Photochemistry and Oxidation–Reduction Reactions of Tin Porphyrins[1]

D. G. Whitten,*[2a] J. C. Yau,[2b] and F. A. Carroll[2c]

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. *Received September 1, 1970*

Abstract: An investigation of the chemistry and interconversion of tin(II) and tin(IV) porphyrins is reported. Tin(IV) porphyrins photoreduce with $SnCl_2 \cdot 2H_2O$ in pyridine to yield first the tin(IV) chlorin and subsequently the corresponding *vic*-tetrahydroporphyrin or bacteriochlorin. The mechanism of the photoreduction evidently involves electron transfer from $SnCl_2$ to the porphyrin excited triplet and subsequent protonation of the resulting tin(IV) porphyrin dianion. Preparation of heretofore unknown tin(II) porphyrins by introduction of anhydrous $SnCl_2$ into the porphyrin in degassed solutions is described. The tin(II) porphyrin is extremely reactive and oxidizes readily to the stable tin(IV) porphyrin on exposure to air or water. Analysis of absorption and nmr spectra of tin(II) octaethylporphyrin indicates that the tin may be relatively far out of the porphyrin plane. Activation of the tin(II) porphyrin by heat or light yields ring-reduced porphyrintin(IV) species. This transformation may proceed *via* intramolecular electron transfer.

The structures, reactivity, and biological functions of metalloporphyrins and their complexes continue to be the subjects of considerable investigation. Vital to an understanding of the biological function of metalloporphyrins is a knowledge of the interactions between the metal, the porphyrin ring, and associated molecules. Recent crystallographic studies on the structures of metalloporphyrins in the solid phase have shown that there can be considerable geometric flexibility in the conformation of the porphyrin ring and location of the metal atom.[3–6] These studies, together with spectroscopic investigations in solution[7–9] and theoretical work,[10,11] have yielded considerable information as to the stereochemistry and interactions of porphyrin and metal. Such information promises[12] to be of great value in unraveling the mechanisms of porphyrin catalysis.

In previous studies[13,14] we have investigated photochemical energy transfer between metalloporphyrins and associated molecules in solution, in part as an effort to determine possible mechanisms for catalysis. In the course of our investigations, we became interested in the possibility that photochemically or thermally induced intramolecular electron transfer processes between metal and porphyrin might be important for metalloporphyrins where more than one stable oxidation state of the metal can exist. The tin porphyrins appeared to offer these possibilities since both tin(II) and tin (IV) complexes of porphyrins had been reported previously.[15–18] Additionally, the tin complexes appeared to be attractive candidates for photochemical investigation since the presence of a diamagnetic, closed-shell configuration of the metal in each state would be expected to result in relatively long excited state lifetimes. In the present paper we report an investigation of the photochemical and thermal oxidation–reduction reactions of porphyrin–tin complexes. Interesting aspects of this study include the finding that porphyrin–tin(IV) complexes undergo photochemically induced reduction at the porphyrin ring to yield a porphyrintin(IV) dianion which yields stable ring-reduced porphyrins following protonation. Porphyrin–tin(II) complexes, which cannot be produced by reduction of the corresponding porphyrintin(IV), have been prepared; spectroscopic studies reveal that these highly reactive compounds have unusual structures in which the metal is considerably out of the plane of the porphyrin.

Results and Discussion

Photoreduction of Sn(IV) Porphyrins. Irradiation of degassed pyridine solutions of octaethylporphyrin-tin(IV) dichloride (**1**) saturated with $SnCl_2 \cdot 2H_2O$ with light absorbed only by the porphyrin leads slowly to formation of octaethylchlorintin(IV) dichloride (**2**) and subsequently to *vic*-tetrahydrooctaethylporphyrin-tin(IV) dichloride (**3**) (isobacteriochlorin) (eq 1).[19]

(1) A preliminary account of the photochemical reduction of octaethylporphyrintin(IV) to the isobacteriochlorin has appeared: D. G. Whitten and J. C. Yau, *Tetrahedron Lett.*, 3077 (1969).

(2) (a) Fellow of the Alfred P. Sloan Foundation, 1970–1972; (b) National Science Foundation Undergraduate Research Participant, 1969–1970; (c) National Science Foundation Undergraduate Research Participant, 1968–1969.

(3) J. L. Hoard in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968, p 573.

(4) J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Amer. Chem. Soc.*, **89**, 1992 (1967); M. D. Glock, G. H. Cohen, and J. L. Hoard, *ibid.*, **89**, 1996 (1967).

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(11) M. S. Fischer and C. Weiss, Jr., *ibid.*, in press. We thank Dr. Weiss for providing us with a preprint of this paper.

(12) See, for example, J. H. Wang, *Accounts Chem. Res.*, **3**, 105 (1907).

(13) D. G. Whitten, I. G. Lopp, and P. D. Wildes, *J. Amer. Chem. Soc.*, **90**, 7196 (1968); D. G. Whitten, P. D. Wildes, and I. G. Lopp, *ibid.*, **91**, 3393 (1969).

(14) I. G. Lopp, R. W. Hendren P. D. Wildes, and D. G. Whitten, *ibid.*, **92**, 6440 (1970).

(15) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier, New York, N. Y., 1964, p 33.

(16) G. D. Dorough, J. R. Miller, and F. M. Huennekens, *J. Amer. Chem. Soc.*, **73**, 4315 (1951).

(17) R. S. Becker and J. B. Allison, *J. Phys. Chem.*, **67**, 2669 (1963).

(18) A. H. Corwin and O. D. Collins, III, *J. Org. Chem.*, **27**, 3060 (1962).

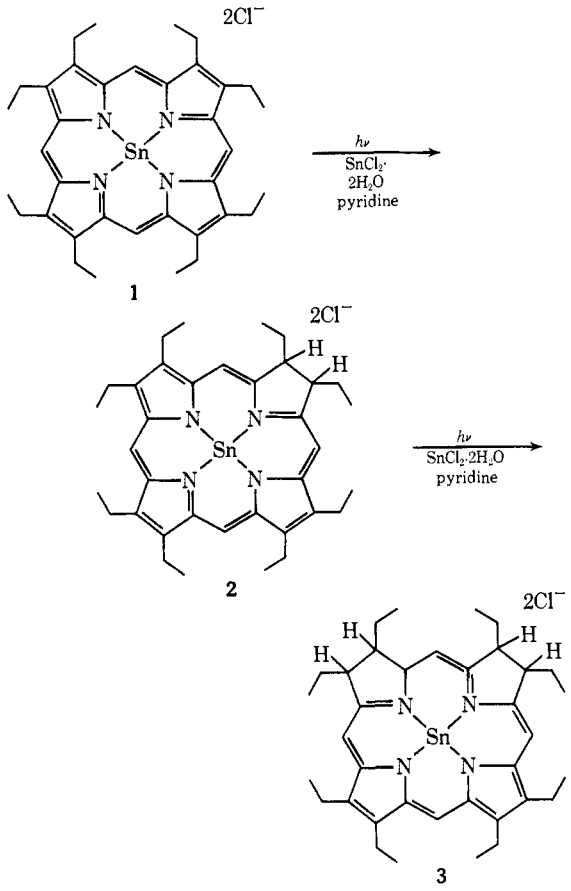
(19) The stereochemistry of the chlorin and isobacteriochlorin was not

Table I. Proton Chemical Shifts of Porphyrins and Reduced Porphyrins[a]

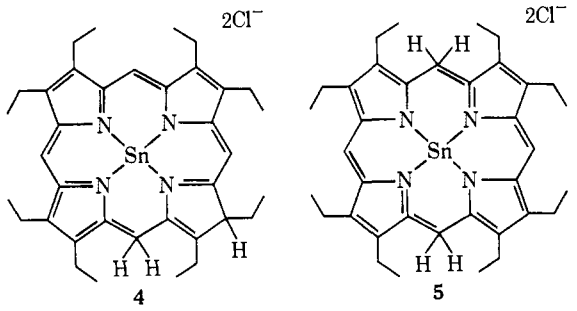
Compd	Compd no.	Solvent	Bridge protons	Ring protons	$-CH_2CH_3$	$-CH_2CH_3$
Octaethylporphyrin		$CDCl_3$	10.17 s (4 H)		4.15 q (16 H)	1.95 t (24 H)
Octaethylporphyrintin(IV) chloride	**1**	$CDCl_3$	10.66 s (4 H)		4.30 q (16 H)	2.10 t (24 H)
Octaethylporphyrintin(II)	**6**	C_5D_5N	10.48 s (4 H)		4.11 q (8 H) 4.13 q (8 H)	1.87 t (24 H)
Octaethylporphyrinlead(II)	**7**	C_5D_5N	10.44 s (4 H)		4.14 q (8 H) 4.16 q (8 H)	1.90 t (24 H)
Octaethylchlorintin(IV) chloride	**2**	$CDCl_3$	9.75 s (2 H) 8.85 s (2 H)	4.50 m (2 H)	3.75 q (2 H) 2.25 m (4 H)	1.75 t (18 H) 0.91 t (6 H)
1,2,3,4-Tetrahydrooctaethylporphyrintin(IV) chloride	**3**	$CDCl_3$	9.03 s (1 H) 8.02 s (2 H) 7.30 s (1 H)	4.07 m (4 H)	3.55 q (8 H) 2.17 quartet of doublets	1.67 t (12 H) 1.07 t (12 H)

[a] Chemical shifts in parts per million downfield from tetramethylsilane; s = singlet, t = triplet, q = quartet, m = multiplet.

Formation of **2** and **3** can be monitored conveniently by observing the sharp visible absorption bands at 625 and 609 nm, respectively. The products of the photo-



reduction were identified by their nmr spectra (Table I) and comparison of their absorption spectra with those of authentic samples. The conversion of **1** ultimately to **3** is nearly quantitative; the occurrence of several isosbestic points when **2** is the starting material indicates that the second reduction leads exclusively to **3** without formation of the "opposite" tetrahydroporphyrin or bacteriochlorin.[22,23] In the conversion of **1** to the chlorin a small amount of a product having absorption at 445 nm can be observed in the early stages of reaction. This product does not accumulate during the course of the reaction; evidently it is converted to **2** subsequent to its formation. Based on spectral similarities and deuterium studies (*vide infra*) this product could be assigned either the partially bridge-reduced dihydroporphyrin structure (**4**) reported by Seely and Talmadge[24] in the ascorbic acid promoted photoreduction of zinc porphin, or, perhaps more likely, the doubly bridge-reduced α,γ-dihydroporphyrin structure (**5**) obtained by Buchler and Inhoffen[25,26] in reductive protonation of metalloporphyrin anions.



Both photoreduction steps proceed with relatively low quantum efficiency; the conversion of **1** to **2** has $\varphi = 10^{-4}$ with $\lambda = 405$ nm while $\varphi = 2 \times 10^{-4}$ for conversion of **2** to **3**. The reaction occurs equally readily in ethanol and pyridine; attempts to photoreduce **1** with stannous chloride in acetonitrile, acetic acid, or acetic acid–acetic anhydride mixtures were unsuccessful. $\alpha,\beta,\gamma,\delta$-Tetraphenylporphyrintin(IV) chloride also photoreduces with $SnCl_2 \cdot 2H_2O$ in pyridine to yield the corresponding chlorin and *vic*-tetrahydroporphyrin. Although quantum efficiencies have not been measured for the tetraphenylporphyrin, both reactions proceed noticeably faster in this case. Copper, zinc, and magnesium octaethylporphyrins do not photoreduce with stannous chloride under the conditions used for the tin porphyrin. Cobalt(III) porphyrins photoreduce under the conditions used for tin; however, the product is the metal-reduced porphyrin.

determined; however, the proposed mechanism (*vide infra*) suggests that trans rather than cis[20,21] products are likely formed.

(20) H. H. Inhoffen, J. W. Buchler, and R. Thomas, *Tetrahedron Lett.*, 1145 (1969).

(21) H. W. Whitlock, Jr., R. Hanauer, M. Y. Oester, and B. K. Bower, *J. Amer. Chem. Soc.*, **91**, 7485 (1969).

(22) For a recent review on reduced porphyrins, see A. N. Sidorov in "Elementary Photoprocesses in Molecules," B. S. Neoporent, Ed., Plenum Publishing Co., New York, N. Y., 1968, p 201.

(23) U. Eisner, A. Lichtarowicz, and R. P. Linstead, *J. Chem. Soc.*, 733 (1957); U. Eisner, *ibid.*, 3461 (1957).

(24) G. R. Seely and K. Talmadge, *Photochem. Photobiol.*, **3**, 195 (1964).

(25) J. W. Buchler and H. H. Schneehage, *Angew. Chem., Int. Ed. Engl.*, in press. We thank Professor Buchler for a preprint of this paper.

(26) H. H. Inhoffen, *Pure Appl. Chem.*, **17**, 443 (1968).

Although both **2** and **3** are fairly stable and isolable, irradiation of nondegassed pyridine solutions of **2** or **3** results in oxidation back to the porphyrin.

Obvious questions regarding the mechanism of the photoreduction concern the identity of the reactive state in the photoreduction and details of the reaction sequence. Regarding the former, we find that fluoresence of **1** is not quenched by $SnCl_2 \cdot 2H_2O$. Since the quantum efficiency of reduction is so low (*vide supra*), this in itself does not exclude singlet participation. However, flash experiments suggest that the triplet is likely the reactive species. The lifetime of the triplet of **1** degassed in pyridine is *ca.* 180 μsec as determined by decay of the triplet–triplet absorption at 460 nm; the lifetime of the same species in pyridine saturated with $SnCl_2 \cdot 2H_2O$ is 10 μsec. If the shortened lifetime is due to reaction of the porphyrin triplet with stannous chloride,[27] it can be estimated that greater than 90% of the porphyrin triplets is consumed by this route. Although absorption of light by the porphyrin as well as porphyrin fluorescence renders measurements in several regions of the spectrum unreliable, no transients other than the porphyrin triplet could be detected in flash investigations. If, as our experiments suggest, the porphyrin triplet reacts with stannous chloride with high efficiency, subsequent intermediates must have a high probability of returning to starting material.

Previously reported photoreductions of zinc, cadmium, and magnesium porphyrins[22,24] to chlorins and tetrahydroporphyrins have involved hydrogen atom donation as the key step. Clearly such a process does not operate in the present case; no reasonable hydrogen atom donor is present in pyridine–stannous chloride solutions. Furthermore, we find that photoreduction of **1** does not occur when **1** is irradiated in the presence of hydrogen atom donors such as benzhydrol or ascorbic acid.

The most likely mechanism for the present photoreduction appears to be photochemically induced electron transfer from stannous chloride to the porphyrin to yield a dianion which subsequently undergoes protonation. Chemical reductions of porphyrintin(IV) complexes as well as corresponding zinc(II) and aluminum(III) complexes have been found to yield dianions which upon protonation yield the corresponding chlorin *via* a α,γ-dihydroporphyrin intermediate.[25,28] Reduction of tetraphenylporphyrinzinc(II) has been reported to yield anions which lead to the chlorin *via* a phlorin salt intermediate.[29] Electrochemical reduction of tin(IV) porphyrins has been suggested to proceed *via* ring reduction rather than *via* reduction of the metal.[30] Considering the reported two-electron reduction potential of tetraphenylporphyrintin(IV) in dimethyl sulfoxide (−1.01 V *vs.* NHE)[30] and the value for the oxidation potential of stannous chloride in pyridine (~1.2 V *vs.* NHE; supporting electrolyte 0.2 *M* tetra-*n*-butylammonium hexafluorophosphate)[31] it appears quite reasonable that the *ca.* 40 kcal/mol tin porphyrin triplet[13,14] could promote reduction to the corresponding dianion with concurrent oxidation of the stannous chloride. However, since we have been unable to detect transients subsequent to the porphyrin triplet, we have no information as to whether a monoanion or a dianion is the reduction product or if a tin(III) species occurs as an intermediate.

We have reduced **1** with excess sodium–potassium alloy in degassed 2-methyltetrahydrofuran solution. The product of this reduction has a prominent long-wavelength absorption band at 448–450 nm; its identity as the dianion seems reasonable in view of previous reports on the dianions prepared by similar reductions of other metalloporphyrins.[32] Observation of this species in the flash experiments would be difficult due to its spectral overlap with the porphyrin triplet–triplet and Soret transitions.

We have tested the proposed reaction sequence by carrying out the photoreduction of **1** in anhydrous pyridine saturated with $SnCl_2 \cdot 2D_2O$. Analysis of the isolated product indicates that deuterium is incorporated into both "chlorin" and bridge positions of **3**. Integration of the nmr spectrum of **3** thus prepared shows incorporation of 0.94 deuterium atom per molecule at the ring or "chlorin" positions and 3.01 deuterium atoms per molecule at the bridge positions. Control experiments indicate that deuterium is not incorporated into the porphyrin on treatment of **1** with the same reagents in the dark, even on prolonged heating. The fact that both bridge and chlorin positions show deuterium incorporation indicates that initial proton abstraction does indeed occur at the bridge. An isotope effect on the rearrangement of the primary reduced product to **2** is the likely source of the greater bridge proton depletion.

Tin(II) and Tin(IV) Complexes of Porphyrins. One of the initial goals of this study was the preparation of porphyrintin(II) complexes. As with other metals, preparation of tin complexes of porphyrins can be accomplished only by treatment of the porphyrin with divalent tin. Although several workers[15,17] have assumed treatment of various porphyrins with stannous chloride or other divalent tin compounds yields the porphyrintin(II) as the isolated product, Corwin and Collins[18] found that metalation of etioporphyrin with stannous chloride in acetic acid yielded etioporphyrintin(IV) diacetate. Recent studies on the Mössbauer spectra of tin complexes of phthalocyanines and porphyrins confirm that the tetraphenylporphyrintin complexes are tin(IV).[33,34] In the present investigation we found also that metalation with $SnCl_2 \cdot 2H_2O$ in pyridine yields the porphyrintin(IV) as the only isolable product. Absorption and fluorescence spectra of samples prepared by introduction of $SnCl_2 \cdot 2H_2O$ into sealed, degassed pyridine or ethanol solutions were identical with those of samples prepared from analytical **1**. Attempts to reduce tin(IV) complexes with reagents such as dithionite were unsuccessful.

(27) A "heavy atom effect" could certainly contribute to a shortening of the triplet lifetime; however, the observation that fluorescence is unquenched by stannous chloride and the fact that the lifetime of the triplet of **1** is similar to those of other metalloporphyrins[14] suggest that this may not be too important.

(28) H. H. Inhoffen and J. W. Buchler, presented at the 4th International Symposium on Organometallic Chemistry, Bristol, England, 1969, Abstracts P11.

(29) G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 818 (1963).

(30) R. H. Felton and H. Linschitz, *ibid.*, 88, 1113 (1966).

(31) J. Ferguson, unpublished results.

(32) J. W. Dodd and N. S. Hush, *J. Chem. Soc.*, 4607 (1964).

(33) M. O'Rourke and C. Curran, *J. Amer. Chem. Soc.*, **92**, 1501 (1970).

(34) B. F. Burnham and J. J. Zuckerman, *ibid.*, **92**, 1547 (1970).

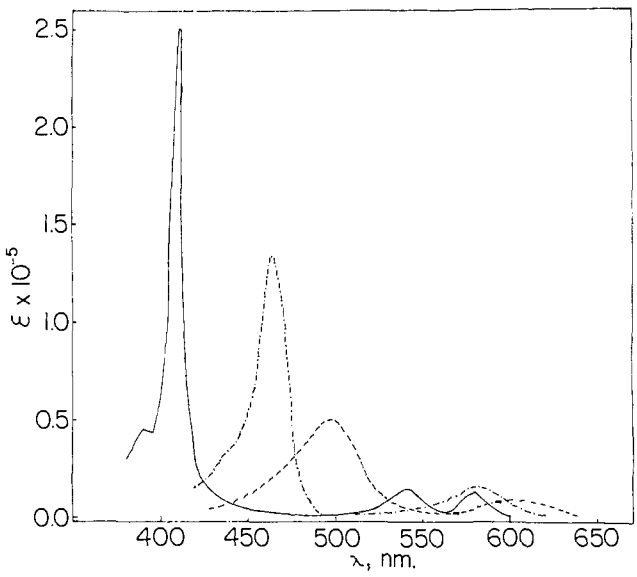


Figure 1. Absorption spectra of pyridine solutions of tin and lead porphyrins: ——, octaethylporphyrintin(IV) dichloride (**1**); -----, octaethylporphyrintin(II) (**6**); -·-·-·-·-, octaethylporphyrinlead(II) (**7**).

As mentioned previously, electrochemical and chemical reduction of tin(IV) porphyrins has been found to yield the ring-reduced tin(IV) porphyrin dianions.[25,30] Comparison of the reported reduction potential for tetraphenylporphyrintin(IV) diacetate of 1.01 V (corrected, *vs.* NHE)[30] with the potential for reduction of water of −0.83 V[35] indicates that equilibrium for the reaction

$$TPPSn^{IV}(OAc)_2^{2-} + 2H_2O \rightleftharpoons TPPSn^{IV}(OAc)_2 + H_2 + 2OH^-$$

should lie to the right.[36] Since the tin(II) porphyn is isomeric with the dianion of the tin(IV) porphyrin, it is conceivable that a similar reaction could occur when $SnCl_2$ is introduced into the porphyrin in the presence of water.

In an effort to bypass possible water-induced oxidation of the tin(II) porphyrin, rigorously dried and degassed pyridine solutions of octaethylporphyrin were treated with freshly prepared anhydrous stannous chloride in a vacuum line apparatus. Upon mixing and heating the anhydrous stannous chloride and octaethylporphyrin solutions a new species, **6**, was obtained. The absorption spectrum of **6** shows rather broad bands at 495 and 600 nm (Figure 1); this spectrum hardly resembles the usual visible-near ultraviolet spectra of other metalloporphyrins and offers few immediate clues as to the structure of **6**. **6** could not be prepared in the presence of air or water; introduction of air or water into solutions of **6** led to immediate production of **1**. Although pyridine could be removed from **6** *in vacuo*, and the solid redissolved in pyridine without chemical change, attempts to dissolve solid **6** in chloroform, ethanol, acetonitrile, or acetic acid resulted in conversion of **6** to **1**.

(35) R. E. Weast and S. M. Shelby, Ed., "Handbook of Chemistry and Physics," 48th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967, p D-86.

(36) Occurrence of this reaction could be a factor in lowering the quantum yield for the photoreduction (*vide supra*).

To test the possibility that **6** might be a "complex" between the porphyrin and metal ion but not a metalloporphyrin,[34,37] solutions of **6** were treated with $Zn(OAc)_2$ and $Cu(OAc)_2$ to determine if the added metal could displace a weakly complexed $SnCl_2$ from the porphyrin. Addition of $Zn(OAc)_2$ to solutions of **6** caused no reaction; addition of $Cu(OAc)_2$ resulted in conversion of **6** to **1**. In no case were we able to regenerate free base porphyrin from **6**. A detailed investigation of the structure of **6** was precluded due to its instability. However, an nmr spectrum (Table I) was obtained following preparation of **6** in perdeuteriopyridine. The nmr spectrum of **6** showed the proton resonances expected for an octaethylporphyrin complex with only small displacements from those of the free base or tin(IV) complexes (however, see below). Consideration of the nmr spectrum together with the evidence that the metal cannot be removed readily from **6** leads to the conclusion that **6** is octaethylporphyrintin(II).[38] Indirect evidence in support of this assignment was obtained in a parallel investigation of the structurally similar octaethylporphyrinlead(II) (**7**). Lead(II) has a similar electronic configuration to tin(II) and although stable lead(II) complexes of porphyrins have been prepared[16] it appears that the ionic radius of lead(II) (0.94–1.2Å depending on coordination number)[41] is probably too large to permit the lead to "sit" in the 1.96–2.06-Å "hole"[11] of the porphyrin π-electron system. The absorption spectrum of octaethylporphyrinlead(II) is compared with that of **6** in Figure 1. The spectra are similar and support the assignment of **6** as the porphyrintin(II); comparison of these spectra with usual metalloporphyrin spectra suggests that the 495- and 450-nm bands of **6** and **7**, respectively, are metalloporphyrin Soret bands, red shifted, somewhat broadened and reduced in intensity. The longer wavelength bands in **6** and **7** are evidently remnants of the metalloporphyrin two-banded visible spectrum, again broadened and reduced in intensity.

The wavelength shifts of the porphyrin Soret band to lower energies are quite large compared to those previously observed with increasing metal size[11] and suggest that both lead(II) and tin(II) may be severely out of plane. Again, this seems reasonable for tin since the ionic radius of tin(II) is reported to vary from 0.94 to 1.22 Å, depending upon coordination number.[41] In addition, the spectral alterations observed for the tin(II) complexes are considerably greater than those observed upon adding a ligand for square-pyramid magnesium and zinc etioporphyrin complexes in solution where the metal atom is estimated to be 0.20–0.30 and 0.30–0.50 Å out of plane, respectively.[7] The dramatic spectral shifts and alterations could be explained either by the stereoelectronic effect[8] or by the "hole size" phenomenon.[11] The nmr spectra of both **6** and **7** show two overlapping quartets of equal in-

(37) E. B. Fleischer and J. H. Wang, *J. Amer. Chem. Soc.*, **82**, 3498 (1960).

(38) Bis(phthalocyanino)tin(IV) complexes have been reported;[6,39,40] however, the tin(II) complexes of phthalocyanine are "conventional."[39] The facile conversion of **6** to **1** together with the presented spectra indicates that **6** is not likely a 2:1 complex.

(39) P. A. Barrett, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, 1719 (1936).

(40) M. Whalley, *ibid.*, 866 (1961); J. A. Elvidge, *ibid.*, 169 (191).

(41) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.*, **25**, 925 (1969).

tensity for the methylene protons but only single methyl and bridge resonances. Although a nonplanar, distorted porphyrin skeleton with the metal preferentially bound to one side could give such a spectrum, a more likely interpretation is that the porphyrin is more or less flat but that the metal lies out of plane on one side so that the geminal protons are nonequivalent when time averaged over rotational isomers. Such nonequivalence of geminal protons has been observed previously in metal complexes of cyclobutadienes,[42] in other axially dissymmetric compounds,[43] and in compounds where a methylene lies near an asymmetric center.[44]

If, indeed, the unusual absorption spectra and the nmr spectra of the lead and tin porphyrins indicate structures with the metal strongly out of plane or bound on one side, the instability of the tin(II) porphyrin and the lack of reduction of the tin(IV) porphyrin to **6** can be understood. The ionic radius of four-coordinate tin(IV) is reported to be 0.69–0.71 Å;[41] clearly this is small enough to allow an "in plane" structure for **1**. Reduction of **1** to the corresponding ring-reduced dianion should require little movement of the metal and thus a relatively low activation energy beyond that required for reduction. On the other hand, reduction of the metal might be expected to involve severe geometric distortion and correspondingly greater activation energy. Conversely, the major factors favoring oxidation of **6** or its rearrangement to the dianion might be relief of strain and stronger metal–nitrogen bonding.

In addition to the above reported oxidations of **6** to **1**, preliminary evidence for the photochemical and thermal intramolecular electron transfer processes originally sought in **6** has been obtained. Irradiation of **6** in pyridine solution containing anhydrous stannous chloride leads ultimately to **3** in *ca.* 70% overall yield. By-products from the pyridine have not been determined and the overall reaction is obviously complex. However, initial irradiation of **6** leads to a product having λ_{max} 448–450 nm. This product, which disappears immediately on exposure to air, is probably the corresponding dianion or, less likely, a protonated anion. Further irradiation of the mixture leads to **2** and finally **3** as the only spectrally detectable product. Although sealed solutions of **6** are relatively stable at room temperature, or below, in the absence of light, heating to 90° induces relatively slow formation of what is evidently the same 448–450 transient formed photochemically. Prolonged heating of the solutions at 90° in the dark results in formation of **1**, **2**, and small amounts of **3**.

Experimental Section

Spectra. Ultraviolet and visible absorption spectra were recorded either on a Unicam or a Cary Model 14 recording spectrophotometer. Fluorescence spectra were recorded on an Aminco-Bowman spectrophotofluorometer using RCA IP21 and EMI 9558Q photomultiplier tubes. Flash spectroscopic studies were performed on a flash photolysis apparatus consisting of a xenon–mercury flash tube (10%–10% time, 15 μsec) for initial excitation, a GE 18A type CPG tungsten lamp as the analyzing lamp, a Bausch and Lomb 500 mm grating monochromator, and a RCA IP28 photomultiplier tube. A polished aluminum sample cavity in the shape of an ellipse was used with the sample cell located at one focus and the flash tube at the other. Transient signals were displayed on a Tektronix type 585 oscilioscope and photographed on Polaroid type 47 film. Samples for flash photolysis were degassed by up to six cycles of the freeze–pump–thaw method and sealed in cylindrical quartz cells (25 mm path). The nmr spectra were recorded on Varian HA-100, Varian A-60, and Jeolco C-60HL spectrometers.

Materials. Octaethylporphyrin and tetraphenylporphyrin were prepared as described, respectively, by Whitlock and Hanauer[45] and by Adler, *et al.*[46] Octaethylchlorin and *vic*-tetrahydrooctaethylporphyrin were prepared by the sodium–isoamyl alcohol reduction of octaethylporphyriniron(III) chloride.[23] Porphyrin-, chlorin-, and *vic*-tetrahydroporphyrin- (isobacteriochlorin-) tin(IV) dichloride complexes were prepared by the procedure of Corwin and Collins.[18] Octaethylporphyrinlead(II) was prepared by a slight modification of the procedure of Dorough, Miller, and Huennekens.[16] Pyridine (B and A Reagent Grade) was distilled from potassium hydroxide and barium oxide immediately prior to use. Other solvents (except spectrograde solvents) were purified by distillation.

Reductions. The dianion of octaethylporphyrintin(IV) dichloride was prepared by a modification of the method of Dodd and Hush[32] for preparation of the mono- and dianions of metalloporphyrins. A solution of the metalloporphyrin in freshly distilled (from $LiAlH_4$) 2-methyltetrahydrofuran was degassed by three cycles of freeze–pump–thaw in a tube with a side arm containing excess sodium–potassium alloy. Anionic species were generated following mixing of the alloy with the solution and their spectra were recorded on a Unicam spectrophotometer.

Irradiations. Irradiations were carried out on samples of Pyrex ampoules degassed by three cycles of freeze–pump–thaw. For stannous chloride photoreductions the tubes used were fitted with a side arm so that the stannous chloride could be mixed with the solution after the sample had been degassed and sealed. Samples were usually irradiated with one of four light sources: for wavelength and quantum yield studies the appropriate region of medium pressure mercury lamp was selected with Corning glass color filters in a "merry-go-round" apparatus;[47] alternatively the solutions were irradiated with a super-high-pressure mercury lamp using a high intensity Bausch and Lomb grating monochromator to isolate the desired wavelength. For product studies both unfiltered sunlight and the light from a tungsten projection lamp proved satisfactory.

Preparative Photoreduction of Octaethylporphyrintin(IV) Dichloride. Free base octaethylporphyrin (60 mg) was dissolved in pyridine (120 ml). $Sn_2Cl_2 \cdot 2H_2O$ was added until the solution was saturated. The solution was heated until all the free base had been converted to the metalloporphyrin. The solution was distributed among 30 13 × 100 mm Pyrex test tubes, which were then degassed three times each by the freeze–pump–thaw method. The tubes were exposed to direct sunlight. After 21 days, spectral analysis indicated that all of the metalloporphyrin had been converted to **3**. The pyridine solutions were combined and reduced in volume *in vacuo*. The concentrated solution was mixed with 120 ml of chloroform and the mixture washed three times with 5% aqueous HCl and then three times with water. The chloroform solution was dried over sodium sulfate and then the solvent was vacuum evaporated. The product was purified by several recrystallizations from acetone–hexane. *Anal.* Calcd for $C_{36}H_{48}N_4SnCl_2$: C, 59.50; H, 6.61. Found: C, 59.31; H, 6.61.

Preparation of Octaethylporphyrintin(II) (6). The tin(II) porphyrin was prepared in a special glass apparatus fitted with Teflon high-vacuum stopcocks, a fritted filter, several removable mixing bulbs, and a distributing outlet where the final solution could be directed into receivers and sealed. The entire preparation was done on a high-vacuum line in the absence of oxygen and moisture. Acetic anhydride (10 ml) was added to freshly prepared anhydrous stannous chloride[48] (250 mg) in a flask fitted with an

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O-ring joint. The mixture was heated and then the flask was connected to the main apparatus on a vacuum line. The acetic anhydride solution was frozen and the space above it was evacuated. After the acetic anhydride had thawed, the solution was filtered through a fritted filter and the anhydrous stannous chloride collected. The solid was washed with previously degassed anhydrous benzene (distilled from sodium). The crystals were then vacuum dried to remove all remaining solvent.

Octaethylporphyrin (3 mg) was dissolved in freshly distilled anhydrous pyridine (30 ml). The solution was degassed by three cycles of freeze–pump–thaw. The degassed porphyrin solution was back-filtered onto the anhydrous stannous chloride and the mixture heated. The resulting brown solution was filtered into a receiving flask and subsequently passed through the distributing outlet into appropriate sample tubes for spectral analysis or further reaction.

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Studies on Transfer Ribonucleic Acids and Related Compounds. III.[1] Synthesis of Hexanucleotide Having the Sequence of the Yeast Alanine Transfer Ribonucleic Acid 3′ End

Eiko Ohtsuka, Masaru Ubasawa, and Morio Ikehara

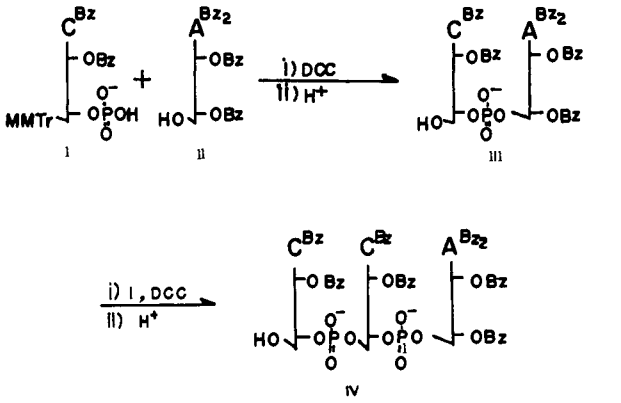
Contribution from the Faculty of Pharmaceutical Sciences, Osaka University, Toyonaka, Osaka, Japan. *Received July 18, 1970*

Abstract: A hexanucleotide with the base sequence of the 3′ end in some tRNA's, CpCpApCpCpA, was synthesized by condensation of the trinucleotide blocks, MMTr-C^{Bz}(OBz)-*p*-C^{Bz}(OBz)-*p*-A^{Bz}(OBz)-*p* and C^{Bz}(OBz)-*p*-C^{Bz}(OBz)-*p*-A^{Bz_2}(OBz)$_2$ using triisopropylbenzenesulfonyl chloride as the condensing reagent. The hexanucleotide was isolated in protected form as C^{Bz}(OBz)-*p*-C^{Bz}(OBz)-*p*-A^{Bz}(OBz)-*p*-C^{Bz}(OBz)-*p*-C^{Bz}(OBz)-*p*-A^{Bz_2}(OBz)$_2$ and can be further condensed with oligonucleotide blocks containing a 3′-phosphate end. A polymerization of C^{Bz}(OBz)-*p*-C^{Bz}(OBz)-*p*-A^{Bz}(OBz)-*p* yielded the hexanucleotide with the 3′-terminal phosphate. The circular dichroism spectra of CpCpA and CpCpApCpCpA were measured.

The synthesis of ribopolynucleotides may be facilitated by using preformed oligonucleotide blocks. In a previous paper we reported the synthesis of protected ribooligonucleotides with 3′-phosphate end groups.[1,2] In this report we present the synthesis of the hexanucleotide MMTr-C^{Bz}(OBz)-*p*-C^{Bz}(OBz)-*p*-A^{Bz}(OBz)-*p*-C^{Bz}(OBz)-*p*-C^{Bz}(OBz)-*p*-A^{Bz_2}(OBz)$_2$ (VIa) by condensation of the trinucleotides C^{Bz}(OBz)-*p*-C^{Bz}(OBz)-*p*-A^{Bz_2}(OBz)$_2$ (IV) and MMTr-C^{Bz}(OBz)-*p*-C^{Bz}(OBz)-*p*-A^{Bz}(OBz)-*p* (V).[3] A hexanucleotide of this sequence constitutes the 3′ end of yeast alanine tRNA,[4] *E. coli* tyrosine tRNA,[5] methionine tRNA,[6] valine tRNA,[7] and *Torulopsis utilis* isoleucine tRNA.[8] Selective removal of the 5′-*O*-methoxytrityl group of compound VIa gave the properly protected hexanucleotide VIb for further elongation of the chain.

Synthesis of C^{Bz}(OBz)-*p*-C^{Bz}(OBz)-*p*-A^{Bz_2}(OBz)$_2$. The terminal trinucleoside diphosphate was synthesized by stepwise condensation of the suitably protected mononucleotides as shown in Chart I. *N,N*′,2′,3′-*O*-

Chart I



Tetrabenzoyladenosine (II) and 5′-*O*-monomethoxytrityl-*N*,2′-*O*-dibenzoylcytidine 3′-phosphate (I) were condensed by a procedure similar to that used for the 5′-*O*-dimethoxytrityl derivatives.[9] After removal of the trityl group and ion exchange chromatography of the reaction mixture, III was obtained in a yield of 58%.

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