

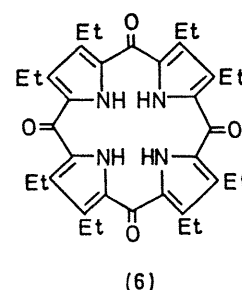
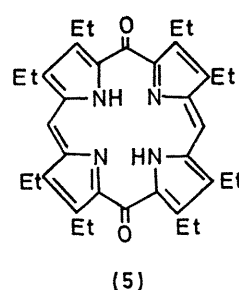
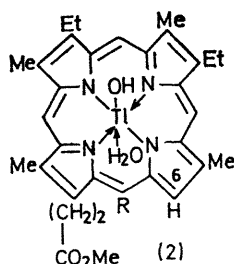
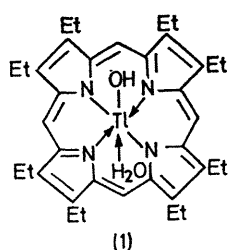
Reactions of Porphyrins with Thallium(III) Trifluoroacetate

By K. M. SMITH

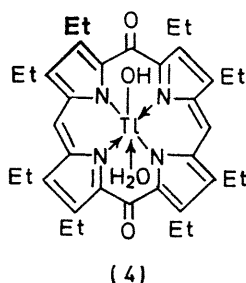
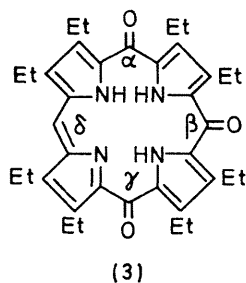
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Summary Treatment of porphyrins with thallium trifluoroacetate gives thallium(III) porphyrin chelates and, in the presence of trifluoroacetic acid gives further products by oxidation at the porphyrin *meso*-positions.

THE chemistry of many metalloporphyrins has been studied^{1,2} but little is known of thallium(III) porphyrin complexes. These might be expected to exhibit interesting physical and chemical properties in view of recent publications on organo-thallium chemistry.³ The only references^{4,5} to thallium porphyrins are brief comments in the blanket coverage of whole groups of metals, and the oxidation state of the thallium in the uncharacterised products was not known with certainty.



Brief treatment of octaethylporphyrin (in dichloromethane and tetrahydrofuran) with an excess of thallium trifluoroacetate^{3,6} followed by chromatography on deactivated alumina gave the chelate (1) (>90%).[†] [m.p. >300°, λ_{\max} (CH₂Cl₂) 415 (ϵ 327,000), 543 (18,200), and



581 nm (14,200); mass spec.[‡] m/e (%), 772(5), 770(2) P^+ ; 737(4), 735(2) $P^+ - OH - H_2O$; 534(100): n.m.r. spectrum (CDCl₃), τ -0.32 (4 *meso*-H, d, J 45 Hz), 5.7—6.2 (16H, m, $-CH_2-$), and 8.05 (24H, t, $-CH_3$).] The *meso*-protons were split as a result of coupling with the thallium atom,[§] which bears a nuclear spin of $\frac{1}{2}$. Similar splittings were also experienced by the 6-proton of (2; R = H)[†] [τ 0.75 (1H, d, J 70 Hz)]; the magnitude of this coupling is larger than that of the *meso*-protons in (1) since it has a more favourable zig-zag arrangement of the four bonds. The *meso*-methyl

group of (2; R = Me)[†] also showed a thallium splitting [τ 5.26 (3H, d, J 28 Hz)]. The base (100%) peak of the mass spectra of all the thallium compounds discussed corresponded to the metal-free ligand owing to the extrusion of the thallium with transfer of two hydrogens to the macrocycle; the mass spectra of metalloporphyrins⁷ do not normally show loss of the metal atom.

Treatment of porphyrin thallium complexes *e.g.* (1) with trifluoroacetic acid at room temperature resulted in immediate and quantitative demetallation to free porphyrin, indicating that the stability of thallium chelates is comparable with that of zinc analogues. Preliminary experiments show that the thallium can also be removed reductively.

Prolonged treatment of octaethylporphyrin with thallium trifluoroacetate in trifluoroacetic acid and dichloromethane, followed by chromatography as before in dichloromethane resulted in isolation of (1) together with three other, easily separable compounds. The least polar of these was shown to be the $\alpha\beta\gamma$ -trioxo-compound (3)[†], [m.p. 228—230°; λ_{\max} (CH₂Cl₂) 336 (ϵ 35,600), 397 (18,000), and 540 nm (8000): mass spectrum m/e (%) 582(80), 580(100);[§] n.m.r. spectrum (CDCl₃) τ -0.33 (2NH), 3.04 (methine-H), 7.0—7.6 (16H m, $-CH_2-$), and 8.6—9.0 (24H m, $-CH_3$).

The $\alpha\gamma$ -dioxo-porphyrinogenatothallium compound (4)[†] was next eluted, [m.p. 259—263°; λ_{\max} (CH₂Cl₂) 328 (ϵ 34,600), 444 (64,000), 542 inf (12,700), and 575 nm (32,300): mass spectrum,[‡] m/e (%) 802(15), 800(6) P^+ ; 768—765 (5—2) $P^+ - 2OH$ or OH and H_2O ; 564(100): n.m.r. spectrum (CDCl₃) τ 3.34 (2 methine-H d, J 20 Hz), 7.1—7.8 (16H m, $-CH_2-$), and 8.7—9.0, (24H m, $-CH_3$)]. With cold trifluoroacetic acid, this chelate gave an almost quantitative yield of the metal-free ligand (5), [m.p. 271—273° (lit.⁹ 272—274°); λ_{\max} (CH₂Cl₂) 315 (ϵ 33,000), 408 (70,000), and 492 nm (15,000); mass spectrum m/e (%) 566(30), 564(100);[§] n.m.r. spectrum (CDCl₃) τ 3.32 (2 methine-H), 7.29 (8H q), 7.50 (8H q, $-CH_2-$), 8.86 (12H t) and 8.88 (12H t, $-CH_3$)]. (5) and its zinc chelate have been prepared by Fuhrhop,⁹ who found demetallation of the latter compound difficult.

The most polar component of the reaction mixture, eluted

[†] A new compound which gave a satisfactory elemental analysis.

[‡] Measured on A.E.I. MS12 Spectrometer with source temperature *ca.* 250°. Thallium has two isotopes, atomic weights 205 (70.5% abundance) and 203 (29.5%) and this is reflected in the appearance of ions containing thallium.

[§] Both thallium isotopes have a nuclear spin of $\frac{1}{2}$. Only one set of resonances is observed, presumably because of the similar magnetic moments of the isotopes.

in chloroform containing 2% ethanol, was identified as octaethylxanthoporphyrinogen (6), [m.p. 273—274° (lit.¹⁰ 272—276°): mass spectrum *m/e* 596 (100%).] Highest proportions of this compound were obtained in reactions with the longest thallium trifluoroacetate contact times.

Xanthoporphyrinogens have been prepared earlier¹⁰ by the oxidation of porphyrins with lead dioxide in acetic acid; it seems likely that in the reactions reported here, thallium trifluoroacetate behaves similarly as an oxidising agent, and there is ample precedent for this.³ Presumably oxidation

of the $\alpha\gamma$ -dioxo-compound (5) or its complex (4) leads to the $\alpha\beta\gamma$ -trioxo-material (3) which is not sufficiently basic to give a thallium chelate able to survive the work-up. Either the thallium chelates or the metal-free ligands might be substrates for the oxidation; both are probably present in the trifluoroacetic acid-dichloromethane solution.

I thank Professor H. H. Inhoffen (Braunschweig, Germany) for his gift of octaethylporphyrin.

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¹⁰ H. H. Inhoffen, J.-H. Fuhrhop, and F. v. d. Haar, *Annalen*, 1966, **700**, 92; H. Fischer and A. Treibs, *ibid.*, 1927, **457**, 209.