

RING CLEAVAGE OF MESO-TETRAPHENYLPORPHYRIN

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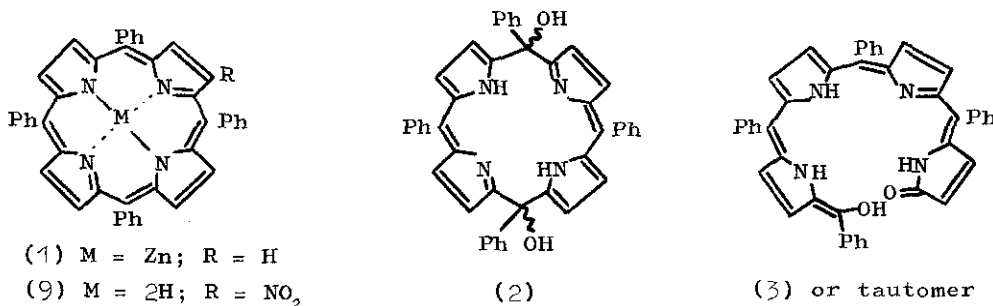
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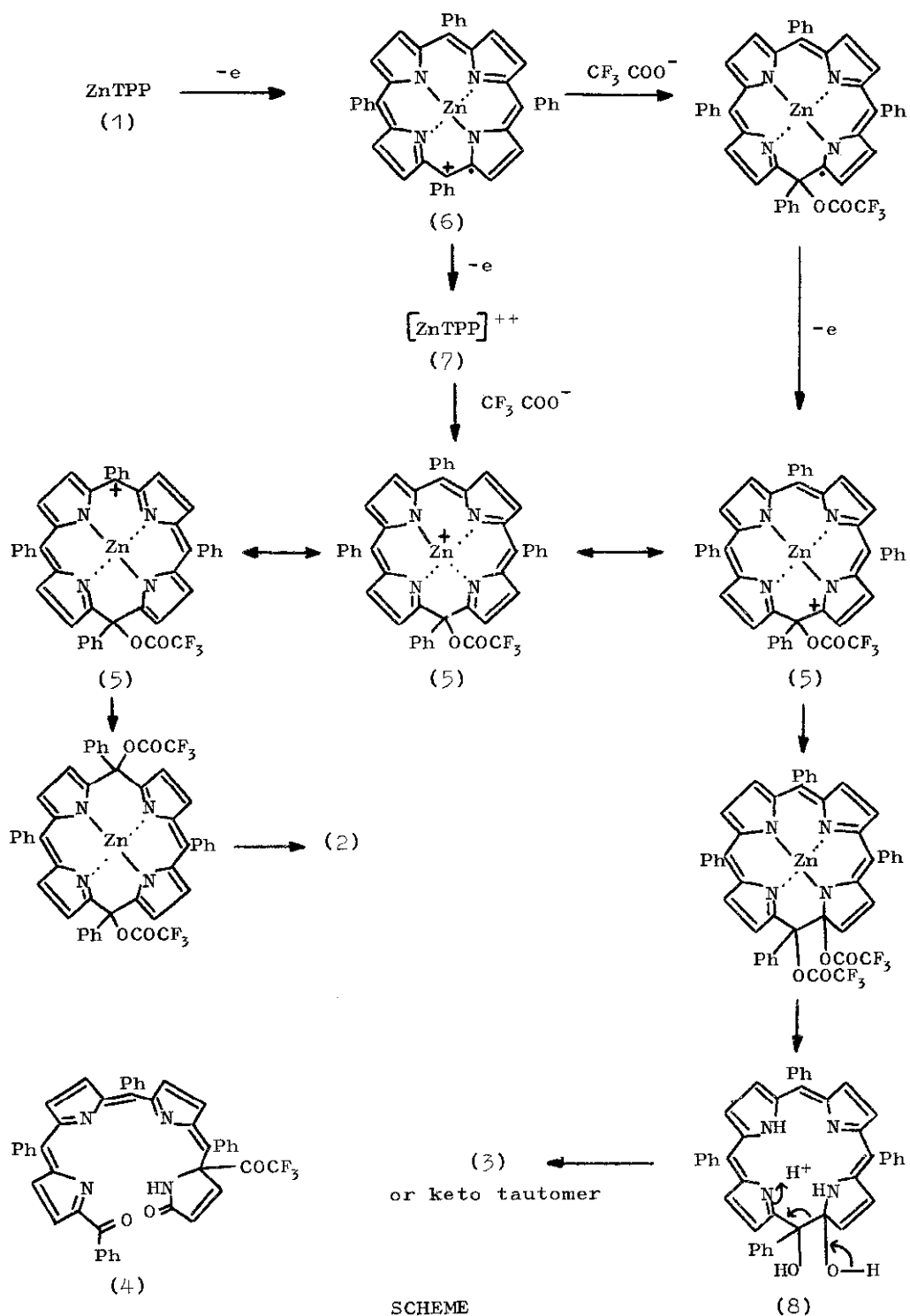
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(Received in UK 25 October 1976; accepted for publication 14 November 1976)

Reactions which accomplish rupture of the porphyrin or chlorin macrocycle have recently assumed importance owing to the relationship of this overall transformation to the natural processes of haem catabolism and of formation of algal and plant biliproteins.¹ Certain photo-oxidations, in which the meso-carbon at the point of rupture is retained as a carbonyl function (instead of being extruded as carbon monoxide) have also been reported.²⁻⁴ In this Letter we describe the reaction between zinc(II) meso-tetraphenylporphyrin (ZnTPP; 1) and thallium(III) salts, from which a major product is the ring-opened bilitriene (3); so far as we are aware, this represents the first example of rupture of the meso-tetraphenylporphyrin macrocycle to afford a bilitriene.



Treatment of ZnTPP in CH₂Cl₂ with 1.1 equiv of thallium(III) trifluoroacetate gave rapidly a yellow-green solution which was filtered through a bed of Kieselgel G (elution with 5% MeOH in CH₂Cl₂) to remove precipitated thallium(I) by-products, and then evaporated to dryness. Demetallation was accomplished with trifluoroacetic acid, and the products



were chromatographed on alumina (elution with CH_2Cl_2). Unconsumed meso-tetraphenylporphyrin was first eluted, followed by a yellow-brown fraction which was crystallised from CH_2Cl_2 - n-hexane to give the separable dihydroxy derivatives (2)⁵ (13% based on consumed ZnTPP). A violet band was finally eluted, and this was identified from its spectroscopic data (vide infra) as the bilitriene derivative (3) (17% yield). A small amount of a less polar red-purple substance was usually obtained (5-12% yield, depending on the excess of oxidant used); this was undoubtedly a further reaction product from (3), and taking into account the literature,⁶ one of several possible structures is given in (4). Unlike (3), the CO.CF_3 containing product (4) did not form a zinc complex under standard conditions.

We envisage the zinc(II) isoporphyrin (5) as an intermediate in the formation of (2), (3), and (4), this being formed either by reaction of the π -cation radical (6) or the π -dication (7) with trifluoroacetate as a nucleophile⁷ (Scheme). Resonance forms of the isoporphyrin (5) can readily explain the formation of compounds (2) and (3), the last being produced⁸ from a type of reverse-aldol reaction (8). Compounds such as (8) in which the " α -pyrrole" carbon atom is substituted are known⁹ to be unstable with respect to ring-opening.

Use of thallium(III) nitrate (in place of trifluoroacetate) also afforded compounds (2) and (3), presumably via nitrate substituted intermediates. As might be expected, compound (4) was not obtained, but a by-product was shown to be β -nitro-meso-tetraphenylporphyrin (9), and identified with an authentic sample prepared by treatment of ZnTPP with nitronium tetrafluoroborate. Insertion of "nitro" from "nitrate" has several precedents;¹⁰ significantly, treatment of zinc(II) aetioporphyrim-I with thallium(III) nitrate gives a 60% yield of meso-nitro-aetioporphyrim-I. This and similar observations are the subject of further study.

(2): (Polar band, silica; cf Ref. 5). M.p. 250-251^o(dec.). Found: C, 80.58, 80.35; H, 5.15, 5.15; N, 8.38. $\text{C}_{44}\text{H}_{32}\text{N}_4\text{O}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ requires: C, 80.34; H, 5.06; N, 8.52%. NMR (τ , CDCl_3) -3.52 (2NH, br), 6.30 (2 OH).

(3): M.p. 136-139^o. Found: C, 79.21, 79.45; H, 5.03, 5.20; N, 8.54. $\text{C}_{44}\text{H}_{32}\text{N}_4\text{O}_2 \cdot \text{H}_2\text{O}$ requires: C, 79.26; H, 5.14; N, 8.40%. NMR (τ , CDCl_3) -2.45, -0.80, +0.04 (3 NH); 2.12 (2H, d J=10 Hz) o-Ph; 2.4-2.7 (18H, m) Ph; 3.12 (1H, d J=6

Hz), 3.16 (1H, t J=2 Hz), 3.23 (1H, d J=5 Hz), 3.52 (1H, d J= 5 Hz), 3.68 (1H, d J=5 Hz), 3.82 (3H, d J=5 Hz) 8 β -H; A D₂O shake caused disappearance of the NH and OH peaks, and the triplet at 3.16 τ became a doublet J=5 Hz. λ_{max} in CHCl₃, 345 (ϵ 36,900), 565 (23,400), and 587 nm (21,600); in CHCl₃ + 1% TFA, 375 (ϵ 27,500), 431 (16,800), and 585 nm (27,500). IR (KBr) 1667 cm⁻¹ (C=O). MS, m/e 650 (80%), 648 (100), 543 (60; M⁺ - CO.Ph).

(9): M.p. >300°. Found, C, 79.89; H, 4.46; N, 10.76. C₄₄H₂₉N₅O₂ requires, C, 80.10; H, 4.43; N, 10.62%. NMR (τ , CDCl₃) 0.96 (1H, s), 0.98 (1H, d J=5 Hz), 1.06 (1H, d J=5 Hz), 1.08 (1H, d J=5 Hz), 1.11 (1H, d J=5 Hz), 1.28 (2H, s) 7 β -H; 1.7-1.85 (8H, m) o-Ph; 2.2-2.3 (12H, m) m,p-Ph; 12.60 (2NH). λ_{max} in CHCl₃, 425 (ϵ 172,300), 534 (13,300), 559 (3400), 600 (3100), and 661 nm (6900). MS m/e 659 (100%), 613 (60).

Acknowledgement: The violet compound, to which we have assigned structure (3), has been obtained independently by Professor H. J. Shine (Lubbock, Texas). We thank him for providing a comparison sample of this material.

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