Cyclisations Involving *meso*-Substituents of Crowded Porphyrins

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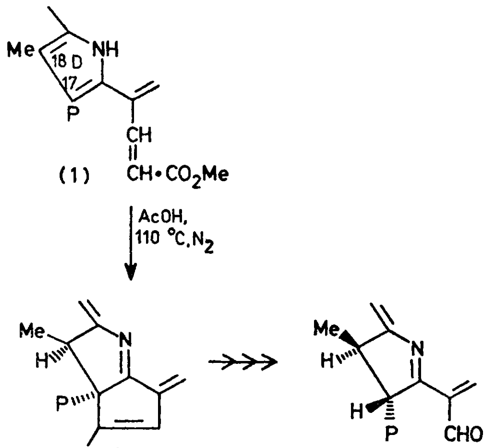
Summary *meso*-Acrylic derivatives of octaethylporphin may be cyclised by acids either to purpurin derivatives (**5**) or to a novel modified porphin containing a fused benzene ring (**7**), depending on the presence or absence of metal and the experimental conditions.

A novel feature of Woodward's classical chlorophyll synthesis was the method used for the reduction of ring D of the unsymmetrical porphin to the corresponding chlorin.[1] It was found that when the porphyrin (**1**) containing an acrylic ester side-chain was heated in acetic acid, cyclisation occurred to give the corresponding purpurin (**2**) which was then subjected to further manipulations in order to produce the C-17 hydrogen substituent in (**3**). The cyclisation, which was a consequence of steric crowding, remained a unique observation until recently when Fuhrhop[2] reported that in the octaethylporphin (OEP) series, the unsaturated dicarboxylic acid monomethyl ester (**4a**) was cyclised by heating in toluene to the purpurin (**5a**) whereas the diacid (**4b**) was cyclised by treatment with concentrated H_2SO_4 to the ketone (**6**). Cyclisation reactions of the *meso*-acrylic ester derivative (**4c**) were not reported although the ethyl ester was prepared.



$CH=CH\cdot CO_2Me$

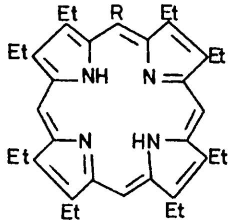
(1)

CO_2Me

(2)

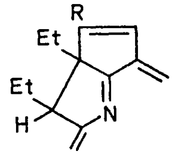
(3)

In the course of our work on *meso*-substituted OEP's, we have examined the metal-free *meso*-acrylic ester (**4c**) produced by acid demetallation of its nickel complex,[3] and find that, as with Woodward's example, it cyclises smoothly to the purpurin (**5**) when it is heated under reflux in acetic acid solution in an atmosphere of nitrogen for 24 h, although it is unaffected by heating in toluene solution. Meanwhile, we have found that the corresponding *meso*-acrylaldehyde of nickel OEP (**4d**) can be prepared in 85% yield from the *meso*-vinyl derivative (**4e**) by Vilsmeier formylation in 1,2-dichloroethane (*meso*-ring substitution occurs also but can be minimised by short reaction time), and that the aldehyde (**4d**) can be reduced to the alcohol (**4f**) with borohydride. When the aldehyde (**4d**) was treated with concentrated H_2SO_4 for 3 min at room temperature, a 37% yield of the metal-free porphin aldehyde (**4g**) could be isolated as well as a green product (**7**). Longer exposure to H_2SO_4 led to decomposition of the aldehyde (**4g**) and after 2 h at room



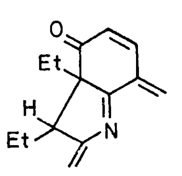
(4)

a, $R = CH{=}C(CO_2Me)(CO_2H)$
b, $R = CH{=}C(CO_2H)(CO_2H)$
c, $R = CH{=}CH\cdot CO_2Me$
d, $R = CH{=}CH\cdot CHO$; nickel complex
e, $R = CH{=}CH_2$; nickel complex
f, $R = CH{=}CH\cdot CH_2OH$; nickel complex
g, $R = CH{=}CH\cdot CHO$

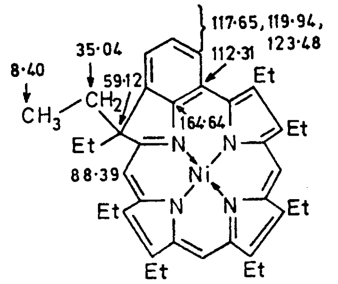


(5)

a, $R = CO_2Me$
b, $R = CHO$



(6)



(7)

temperature the product was mainly the green compound (**7**), m.p. 224—225 °C, 40% yield, which possesses a fused benzene ring and a *gem*-diethyl group. The compound (**7**) was also obtained in 15% yield when the alcohol (**4f**) was heated with H_2SO_4 in dimethylformamide. The structure of (**7**) was deduced from the mass spectrum which showed the loss of an oxygen atom from the initial aldehyde (**4d**) and from the ^1H n.m.r. spectrum, which clearly demonstrated the presence of the *gem*-diethyl group, with signals at δ 0·04 (t) and 2·28 (q) (*cf.* the *gem*-porphin ketones of Inhoffen[4]). The protons of the benzene ring appeared at δ 7·70 (br.d, 2H) and 8·9 (br.t, 1H) while the *meso*-protons appeared as singlets at δ 7·72, 8·45, and 8·82. This structure was confirmed by the ^{13}C n.m.r. spectrum and the relevant assignments which are fully supported by off-resonance decoupling, are shown on the formula. The electronic spectrum of (**7**) exhibited a strong chlorin-like band at 677 nm (ϵ 36,700) as well as a Soret band at 416 nm (ϵ 69,200). The cyclisation of the acrylaldehyde side-chain to form a benzene ring formally involves a reduction step, the mechanism of which is still unknown, although nickel porphyrin complexes are known to act as electron donors under acidic conditions.[5]

When the metal-free aldehyde (**4g**) was heated under reflux in acetic acid under nitrogen, it gave an isomeric compound, the n.m.r. and electronic spectra of which suggested a purpurin aldehyde structure (**5b**) (λ_{max} 440, 505, 554, 592, 672, and 734 nm). The corresponding nickel complex (**4d**) was unaffected under these conditions. Thus the *meso*-acrylaldehyde can be cyclised by acids in either of two ways [to give (**5b**) or (**7**)] depending on experimental conditions and the presence or absence of nickel.

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[3] H. Callot, *Bull. Soc. chim, France*, 1973, 3413.
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[5] D. Arnold, A. W. Johnson, and M. Winter, *J.C.S. Perkin I*, 1977, 1643.