Tetrahedron Letters No. 36, pp 3155 - 3158, 1974. Pergamon Press. Printed in Great Britain.

HOMOPORPHYRINS I
PREPARATION - STRUCTURE

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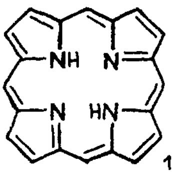
(Received in UK 29 July 1974; accepted for publication 31 July 1974)

The comparison of the properties of the macrocycles, porphin 1 and corrole 2, to those of benzene and cyclopentadiene respectively, has been brilliantly illustrated by the formation of an aromatic anion by base treatment of a metallocorrole (1,2).

In order to complete the comparison it only remained to prepare and study the behaviour of "homoporphin" system 4, homologous to cycloheptatriene.

The only compound of this type so far described is the substituted azahomoporphin 5 obtained by Grigg (3), by the treatment of octaethylporphin with carbethoxynitrene. This compound readily rearranges to 6, an instability which has not allowed a more profound study.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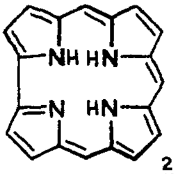
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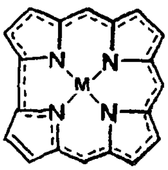
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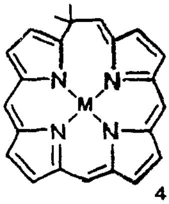
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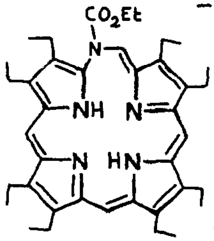
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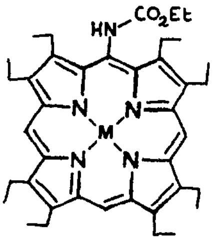
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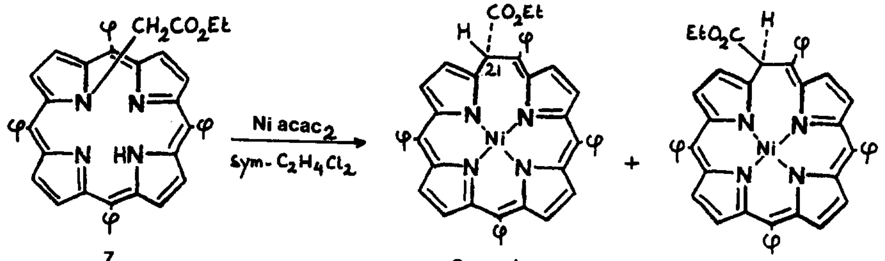
We wish to report the preparation of the homoporphin system via a rearrangement of a N-substituted-m-tetraphenylporphin.

Treatment of compound 7 (4,5) with Niacac$_2$ leads to two neutral products formulated 8 and 9, together with a little NiTPP :



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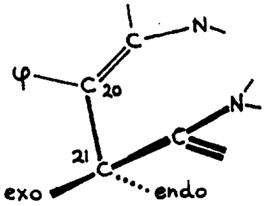
8 endo 57%

9 exo 4%

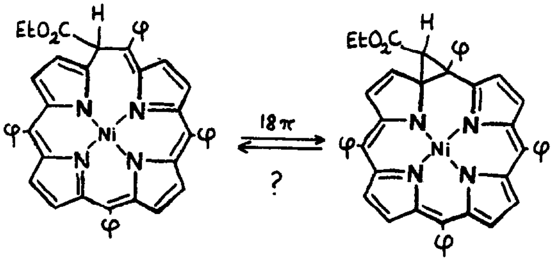


The compound 8 possesses a saturated carbon bearing an ester function [IR(KBr) 1735 cm^{-1}, n.m.r. ($CDCl_3$,TMS $\delta = 0$) CH_3: -0.12ppm, CH_2: 2.84ppm] and a singlet hydrogen [H_{21} $\delta = 5.14$ppm] ; mass spectrum: $M^+ = 756$ (52%), m/e = 683 (100%, -COOEt). 9 exhibits the same structural features: ester [1745 cm^{-1} ; CH_3: 1.0ppm, CH_2: 3.92ppm], singlet H_{21}[0,16ppm]; mass spectrum: $M^+ = 756$ (70%), m/e = 683·(100%, -COOEt). The visible spectra of the two compounds 8 and 9 are very similar:

8 λmax = 453nm (ε = 87000), 584 (6350), 688 (17300)
9 λmax = 449nm (ε = 86700), 579 (6760), 675 (14700).

This confirms the presence of the same conjugated system, in agreement with the literature data: azahomoporphin (3), bilatrienes (12), phlorins (13). (In particular all these compounds exhibit an intense band in the region where the Soret band appears for porphins). The large differences in chemical shifts in the n.m.r. of 8 and 9 [$\Delta\delta_{8-9} = -1.12$, -1.08 and 4.98ppm for CH_3, CH_2 and H_{21} resp.] demonstrate that 8 and 9 constitute a pair of epimers, endo and exo respectively.

If these two compounds are in fact porphin analogues of cycloheptatriene, it remains to exclude the possibility of a "norcaradiene" structure, always possible by a disrotatory electrocyclic reaction involving 18π electrons (as previously evoked by Grigg):



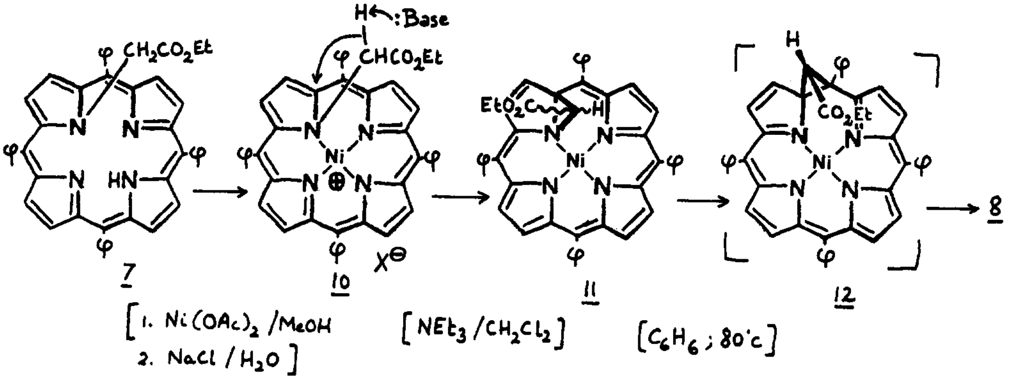
The ^{13}C n.m.r. of 8 [Varian XL100, $CDCl_3$, TMS $\delta = 0$] confirms the proposed structure: the only high field observable signals are due to the ethyl ester [$^{13}CH_3$: 12.4ppm, $^{13}CH_2$: 60.6ppm, $^{13}C{=}O$: 167.6ppm] and to $^{13}C_{21}$ [47.1ppm], accompanied by an unassignable group of signals due to all the aromatic carbons.

The X-ray structural determination of 8 published elsewhere (6), not only confirms these hypotheses but also demonstrates the large deformation of the whole conjugated system.

We have shown that at higher temperature (110°, toluene) there is an equilibrium $8 \rightleftarrows 9$ (60/40) which can be explained by ring inversion. Kinetic measurements (n.m.r. or isolation of products followed by visible spectroscopy) allows an inversion barrier $\Delta G^{\neq} = 30.0 \pm 0.2$ kcal/mole ($8 \rightarrow 9$) and $\Delta G^{\neq} = 29.8 \pm 0.2$ kcal/mole ($9 \rightarrow 8$) to be determined: it is of the same order as those obtained for various polybenzocycloheptatrienes (7).

The reaction $7 \rightarrow 8 + 9$ is apparently therefore stereospecific, the small amount of 9 arising from ring inversion of 8, a process which is slow at the reaction temperature used.

The following mechanism is therefore proposed for the formation of 8 and has been confirmed by isolating and characterising the intermediates 10 (X = Cl) and 11, made possible by modifying the reaction conditions (reagents shown in brackets):



Like Ni-N-CH_3-octaethylporphin iodide (8) the salt 10 is paramagnetic (μ_{eff}= 1.8BM) but in contrast is apparently stable at room temperature. The aziridine 11, also stable at 25°, is rapidly converted to 8 (+ a trace of 9) in refluxing benzene. The IR and n.m.r. spectra [1735 cm^{-1} ; CH_3: 0.07ppm, CH_2: 2.53ppm, H_{21}: -0.35ppm] are compatible with the proposed structure. It is interesting to note that only one of the two possible epimers 11 is obtained.

The determination of the stereochemistry of 11, at present under study, should allow the course of the [1,17]-migration $11 \rightarrow 12$ to be specified, since the ring-opening of 12 would in any case lead to a single product 8. This [1,17]-migration is homologous to the known [1,5]-migration, the detailed stereochemistry of which is still being investigated (14).

The cyclisation 10 → 11 is a novel example of nucleophilic attack on the porphin nucleus, the only previous example involving metalloporphin dications (9).

Finally it is surprising to note (11) that the analogs of 10 in which Ni has been replaced by Cu, Zn, or Co^{II} are stable under the cyclisation conditions and only undergo cleavage of the chain, followed, under more drastic conditions, by a little C-alkylation of the pyrrole ring (4).

The thermal rearrangements of the homoporphyrins 8 and 9 are described in the following publication.

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