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HOMOPORPHYRINS II
THERMAL REARRANGEMENTS

by H.J. CALLOT* and Th. TSCHAMBER

Institut de Chimie, Laboratoire associé au CNRS,
Université Louis Pasteur, 1 rue Blaise Pascal, 67-STRASBOURG, France.

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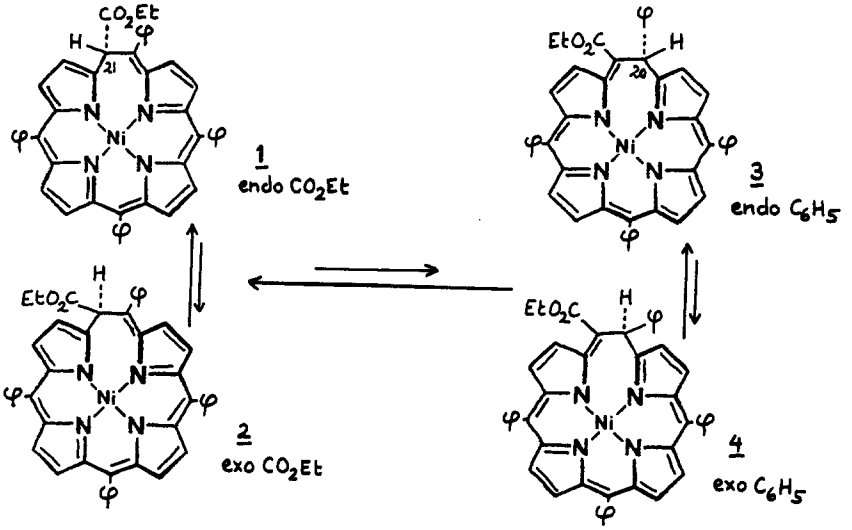
In the preceding publication (1), the preparation and characterisation of the homoporphyrins 1 and 2 have been described. In addition to a ring inversion 1 ⇄ 2, at higher temperatures these compounds also exhibit hydrogen migration followed eventually by cyclopropane migration.

A. Hydrogen migration:

When 1 or 2 is heated at temperatures greater than 160°C, an equilibrium is attained between the four products 1, 2, 3 and 4 (41, 29, 23, 7% resp.):



The compounds 3 and 4 possesses a conjugated ester function [IR(KBr) 1685 and 1690 cm^{-1}, n.m.r. ($CDCl_3$, TMS δ = 0), CH_3: 1.58 and 1.06ppm, CH_2: 4.70 and 4.23ppm], a singlet H [1.11 and 0.31ppm] and a sp_3 carbon bearing a phenyl group [3: 5.1-6.0ppm (multiplet), 4: 7.10ppm (singlet)]. The visible and mass

spectra are similar to those of 1 and 2:

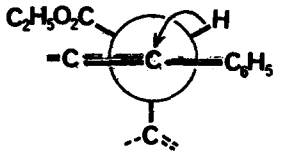
3: λmax = 452nm (ε = 68000), 695 (13600) ; M^+ = 756 (100%), m/e = 683 (29%, -COOEt)

4: λmax = 450nm (ε = 72400), 688 (13800) ; M^+ = 756 (100%), m/e = 683 (47%, -COOEt)

The two compounds are therefore another pair of epimers and from the proton chemical shifts 3 and 4 be recognised as the endo and exo epimers respectively [$\Delta\delta_{3-4}$: phenyl ca. -1.5ppm, H_{20} + 0.8ppm].

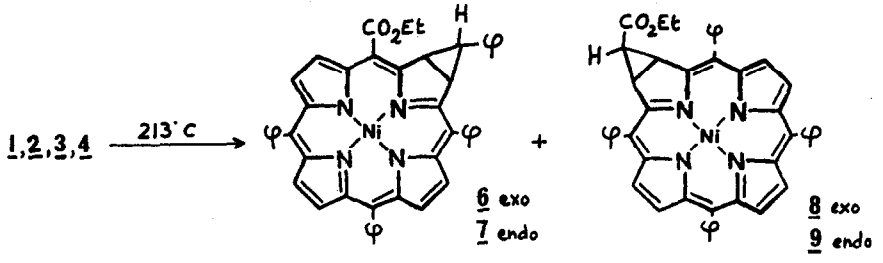
The ring inversion barrier $3 \rightleftarrows 4$, $\Delta G^{\neq}_{3 \rightarrow 4}$ = 26.8 kcal/mole (C_6H_6, 80°C) is significantly lower than for the inversion $1 \rightleftarrows 2$.

The equilibrium between the compounds 1, 2, 3 and 4 is explained by reversible hydrogen transfer between carbons 20 and 21 of the two carbon bridge. If this reaction is intramolecular, the selection rules (2) impose for this migration between the 1 and 19 positions of the conjugated system an antara-supra stereochemistry. Consideration of the molecule 1 along the axis of the C-20-C-21 bond clearly shows that the H-21 ("lower" face) is very favourably placed for migration onto the C-20 by way of the "upper" face(3). The same reasoning is equally applicable to the other three compounds of the equilibrium. The rapidity of the ring inversions $1 \rightleftarrows 2$ and $3 \rightleftarrows 4$ at the temperature employed does not unfortunately allow any stereochemical verification of the proposed mechanism. A study of the reaction by double labelling is foreseen.



B. Cyclopropane migrations:

On heating the equilibrium mixture of compounds 1, 2, 3 and 4 at temperatures higher than 200°C a mixture of 4 cyclopropyl chlorins 6, 7, 8 and 9 is obtained (65, 15, 15, 5% resp.):

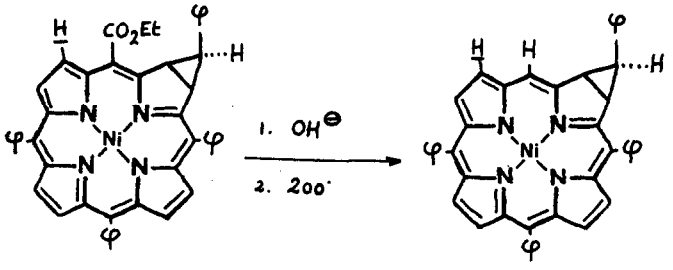


These compounds exhibit visible spectra typical of chlorins (dihydroporphins) and can be compared to the known compounds obtained from the reaction of m-tetraphenylporphin with carbenes (4). 8 and 9 have been synthesised by

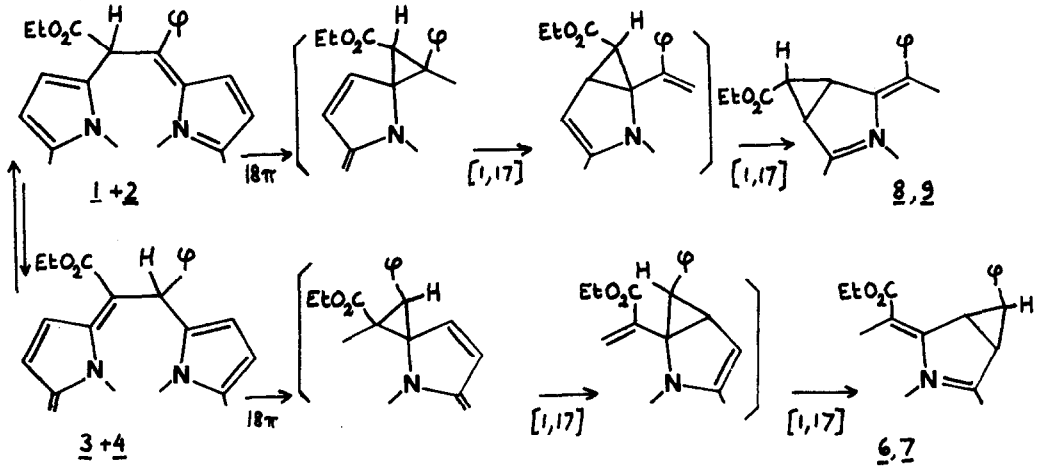
the following reaction sequence:

$$ZnTPP \xrightarrow[CuI]{N_2CHCO_2Et} \xrightarrow{\text{separation}} \xrightarrow[2)\ Niacac_2]{1)\ H^+} \underline{8} \text{ and } \underline{9}$$

$\underline{6}$ and $\underline{7}$ present, as well as a conjugated ester group [IR(KBr) 1705 cm^{-1} ; n.m.r. ($CDCl_3$) CH_3: 1.15 and 1.50ppm, CH_2: 4.51 and 4.58ppm], a phenyl on a sp_3 carbon [$\underline{6}$: 7.25ppm (multiplet), $\underline{7}$: 6.35-6.65ppm (multiplet)] and the expected signals for the cyclopropyl protons. The stereochemistry of $\underline{6}$ (exo) and $\underline{7}$ (endo) can be unequivocally assigned from the chemical shift differences $\Delta\delta_{\underline{6}-\underline{7}}$ for the phenyl protons (ca. 0.75ppm) and for the hydrogen of the same carbon atom (-1.2ppm). Moreover $\underline{6}$ and $\underline{7}$ show a doublet at 8.78 and 8.68ppm respectively, due to the pyrrolic proton (underlined in the figure) nearest to the ester group. Saponification and decarboxylation of $\underline{6}$ causes this signal to disappear in the aromatic proton multiplet.



For this homoporphyrin → cyclopropyl-chlorin rearrangement it seems reasonable to envisage the involvement of a "norcaradiene" form, present in very low concentration, followed by two [1,17]-migrations of a carbon-carbon bond:



This reaction would therefore be a higher homologue of cyclopropyl 1,5 -migrations, well known in the norcaradiene series[5,6]. In the present case, the migration stops as soon as an aromatic system is obtained. If the two successive steps of the migration have the same stereochemical requirements (retention or inversion), then the proportion of the products reflects the relative ease of migration of endo or exo carbethoxycyclopropanes or phenylcyclopropanes:

starting	exo 36%	phenyl on sp_3 carbon	30%
equilibrium	endo 64%	ester on sp_3 carbon	70%
products	exo 80%	phenyl on sp_3 carbon	80%
	endo 20%	ester on sp_3 carbon	20%

If the original assumption is correct, the reaction is therefore more rapid when the cyclopropane bears an exo substituent, and when this substituent is a phenyl rather than an ester group.

References

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