Reactions of Some Metalloporphyrin and Metallochlorin π-Cation Radicals with Nitrite

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Summary Treatment of π-cation radicals of magnesium(II) and cadmium(II) octa-alkylporphyrins with sodium nitrite affords good yields of *meso*-mononitroporphyrins after demetallation; with zinc(II) *trans*-octaethylchlorin, *meso*-substitution occurs adjacent to the partially reduced ring.

SUBSTITUENTS are usually introduced into the *meso*-positions of porphyrins, chlorins, and their metal chelates by means of electrophilic substitution.[1] A novel alternative[2] for synthesis of *meso*-acetoxyporphyrins is treatment of metalloporphyrin π-dications with acetate as a nucleophile. We have interpreted the mechanism of our syntheses of *meso*-trifluoroacetoxy-porphyrins and -chlorins in these terms.[3] However, on account of the unexpected stability of metalloporphyrin π-cation radicals in methanol, it has been generally accepted that such species are resistant to attack by nucleophiles; this has been rationalised in terms of the stability afforded by delocalisation of the unpaired electron in the π-cation radical over the π-cloud of the porphyrin macrocycle.[2] We now report the ready reaction of metalloporphyrin and metallochlorin π-cation radicals with nitrite, which furnishes a simple route to the corresponding *meso*-nitro macrocycles.

Treatment of magnesium(II) aetioporphyrin-I (**1a**) with an excess of iodine gave[4] the π-cation radical which, as expected, was stable in methanol. Addition of sodium nitrite[5] to the mixture caused a rapid change in colour, and after a mild acid work-up an 85% yield of mononitroaetioporphyrin-I† (**2**)[6] was obtained.‡ A high yield of a readily separable mixture[8] of αβ-† and αγ-dinitro-octaethylporphyrins† was obtained when magnesium(II) octaethyl-

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† A satisfactory elemental analysis was obtained, and m.p., n.m.r., visible, and mass spectra were compatible with this formulation. The compound was also identified by comparison with authentic material prepared using literature methods.

‡ Similar results were obtained using cadmium(II) aetioporphyrin-I (**1b**) and with the corresponding chelates of octaethylporphyrin. The oxidation potential of cadmium(II) octaethylporphyrin is sufficiently low[7] for the π-cation radical to be obtained using iodine.

porphyrin was stirred during 6 h with excess of silver(I) nitrite§ in chloroform–methanol, followed by demetallation.

When zinc(II) *trans*-octaethylchlorin (**3**) was oxidised with excess of iodine and the resulting π-cation radical treated with sodium nitrite, a 65% yield¶ of γ-nitro-*trans*-octaethylchlorin† (**4a**)[8] was isolated after an acidic work-up. The π-cation radical from the zinc(II) chelate of (**4a**) reacted further with sodium nitrite to give the γδ-dinitrochlorin† (**4b**)[8] after demetallation of the zinc complex.

We consider that the above reactions involve the novel nucleophilic attack of nitrite upon macrocyclic π-cation radicals, followed by abstraction of a second electron by the excess of oxidant and then loss of a proton from the resultant metallo-isoporphyrin. π-Dications cannot be involved in these transformations because the oxidation potential of iodine is not high enough to abstract *two* electrons from the metalloporphyrins employed. Moreover, the reactions can be carried out in presence of methanol, and powerful electrophiles such as metalloporphyrin π-dications[2,9] would be expected to react with solvent, producing side-products (which were not observed).

Preliminary experiments have indicated similar, though less efficient, reactions of π-cation radicals of metalloporphyrins with other nucleophiles; a comprehensive study of these is in progress.

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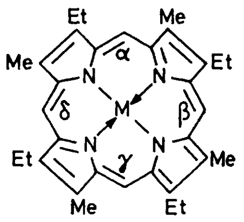
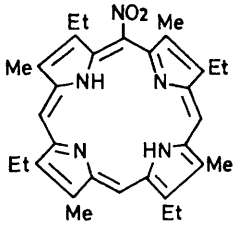
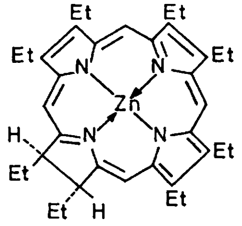


(1)

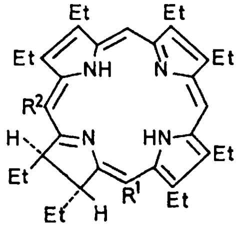
a; M = Mg
b; M = Cd



(2)



(3)



(4)

a; $R^1 = NO_2, R^2 = H$
b; $R^1 = R^2 = NO_2$

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§ αβγ-Trinitroporphyrin was not obtained, presumably because the first oxidation potential of the magnesium(II) dinitroporphyrins is too high to be achieved by reduction of silver(I).

¶ Major by-products were zinc(II) octaethylporphyrin and its mono-nitro derivative; these were separable from the required product by chromatography.

[1] For a review see H. H. Inhoffen, J. W. Buchler, and P. Jäger, *Fortschr. Chem. org. Naturstoffe*, 1968, **26**, 284.
[2] D. Dolphin, Z. Muljiani, K. Rousseau, D. C. Borg, J. Fajer, and R. H. Felton, *Annals New York Acad. Sci.*, 1973, **206**, 177.
[3] G. H. Barnett, M. F. Hudson, S. W. McCombie, and K. M. Smith, *J.C.S. Perkin I*, 1973, 691; J. A. S. Cavaleiro and K. M. Smith, *ibid.*, 1973, 2149.
[4] J.-H. Fuhrhop, and D. Mauzerall, *J. Amer. Chem. Soc.*, 1969, **91**, 4147.
[5] *Cf.* C. V. Ristagno and H. J. Shine, *J. Amer. Chem. Soc.*, 1971, **93**, 1811; H. J. Shine, J. J. Silber, R. J. Bussey, and T. Okuyama, *J. Org. Chem.*, 1972, **37**, 2691.
[6] A. W. Johnson and D. Oldfield, *J. Chem. Soc.*, 1965, 4303.
[7] J.-H. Fuhrhop, K. M. Kadish, and D. G. Davis, *J. Amer. Chem. Soc.*, 1973, **95**, 8140.
[8] R. Bonnett and G. F. Stephenson, *J. Org. Chem.*, 1965, **30**, 2791.
[9] D. Dolphin, R. H. Felton, D. C. Borg, and J. Fajer, *J. Amer. Chem. Soc.*, 1970, **92**, 743.