Radical Reactions in the Porphyrin Series. The Benzoyloxylation of Octaethylporphyrin

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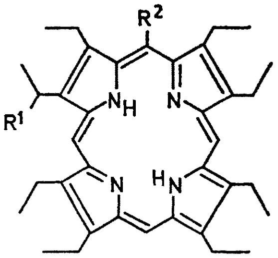
Summary The reaction of benzoyl peroxide with octaethylporphyrin (1,2,4-trichlorobenzene, 95°, N_2) leads to side-chain and *meso*-substitution products (benzoyloxy-derivatives).

The postulate[1] that the *meso*-hydroxylation of bis-pyridine octaethylhaemochrome, a reaction which is thought to have a bearing on the chemistry of haem catabolism,[2] proceeds by a radical process has led us to search for examples of radical attack on the porphyrin system. The reaction[3] of octaethylporphyrin (I) with benzoyl peroxide (2·2 mol., 15 min., 95° in 1,2,4-trichlorobenzene) presumably involves radical intermediates, and shows an interesting dependance of reactivity on oxygen tension and on the presence of a co-ordinated ferrous ion.

Conducted under *nitrogen*, the reaction gave seven major substitution products, which were separated (t.l.c.), crystallised, and identified as follows:†



(I) $R^1 = R^2 = H$
(II) $R^1 = OCOPh, R^2 = H$
(III) $R^1 = H, R^2 = OCOPh$

2-(1′-benzoyloxyethyl)heptaethylporphyrin (II), 14%;
5-benzoyloxyoctaethylporphyrin (III),[3] 18%;
di-(1′-benzoyloxyethyl)hexaethylporphyrin (IV),‡ 8%;
(1′-benzoyloxyethyl)-*meso*-benzoyloxyheptaethylporphyrin (V),‡ 17%;
di-(*meso*-benzoyloxy)octaethylporphyrin (VI),‡ 15%;
5,10,15-tribenzoyloxyoctaethylporphyrin (VII), 8%;
5,10,15,20-tetrabenzoyloxyoctaethylporphyrin (VIII), 2%

The structural assignments rest on elemental analyses (II, III), accurate molecular-ion determinations (III, VI, VII, VIII), and spectroscopic data (i.r., n.m.r., visible, mass). In the i.r. spectra the *meso*-benzoyloxy-group gave rise to a peak at *ca.* 1740 cm^{-1} (νC=O), while for the side-chain benzoyloxy-derivatives this absorption appeared at *ca.* 1720 cm^{-1}: both peaks occurred in the spectrum of (V). All the products (II—VIII) possessed four-banded visible spectra, those of (VI) and (VII) being of the phyllo type.[4] Whereas the compounds (III, VI, VII, VIII) substituted solely at *meso*-positions gave strong molecular ions, in the mass spectra of the side-chain derivatives the molecular ion was weak or absent, due to the ready loss of benzoic acid. Thus the mass spectrum of (II) showed strong peaks at *m/e* 532 ($M - PhCO_2H$) and 122 ($PhCO_2H$). Pyrolysis (250—260°, 0·1 mm., 3 min.) of (II) gave benzoic acid (88%) and vinylheptaethylporphyrin (65%).

The products mentioned above, together with recovered octaethylporphyrin give >80% material balance: products arising from phenylation have not been recognised.

When the reaction was carried out under *oxygen*, side-chain substitution virtually ceased. Using 2·2 mol. of benzoyl peroxide as before, but under oxygen, the products were: (II) 1%; (III) 30%; (V) 2%; (VI) 22%; (VII) 10%; and (VIII) 3%. A similar product distribution was observed (expect that in this case only trace amounts of side-chain-substituted products were detected) when bis-pyridine octaethylhaemochrome was subjected to benzoyloxylation under *nitrogen*. The mechanistic implications of these results will be discussed in the full paper.

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† Presented in order of decreasing mobility on the t.l.c. system (silica gel, 20% acetone–60—80° light petroleum).

‡ The disubstituted compounds are presumably mixtures of positional isomers which have not been separated.

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