Synthesis of a *Meso*-Substituted Porphyrin *via* *N*-Alkylation

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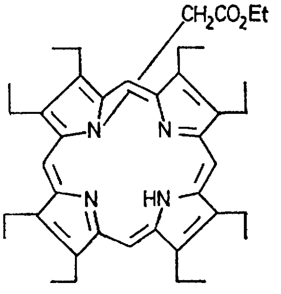
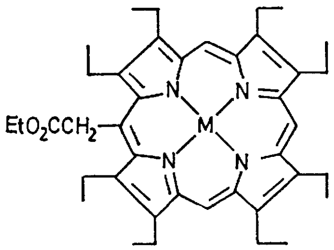
Summary *Meso*-Alkylation of octaethylporphyrin was achieved *via* rearrangement of an *N*-substituted derivative.

Alkylation of octa-alkylporphyrins at the *meso*-position can be achieved using various methods: Vilsmeier formylation[1,2] followed eventually by Wittig reaction,[3] electrophilic reaction of a porphyrin-dianion,[4] nucleophilic attack on an oxidised substrate,[5] action of FSO$_3$Me[1] or CH$_2$Cl$_2$–N$_2$O$_4$,[6] or reaction of a diazoester in the presence of a copper(I) halide.[7]

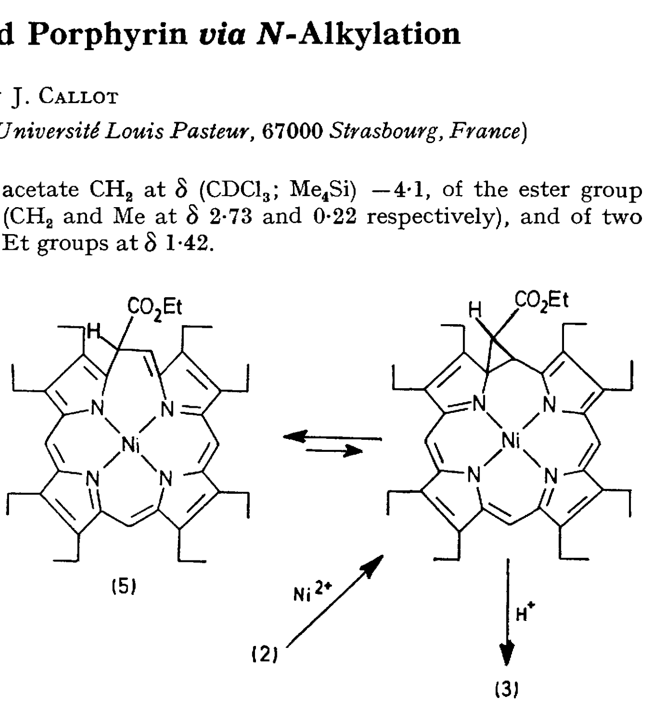


(2)



(3) M = Ni
(4) M = H$_2$

We describe here the preparation of *meso*-ethoxycarbonylmethyloctaethylporphyrin *via* an *N*-substituted macrocycle. Reaction of the Zn-complex of octaethylporphin (**1**) with N$_2$CHCO$_2$Et in refluxing bromobenzene, followed by demetallation (HCl), gave the *N*-substituted base (**2**) (45—55%), identical with a recently described product,[8] the structure of the hydriodide of which has been determined by *X*-ray crystallography.[9] Direct alkylation of octaethylporphyrin using ICH$_2$CO$_2$Et also gave the base (**2**) in lower yield (*ca.* 25%). All the spectral data for the base (**2**) fit the proposed structure well; there is strong shielding of the acetate CH$_2$ at δ (CDCl$_3$; Me$_4$Si) −4·1, of the ester group (CH$_2$ and Me at δ 2·73 and 0·22 respectively), and of two Et groups at δ 1·42.



Reaction of the base (**2**) with bis(acetylacetonato)nickel in refluxing benzene gave, in addition to some nickel-octaethylporphyrin (16%), the *meso*-substituted nickel complex (**3**) (40%). Demetallation of complex (**3**) using conc. H$_2$SO$_4$ gave quantitatively the free base (**4**).

The base (**4**) was identical with the known product[7] from Cu–octaethylporphyrin + N$_2$CHCO$_2$Et in the presence of CuI, followed by demetallation. The n.m.r. spectrum of complex (**3**) displayed the expected signals due to the acetate CH$_2$ (δ 5·52) and the ester group (CH$_2$ and Me at δ 3·68 and 0·77 respectively).

To explain this acetate chain migration we postulate, as in a recently described rearrangement,[10] an initial nickel cationic complex. Cyclisation of this salt to an aziridine, followed by migration and 18π-electrocyclic ring-opening leads to the homoporphyrin (**5**). While monitoring the reaction using alumina t.l.c. we observed the formation of a green product, which could be the homoporphyrin (**5**). At this stage the visible spectrum of a dilute solution showed two maxima at 428 and 660 nm, comparing favourably with the known nickel-homoporphyrins (*ca* 450 and 680 nm).[10] This intermediate was too unstable to allow isolation in a pure state and gave complex (**3**) when kept. This behaviour recalls the relative instability of Grigg's azahomooctaethylporphyrin.[11] Proton-catalysed ring-opening of the intermediate cyclopropane should lead to the observed product (**3**).

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