Reaction of Dinitrogen Tetroxide with Octaethylhemin in Dichloromethane: A *meso*-Substitution Reaction

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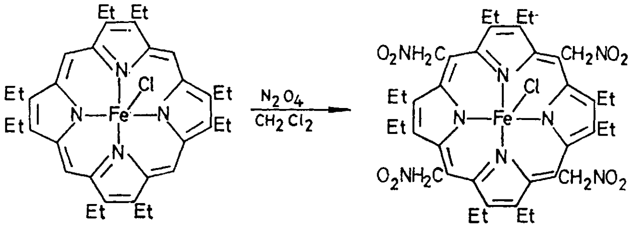
Summary Octaethylhemin(I) reacts rapidly with N_2O_4 in $CHCl_2$ to produce *meso*-tetranitromethyloctaethylhemin(II), a high-spin iron(III) complex with a porphyrin ligand fully substituted in all β- and *meso*-positions.

The *meso*-reactivity of porphyrins and metalloporphyrins has recently been under study[1] and iron(III) porphyrins have been shown to be rather unreactive to *meso*-oxidation.[1a] We report that octaethylhemin(I) reacts rapidly with N_2O_4 (1:10) in CH_2Cl_2 at room temperature in air, producing *meso*-tetranitromethyloctaethylhemin(II) in 48% yield. Compound (II) is an iron(III) complex with a porphyrin ligand having total β- and *meso*-substitution. A large excess of N_2O_4 was used in order to reduce the amount of partially substituted products and the separation problems that would result. Impurities were removed from compound (II) by dissolving it in CH_2Cl_2 and using columns of Sephadex LH-20 and talc. Compound (II) gave a satisfactory analysis, and its i.r. spectrum in CH_2Cl_2 shows strong bands at 1537 and 1362 cm^{-1} indicative of covalently bound NO_2 groups. The same solution has visible absorption bands at 642 (3800), 540 infl (7400), 510 (8300), and 375 nm (38,600) (molar absorbances in parentheses)—a spectrum typical of iron(III) porphyrins. A saturated $CDCl_3$ solution of (II) has an ^1H n.m.r. spectrum displaying large paramagnetic shifts which would be expected for a high-spin iron(III) complex: δ (Me_4Si) CH_2Me −40·1, −37·5, −35·2, and −33·2; Me −4·4; and CH_2(*meso*) −1·4, +0·2, +1·3, and +3·2. These assignments are based upon peak areas and a comparison with the ^1H n.m.r. spectrum of (I) in $CDCl_3$: CH_2 −33·4 and −41·6; Me −4·8; and *meso*-H, +55br.[2] The signals from (II) at −1·4 and +3·2 are broad (*ca.* 300 Hz) and of low intensity, while the other two *meso*-CH_2 signals are sharp with about ten times the intensity of the broad peaks.



(I) (II)

The splitting of the CH_2 peaks is a result of the asymmetric nature of the square-pyramidal porphyrin complex and the distortion of the porphyrin ring by the *meso*-substituents. Models show that the four pyrrole rings with β-ethyl groups will undergo skeletal 'ruffling' in order to accommodate the four bulky CH_2NO_2 groups. This forces the *meso*-CH_2 groups out of the porphyrin ring plane and either close to the out-of-plane iron or away from it, on the opposite side of the porphyrin plane. The variation in the line shapes of the *meso*-CH_2 signals may be due to the non-equivalency of the groups or a difference in their rotational correlation times.

meso-Substitution of porphyrins and metalloporphyrins may be achieved by either electrophilic or free-radical attack.[1a] The path of the *meso*-nitromethylation reaction is not known and is now under study. Both NO_2 and N_2O_4 are present in the solution, but N_2O_4, present in high concentration at room temperature[3] is probably involved in the nitromethylation reaction. NO_2, since it is known to abstract hydrogen atoms from CH_2Cl_2,[5] is less likely to be involved.

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