New Syntheses of Chlorocruoro- and Isochlorocruoro-porphyrins from Protoporphyrin-IX

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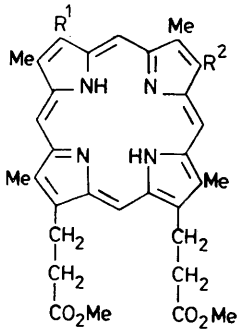
Summary Treatment of protoporphyrin-IX dimethyl ester with picryl azide affords an equimolar mixture of chlorocruoro- and isochlorocruoro-porphyrin dimethyl esters.

VINYL substituents in porphyrins have been characterised both chemically[1] (*e.g.* by reaction with diazoacetic ester) and spectroscopically[2] (by noting the small hypsochromic shift which occurs on reduction and the change in molecular weight by two mass units). In the course of searching for a reagent which would both detect vinyl groups and convert them into alternative useful functional groups we examined the reaction between protoporphyrin-IX dimethyl ester (Ia) and picryl azide.[3] This reagent reacts with olefins by a 1,3-dipolar addition mechanism affording triazolines which are generally thermally unstable[4] and lose nitrogen rapidly to give aziranes or anils.[5] The latter can be hydrolysed readily to ketones and picramide.

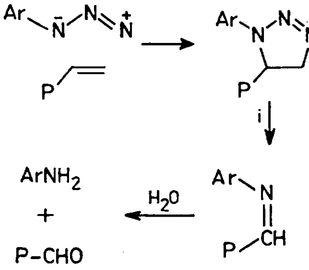
Protoporphyrin-IX dimethyl ester was heated with picryl azide in refluxing chloroform, and chromatographic investigations showed the presence of three porphyrinic fractions. Isolation by t.l.c. followed by field desorption mass spectrometry[6] indicated that the three components isolated (in order of increasing polarity) were (i) unchanged starting material (*m/e* 590), (ii) the major product (*m/e* 592), and (iii) a very polar product (*m/e* 594). There was no evidence for the formation of the expected diacetyldeuteroporphyrin dimethyl ester (Ib), an authentic sample of which was prepared[7] from haematoporphyrin dimethyl ester (Ic). Visible spectroscopic studies showed that the major component corresponded to a mixture of monoformyl monovinyl deuteroporphyrin esters (Id) and (Ie) (*i.e.* chlorocruoroporphyrin and its isomer), whilst the very polar band was the 2,4-diformyldeuteroporphyrin ester (If).



a; $R^1 = R^2 = CH{=}CH_2$
b; $R^1 = R^2 = COMe$
c; $R^1 = R^2 = CH(OH)Me$
d; $R^1 = CH{=}CH_2, R^2 = CHO$
e; $R^1 = CHO, R^2 = CH{=}CH_2$
f; $R^1 = R^2 = CHO$

(I)

Subsequently more detailed investigations were carried out using h.p.l.c.[6] to follow the time course of the reactions Conditions were worked out so that reaction only proceeded to the first stage, and an almost quantitative yield of the mixed isomers (Id) and (Ie) was obtained (allowing for recovered protoporphyrin ester). Careful preparative h.p.l.c.† enabled the two isomers to be separated and their identities were confirmed by comparison with authentic materials.



SCHEME. P = Porphyrin

Two possible mechanisms may be envisaged for the overall reaction (see Scheme): (i) a concerted cycloreversion reaction with loss of diazomethane and (ii) opening of the initially formed triazoline to a zwitterion which then fragments with loss of diazomethane.[8] In either event the picryl Schiff's base[2] is formed and readily undergoes hydrolysis (even by water absorbed on the columns, or in the solvent) to the formyl porphyrin. Similar extrusions of diazoalkane have been observed in the addition of tosyl azide to enamines[8,9] and to alkyl vinyl ethers.[8,10]

The formation of formyl porphyrins from protoporphyrin-IX dimethyl ester is the first case in which such a fragmentation reaction has been observed for an arylethylene. Styrene itself polymerises[11] under the reaction conditions used, but studies of other arylethylenes and of the mechanism are in progress.

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† 5 μ Partisil, 15 cm × 5 mm column, ethyl acetate–light petroleum (b.p. 60—80 °C) (1 : 1, v/v), flow rate 2 ml min⁻¹.

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