.60 (t, $J = 5.4$ Hz, 2H, *meta* H of 20-Ph), 7.62 (m, 2H, *para* H of 5-Ph and of 20-Ph), 7.63 (t, $J = 6.9$ Hz, 2H, *meta* H of 5-Ph), 7.70 (t, $J = 6.8$ Hz, 2H, *meta* H of 15-Ph), 7.71 (m, 2H, *para* H of 10-Ph and of 15-Ph), 7.72 (t, $J = 6.4$ Hz, 2H, *meta* H of 10-Ph), 7.95 (dd, $J = 6.4$, 2.6 Hz, 2H, *ortho* H of 20-Ph), 8.05 (d, $J = 6.9$ Hz, 2H, *ortho* H of 5-Ph), 8.08 (dd, $J = 6.8$, 2.1 Hz, 2H, *ortho* H of 15-Ph), 8.11 (dd, $J = 6.4$ Hz, $J = 2.5$ Hz, 2H, *ortho* H of 10-Ph), 8.35 (d, $J = 5.3$ Hz, 1H, 7-H), 8.37 (d, $J = 5.6$ Hz, 1H, 18-H), 8.49 (s, 2H, 12-H and 13-H), 8.53 (d, $J = 5.6$ Hz, 1H, 17-H), 8.56 (d, $J =$ 5.3 Hz, 1H, 8-H); UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [$M^{-1}cm^{-1}$]) = 444 (123000), 543 (15500), 624 (8500); LR-MS: m/z (%): 673.3 (100, $[M+1]^+$), 595 (12), 469 (23).
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