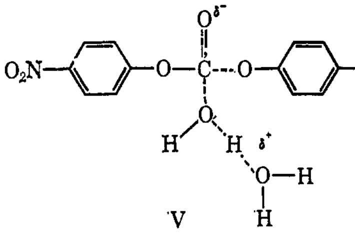
N-acylimidazoles,[1,18] and Schiff bases.[22] These reactions all involve participation by water in the transition state. The observed rate decreases have been explained by the decrease in water activity as acid concentration is increased[18] or by a possible change in rate-determining step.[18]

The pH-independent reactions are undoubtedly water-catalyzed reactions, and, as discussed above, the large D_2O solvent isotope effect indicates that proton transfer is taking place in the transition state. The most likely mechanism can therefore be represented by V or a kinetic equivalent.


V

The Hammett ρ value[23] for water-catalyzed hydrolysis of the dichloroacetate esters is 1.3 calculating it from the k_0 values for the nitro- and methoxy-substituted compounds. It can be seen in Table IV that the value of ρ is highly dependent on the ionic strength of the medium since the rate decrease produced by increasing acid concentrations is much greater for the nitrophenyl ester than for the methoxyphenyl ester. This is again very likely a reflection of the importance of solvation factors in the hydrolysis of nitrophenyl esters.

The magnitude of the water-catalyzed reactions is of considerable interest since such large water catalysis is not observed with other nitrophenyl esters (see the k_0 values in Table III). Thus, the carbonate ester is especially susceptible to water catalysis. This indicates a very low Brønsted coefficient for classical general base catalysis of carbonate ester hydrolysis. A Brønsted coefficient of 0.3 was observed for bis(4-nitrophenyl) carbonate.[24] An enhanced water catalysis has been noted previously with acyl activated esters by a positive deviation from Brønsted plots for nucleophilic catalysis.[25]

Acknowledgment. This work was supported by a research grant from the National Institutes of Health.

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[22] E. H. Cordes and W. P. Jencks, *J. Am. Chem. Soc.*, **84**, 832 (1962).

[23] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII; H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

[24] The hydrolysis of bis(4-nitrophenyl) carbonate is strongly catalyzed by the base species of various buffers. Rate constants for these reactions will be presented in a subsequent publication.

[25] K. Koehler, R. Shora, and E. H. Cordes, *J. Am. Chem. Soc.*, **88**, 3577 (1966).

Diimide Reduction of Porphyrins

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*Contribution from the Department of Chemistry, University of Wisconsin,
Madison, Wisconsin.* *Received December 26, 1968*

Abstract: A study of the diimide reduction of α,β,γ,δ-tetraphenylporphyrin and 1,2,3,4,5,6,7,8-octaethylporphyrin has been carried out. Diimide selectively *cis*-hydrogenates porphyrins. The stereoselective synthesis of *cis*- and *trans*-octaethylchlorin is described.

The central role played by oxidation/reduction reactions of porphyrins in photosynthesis and electron-transport mechanisms[1] coupled with the well-recognized cryptoolefinic nature of the peripheral double bonds in porphyrins[2-5] has prompted us to investigate the diimide reduction of *meso*-tetraphenylporphyrin and 1,2,3,4,5,6,7,8-octaethylporphyrin. We have been able to demonstrate that (1) porphyrins and chlorins are indeed readily reduced by diimide produced from the standard diimide precursor *p*-toluenesulfonylhydrazine,[6] (2) reduction of octaethylporphyrin proceeds with a high degree of stereoselectivity to *cis*-octaethylchlorin, (3) diimide reduction is the best synthetic procedure for preparing reduced derivatives of the tetraphenyl porphyrin ring system. These results are to be compared with one electron reduction of metal-free porphyrins which, with the possible exception of photoreduction of tetraphenylporphyrin with benzoin,[7] normally[8-11] afford the isomeric but less stable[10] phlorins. (See Figure 1.)

To the extent that one can equate ring currents and "aromaticity" with lack of reactivity toward nonpolar cycloaddition reagents we view the surprisingly facile diimide reduction of porphyrins as strong evidence for the picture of them as having marked and mutually distinct regions of π localization and aromaticity suggested by X-ray crystallographers.[2-4] An interesting

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[1] A. A. Krasnovskii, *Ann. Rev. Plant Physiol.*, **11**, 363 (1960).

[2] L. E. Webb and E. B. Fleischer, *J. Amer. Chem. Soc.*, **87**, 667 (1966).

[3] S. J. Silvers and A. Tulinsky, *ibid.*, **89**, 3331 (1967).

[4] J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *J. Amer. Chem. Soc.*, **87**, 2312 (1965).

[5] R. Grigg, A. W. Johnson, and A. Sweeney, *Chem. Commun.*, 697 (1968).

[6] E. E. van Tamelen, R. S. Dewey, and R. J. Timmons, *J. Amer. Chem. Soc.*, **83**, 3725 (1961).

[7] G. R. Seely and M. Calvin, *J. Chem. Phys.*, **23**, 1068 (1955).

[8] D. Mauzerall, *J. Amer. Chem. Soc.*, **84**, 2437 (1962).

[9] H. H. Inhoffen, P. Jaeger, R. Mahlhop, C. D. Mengler, *Ann.*, **704**, 188 (1967).

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

[11] A. N. Sidorov, *Usp. Khim.*, **35**, 366 (1966).

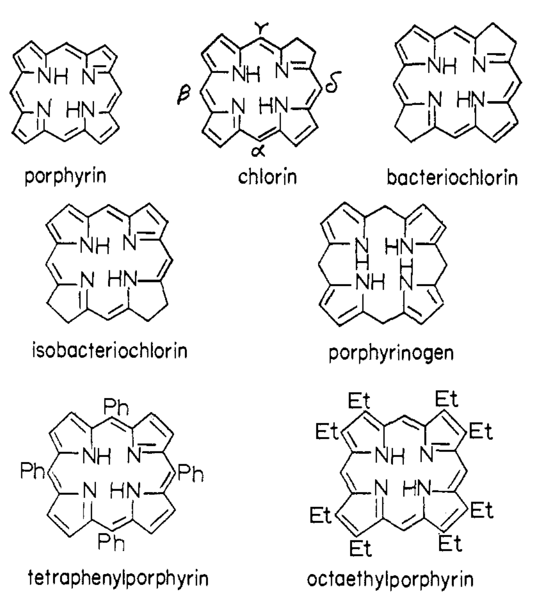

Figure 1. Nomenclature used for the ring systems discussed in the paper.

corollary of this, however, is that chlorins and metallochlorins differ significantly in this respect (see below).

Reduction of Tetraphenylporphyrin. The behavior of tetraphenylporphyrin (prepared according to Adler, *et al.*[12]) tetraphenylchlorin, zinc tetraphenylporphyrin, and zinc tetraphenylchlorin toward *p*-toluenesulfonylhydrazine in pyridine is summarized in Scheme I. Our observations as to the sequential nature of these reductions (Scheme I) are in good qualitative agreement with the spectroscopic studies of Sidorov on the hydrazine–aerobic pyridine reduction of tetraphenylporphyrin.[13] It seems clear that the processes observed are in fact reductions of the peripheral double bonds of the porphyrins by diimide[14–16] and do not involve poorly defined complexes between porphyrin or hydrazine and oxygen.[13]

Scheme I. Reduction of Tetraphenylporphyrin (TPP), Tetraphenylchlorin (TPC), Zinc TPP (ZnTPP), and Zinc TPC (ZnTPC) with Diimide in Pyridine[a]

$$\begin{tikzcd} \text{TPP} \arrow[r] \arrow[d, "\text{Zn}^{2+}"] & \text{TPC} \arrow[r] \arrow[d, "\text{Zn}^{2+}"] & \text{TPBC} \\ \text{ZnTPP} \arrow[r] & \text{ZnTPC} \arrow[r] & \text{ZnTP-}i\text{-BC} \end{tikzcd}$$

[a] TPBC = tetraphenylbacteriochlorin; ZnTP-*i*-BC = zinc tetraphenylisobacteriochlorin.

A remarkable feature of these reductions is the influence on the course of reaction of the presence of chelated zinc. Diimide reduction of metal-free tetraphenylchlorin affords tetraphenylbacteriochlorin contaminated by no more than 2–4% of tetraphenylisobacteriochlorin as determined by its uv-visible spectrum. Reduction of zinc tetraphenylchlorin affords the zinc complex of tetraphenylisobacteriochlorin with a similar degree of selectivity. The product mixtures from these reductions are kinetically determined as is shown by the stability of tetraphenylisobacteriochlorin and zinc tetraphenylbacteriochlorin under the reaction conditions associated with formation of their isomers. Our present understanding of the factors governing rates of diimide reduction of olefins[17] predicts that differences in π-bond order, localization energies or magnitude of the atomic orbital coefficients of the highest filled porphyrin molecular orbitals should determine the difference in reactivity of chlorin and metallochlorin. Huckel molecular orbital calculations[18,19] to this end were inconclusive.[20]

There are two other noteworthy features of the preparative aspects of diimide reduction of these porphyrin derivatives. *o*-Chloranil dehydrogenation[21,22] of tetraphenylbacteriochlorin to tetraphenylchlorin is sufficiently faster than dehydrogenation of the chlorin that the most efficient chlorin preparation involves reduction of tetraphenylporphyrin to a chlorin–bacteriochlorin mixture followed by addition of *o*-chloranil to dehydrogenate the bacteriochlorin. This technique may also be used to advantage in the preparation of octaethylchlorin described below. Separation of the pigments from one another is facilitated by their differing partition coefficients between benzene and phosphoric acid. Tetraphenylporphyrin may be separated from tetraphenylchlorin by extraction of a benzene solution of the two first with 68% (w/w) phosphoric acid, which removes the porphyrin into the acid layer, followed by 82% (w/w) phosphoric acid. Tetraphenylbacteriochlorin may be separated from the porphyrin and chlorin by extraction of benzene solutions of the three with 82% phosphoric acid: the less basic bacteriochlorin remains in the benzene layer. Separation of tetraphenylbacteriochlorin and tetraphenylisobacteriochlorin may be achieved by selective extraction of the latter from benzene with phosphoric acid. Dilution of the acid and extraction enables one to isolate the free porphyrin species. Use of phosphoric acid offers several advantages over, *e.g.*, hydrochloric acid in its decreased antipersonnel properties and minimization of acid-catalyzed autoxidation of the reduced porphyrins. The relative basicities of these porphyrins as inversely equated with the strength of phosphoric acid needed to extract them from benzene solution is: porphyrin > chlorin, isobacteriochlorin > bacteriochlorin.

Reduction of 1,2,3,4,5,6,7,8-Octaethylporphyrin. Reduction of octaethylporphyrin with diimide in hot pyridine or β-picoline affords a single isomer of octaethylchlorin (OEC), mp 216–217°. Reduction of iron(III) octaethylporphyrin chloride by a modification of the procedures of Eisner, *et al.*,[23] and Schlesinger, *et al.*,[24–27] affords in 72% yield an isomeric octaethylchlo-

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(12) A. D. Adler, F. R. Longo, and J. D. Finarellis, *J. Org. Chem.*, 32, 476 (1967).

(13) A. N. Sidorov, *Biofizika*, 10, 226 (1965). Reduction of porphyrins to chlorins by hydrazine has also been observed by E. W. Baker, A. H. Corwin, E. Klesper, and P. E. Wei, *J. Org. Chem.*, 33, 3144 (1968).

(14) E. J. Corey, W. L. Mock, and D. J. Pasto, *Tetrahedron Letters*, 347 (1961), and succeeding papers.

(15) S. Hunig, H. R. Milles, and W. Thier, *ibid.*, 353 (1961).

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(17) E. W. Garbisch, S. M. Schildcrout, D. B. Patterson, and C. M. Sprecher, *J. Amer. Chem. Soc.*, **87**, 2932 (1965).

(18) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, 17, 264 (1949).

(19) W. E. Kurtin and P-S Song, *Tetrahedron*, 24, 2255 (1968).

(20) R. C. Dougherty, H. H. Strain, and J. J. Katz, *J. Amer. Chem. Soc.*, **87**, 104 (1965).

(21) U. Eisner and R. P. Linstead, *J. Chem. Soc.*, 3749 (1965).

(22) J. R. L. Smith and M. Calvin, *J. Amer. Chem. Soc.*, **88**, 4500 (1966).

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

(24) W. Schlesinger, A. H. Corwin, and L. J. Sargent, *J. Amer. Chem. Soc.*, 72, 2867 (1950).

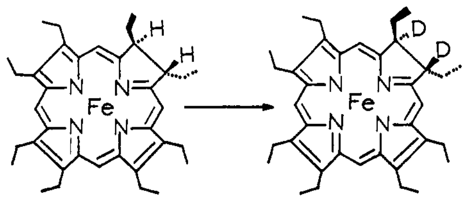
(25) H. Fischer and F. Balaz, *Ann.*, **553**, 166 (1942).

(26) H. Fischer, K. Platz, H. Helberger, and H. Niemer, *ibid.*, **479**, 26 (1930).

rin, mp 231.8–232°. Both reactions are completely stereoselective within the limits of detection of nmr (*ca.* 95%). This is clearly seen on comparison of the bridging methine region of the two spectra: the spectrum of the former OEC shows peaks due to the methine hydrogens as two singlets at δ 9.66 and 8.81 (CDCl$_3$, 100 MHz) while that of the latter OEC exhibited a pair of singlets at δ 9.72 and 8.86 (CDCl$_3$, 100 MHz).[28] A synthetic mixture of the two showed a resolved doublet for each methine peak. Scarcity of material prevented determining the ultimate limits of detection of contamination of one isomer with the other, other than to note that each reduction gave a chlorin that had but a pair of peaks in the methine region. The remainders of the spectra of the two isomers (Figure 2) are also different in a nonconcentration dependent manner.

Which chlorin is the *cis* and which is the *trans*? The simplest (but suspect) reasoning, that the chlorin from alkali metal reduction of the hemin chloride is the *trans*, is correct. Oxidation of this isomer by the procedure of Ficken, *et al.*,[29] afforded *racemic* 2,3-diethylsuccinic acid.[30] It appears then that diimide in β-picoline reduces octaethylporphyrin to *cis*-octaethylchlorin and sodium/alcohol reduces iron octaethylporphyrin chloride to the *trans*-chlorin, both reactions proceeding with a high degree of stereoselectivity.[31]

Consideration of the cause of stereoselective sodium isoamyl alcohol reduction of the hemin chloride to iron *trans*-octaethylchlorin reveals an interesting facet of the chemistry of the iron chlorin. Treatment of iron(III) *trans*-octaethylchlorin chloride with sodium isoamyloxide in isoamyl alcohol-O-*d* under conditions approximating those of the sodium and alcohol reduction results in the selective exchange of two of the 42 aliphatic hydrogens[32] as in eq 1. This conclusion follows from the low voltage mass spectrum of the derived chlorin, 64% d_2,[34] and its nmr spectrum which showed virtual disappearance of the band assigned to the two methine hydrogens. Inasmuch then as H/D exchange is a sufficient condition for *cis*/*trans* isomerization stereoselective reduction of the metalloporphyrin by sodium in alcohol is a reflection of the greater stability of the *trans*-chlorin, regardless of the stereochemistry of the chlorin initially produced.



(1)

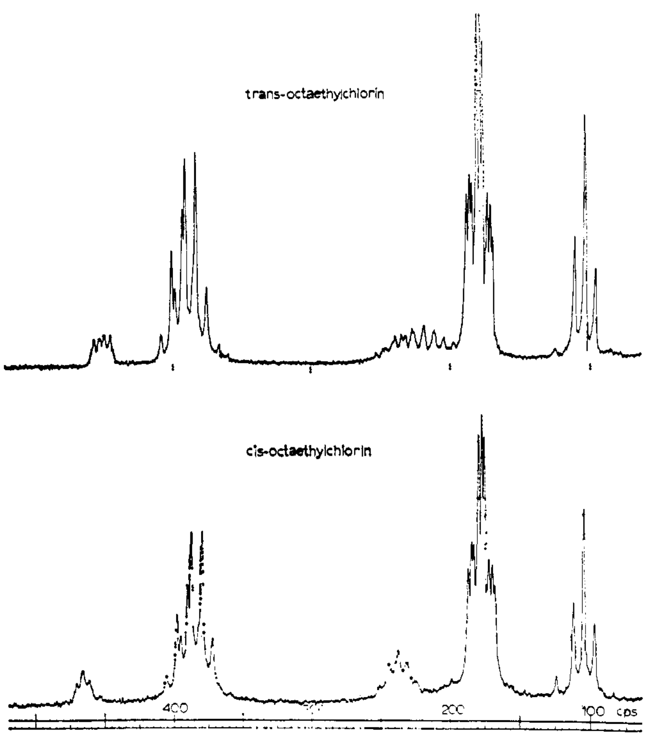


Figure 2. Nmr (CDCl$_3$) at 100 MHz of *cis* and *trans*-octaethylchlorin. The chemical shifts in cycles per second are relative to tetramethylsilane. Peak assignments for the two isomers are δ 1.05, $\mathit{CH_3}\mathrm{CH_2CH}$; 1.75, $\mathit{CH_3}\mathrm{CH_2C}{=}$; 2.0–2.5, $\mathrm{CH_3}\mathit{CH_2}\mathrm{CH}$; *ca.* 3.9, $\mathrm{CH_3}\mathit{CH_2}\mathrm{C}{=}$; 4.5, $\mathrm{CH_3CH_2}\mathit{CH}$. The two singlets for the bridging methine hydrogens are off scale to the left.

The role played by iron in the reduction and hydrogen–deuterium exchange process is poorly understood. Fischer and Gibian[36] have shown that certain optically active (by virtue of substituents on the dihydro ring) chlorins are racemized under Wolff–Kishner reaction conditions, although their conditions are somewhat harsher than ours, and there is, of course, no indication in their work of the positional specificity of deprotonation of metal-free chlorins, if in fact racemization proceeds in that way. It is clear from the work of Schlesinger[24] and Corwin[37] that the path of alkali metal reduction of porphyrins may be influenced by the particular metal complexed by the ligand. Two mechanistic possibilities for the role of iron in the hydrogen–deuterium exchange are the usual superacid role of the metal in facilitating attack of nucleophilic species on the porphyrin and a coupling of deprotonation of the porphyrin species with redox reactions[37] of the metal. In this respect it is interesting to note that sodium/alcohol reduction of iron octaethylchlorin chloride affords the iron complex of octaethyl-*cis*-bacteriochlorin.

Experimental Section

trans-**1,2,3,4,5,6,7,8-Octaethylchlorin.** A solution of 1.0 g (6.17 mmoles) of anhydrous ferric chloride and 0.5 g of anhydrous sodium acetate in 200 ml of glacial acetic acid contained in a 250-ml round-bottomed flask fitted with magnetic stirrer and Sohxlet

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(27) H. Fischer and H. Helberger, *Ann.*, **471**, 285 (1929).

(28) Assignment of the upfield peak to the pair of hydrogens labeled $\gamma\delta$ (Figure 1) is based on hydrogen–deuterium exchange experiments in which the faster exchanging hydrogens give rise to the peak at δ 8.86.

(29) L. Schotte and A. Rosenberg, *Arkiv Kemi*, **8**, 551 (1966).

(30) G. E. Ficken, R. B. Johns, and R. P. Linstead, *J. Chem. Soc.*, 2272 (1956).

(31) Since this paper was submitted, H. H. Infoffen, J. W. Buchler, and R. Thomas [*Tetrahedron Lett.*, 1145 (1969)] have reported the low-yield reduction of octaethylporphyrin to a 5:1 mixture of *cis*- and *trans*-octaethylchlorin by diborane in tetrahydrofuran. The properties of the two isomers quoted by them are in reasonable agreement with those of ours.

(32) Exchange of two labile vinyl hydrogens on the bridging methylenes[20,33] also occurs but is not considered since any deuterium thus introduced is washed out in subsequent acid demetalation of the metal chlorin.

(33) R. B. Woodward and V. Skáric, *J. Amer. Chem. Soc.*, **83**, 4676 (1961).

(34) This reflects the isotopic composition of the recovered solvent, the isotope dilution presumably being caused by a proto-Guerbet[35] reaction.

(35) M. Guerbet, *C. R. Acad. Sci., Paris*, **128**, 511 (1899).

(36) H. Fischer and H. Bibian, *Ann.*, **550**, 208 (1942).

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

extractor containing 1.0 g (1.87 mmoles) of octaethylporphyrin[38] was heated under reflux until the porphyrin was extracted from the thimble. The solution was cooled and the bulk of the acetic acid was removed under reduced pressure. Water (200 ml) was added and the resulting suspension was filtered to afford 1.18 g of crude iron(III) octaethylporphyrin chloride.

Anal. Calcd for $C_{36}H_{44}N_4FeCl$: C, 69.29; H, 7.11; N, 8.98; Cl, 5.68. Found: C, 69.12; H, 7.24; N, 8.39; Cl, 5.37.

Crude iron(III) porphyrin from above was dissolved in 118 ml of isoamyl alcohol in a 250-ml round-bottomed three-necked flask fitted with a stirrer and condenser. The mixture was heated under reflux for 15 min (oil bath, 150°) and then 11.8 g (0.51 g-atom) of sodium was added to the refluxing solution (the color of the solution went from red-brown to red to a dark green). The mixture was refluxed for an additional 15 min (oil bath, 175°), the stirring bar was raised above the surface, and the mixture was cooled in an ice bath. After solidification had occurred 25 ml of methanol followed by 100 ml of water was added and the mixture was stirred at room temperature until the bulk of the reaction mixture had dissolved. The mixture was extracted with 300 ml of benzene and the organic layer was washed successively with water, one portion of 150 ml of concentrated hydrochloric acid, and water until neutral, and then concentrated under reduced pressure to a volume of 75 ml. The resulting dark green solution was added to 500 ml of acetic acid under a nitrogen atmosphere in a 1-l. flask fitted with stirrer. With rapid stirring 50 ml of a saturated solution of ferrous sulfate in concentrated hydrochloric acid was added over 2 min, stirring was continued for 2 min, and the reaction mixture was poured into a cold mixture of 300 ml of saturated aqueous sodium acetate and 200 ml of benzene. The benzene layer was separated, washed and dried, and evaporated to afford 850 mg of a dark solid.

The solid was dissolved in benzene and the benzene solution was extracted with 50% (w/w) phosphoric acid until the acid extracts were colorless. The organic layer was then extracted with 75% (w/w) phosphoric acid (the extract was dark blue) until the extracts were pale. The remaining benzene layer was discarded, and the 75% phosphoric acid extracts were combined, diluted with water to approximately 60% phosphoric acid content, and extracted with benzene. The combined organic extracts were washed and evaporated to afford on crystallization from ethanol–chloroform 715 mg (72% yield) of *trans*-octaethylchlorin: mp (evacuated capillary) 231.8–232° (lit.[23] mp 232°); uv-visible $\lambda_{\max}^{C_6H_6}$ 391 mμ (ϵ 188,500), 487 (12,900), 496 (13,400), 520 (4070), 544 (1620), 593 (4030), 617 (4480), 647 (73,150). Combustion analysis of both *trans*- and *cis*-octaethylchlorin persistently gave results low in carbon.

***cis*-Octaethylchlorin.** In a 100-ml three-necked flask fitted with stirrer, condenser, and addition funnel was placed a mixture of 3.75 g of anhydrous potassium carbonate, 0.50 g (0.94 mmole) of octaethylporphyrin, and 25 ml of freshly distilled β-picoline. The mixture was placed under a nitrogen atmosphere and brought to reflux, and a solution of 5.0 g (25.8 mmoles) of *p*-toluenesulfonylhydrazine in 15 ml of β-picoline was added dropwise over a period of 2.5 hr. The reaction mixture was refluxed a further 2 hr and then cooled and partitioned between benzene and water. The benzene layer was extracted with cold 10% hydrochloric acid followed by three 35-ml portions of 85% (w/w) phosphoric acid. The combined phosphoric acid extracts were diluted to a 60% (w/w) phosphoric acid concentration and extracted with benzene. The combined benzene extracts were then washed with 60% phosphoric acid until the washes were colorless, with saturated bicarbonate solution and with water, and were evaporated to afford, after recrystallization from methanol–chloroform, 56 mg (11% yield) of *cis*-octaethylchlorin: mp 216–217° (vac); $\lambda_{\max}^{C_6H_6}$ 393 mμ (ϵ 182,800), 489 (12,590), 497 (12,600), 522 (3540), 548 (1635), 596 (4050), 620 (4440), 651 (69,100). Extending reaction times in attempts to raise the yield of *cis*-chlorin inevitably resulted in bleaching of the reaction mixture with accompanying formation of octaethylporphyrinogen.[39]

Oxidation of *trans*-Octaethylchlorin. Racemic Dimethylsuccinic Acid. To a solution of 296 mg (0.55 mmole) of *trans*-octaethylchlorin in a mixture of 200 ml of 60% sulfuric acid and 120 ml of 85% phosphoric acid was added a solution of 625 mg of chromium trioxide in 10 ml of water. The reaction mixture was stirred at 0° for 3.5 hr after which time it was diluted with 1 l. of ice water and extracted with five 250-ml portions of ether. The combined ether extracts were dried and evaporated. The dark residue was percolated in ether solution through a small column of silica gel to afford on evaporation 183 mg of a brown oil. Chromatography of this oil on silica gel followed by sublimation and preparative thin layer chromatography[40] of the material eluted with 5% ether in chloroform afforded 57 mg (22% yield) of diethylmaleimide, and 23 mg of a solid that was heated overnight at 100° with 2 ml of 80% sulfuric acid. The acid mixture was diluted and continuously extracted with ether to afford 6.5 mg of crystals, mp 112–113.5°. Repeated sublimation and recrystallization afforded approximately 1 mg of *dl*-α,α'-diethylsuccinic acid, mp 128–130° (lit.[29] mp 131–133°), mixture melting point with an authentic sample[29] of mp 130–131.5°, 130.5–132.0°. The infrared spectra of the two samples were identical and clearly distinct from that of *meso*-diethylsuccinic acid.[29] Subjecting a sample of *meso*-diethylsuccinic acid to the above set of conditions did not isomerize it.

Iron(III) Octaethylchlorin Chloride. A mixture of 300 mg (0.56 mmole) of *trans*-octaethylchlorin, 1.0 g (5 mg formula weight) of ferrous chloride tetrahydrate, and 1.4 g (17 mg formula weight) of sodium acetate in 35 ml of glacial acetic acid was heated under reflux with stirring under nitrogen for 5 min. Solvent was removed *in vacuo* from the cooled reaction mixture and the residue was slurried with water and filtered to afford 337 mg of the iron(III) chlorin. It should be recrystallized from hexane–chloroform: $\lambda_{\max}^{C_6H_6}$ 376 (ϵ 89,000), 471 (8060), 510 sh (5580), 559 (5960), 603 (24,200), 751 (2860).[41]

Anal. Calcd for $C_{36}H_{46}N_4FeCl$: C, 69.06; H, 7.41; N, 8.95; Fe, 8.92; Cl, 5.66. Found: C, 68.80; H, 7.18; N, 9.14; Fe, 9.12; Cl, 5.83.

Hydrogen Exchange of Iron(III) Octaethylchlorin. To a solution of 0.48 g (0.021 mg-atom) of sodium in 15 ml of isoamyl alcohol-O-d_1 (98% OD by nmr) in a glass tube was added 137 mg (0.212 mmole) of iron(II) chlorin prepared as above. The mixture was freeze–thaw degassed (10^{-5} mm), sealed, and heated at 135° for 1 hr. The cooled tube was opened and its contents were poured into water. The aqueous mixture was extracted with benzene and the combined benzene extracts were washed with concentrated hydrochloric acid and water and evaporated. The residue was dissolved in 50 ml of acetic acid, 5 ml of a saturated solution of ferrous sulfate in hydrochloric acid was added, and the mixture was stirred at room temperature for 10 min and poured into 100 ml of saturated aqueous sodium acetate. The mixture was extracted with benzene and the combined benzene extracts were extracted with 85% (w/w) phosphoric acid until the extracts were colorless. The benzene layer was washed with water and evaporated to afford 51 mg (37% yield) of iron(III) octaethylporphyrin, identified by its uv-visible spectrum with that of an authentic specimen prepared as above. The combined phosphoric acid extracts were diluted with an equal volume of water (to *ca.* 50% w/w concentration) and extracted with benzene. The benzene extracts were washed with water and evaporated, and the residue was crystallized from chloroform/methanol to afford 27 mg (24% yield) of *trans*-octaethylchlorin. Its identity was established by its nmr which showed that the signal at δ 4.5 (C*H*CH$_2$CH$_3$) corresponded in area to 0.24 H (88% deuteration at this position). Its mass spectrum (determined at 12 V nominal on an A.E.I. MS-902, using a direct inlet probe at 100°) indicated the following isotope composition:[43] 3.5% d_0, 16.2% d_1, 63.5% d_2, 16.1% d_3, 0% d_4, 0.7% d_5.

Octaethyl *cis*-Bacteriochlorin. In a 50-ml three-necked round-bottomed flask fitted with a condenser and magnetic stirrer were placed under nitrogen 100 mg (0.16 mmole) of iron(III) octaethylporphyrin chloride and 650 mg (28.2 mg-atoms) of sodium in 20 ml of isoamyl alcohol. The mixture was refluxed with stirring for 1.5 hr and cooled to 5°. Methanol, 1 ml, was added followed by 5 ml of a saturated hydrochloric acid solution of ferrous sulfate. The mixture was stirred for 0.5 hr and the blue solution was partitioned between 200 ml of benzene and 20 ml of aqueous ammonia. The benzene solution was washed with water, dried over anhydrous sodium sulfate, and evaporated.[44] Recrystallization of the residue

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[38] H. W. Whitlock and R. Hanauer, *J. Org. Chem.*, 33, 2169 (1968).

[39] R. Hanauer, unreported work.

[40] Thin and thick layer chromatography was carried out on a silica gel PF$_{254}$ (Brinckmann) with chloroform as eluent.

[41] The spectrum of this substance by Eisner[42] is different from this. However, washing benzene solutions of the iron chlorin prepared as above with aqueous ammonia produces a material having spectra similar to that reported by Eisner.

[42] U. Eisner, *J. Chem. Soc.*, 3461 (1957).

[43] From the raw data (*m/e*, relative intensity): 536, 5; 537, 25; 538, 100; 539, 62; 540, 17; 541, 3. The values of $(P + 1)/P = 41.2\%$ and $(P + 2)/P = 9.0\%$ were calculated *via* the formulas in "Mass and Abundance Tables for Use in Mass Spectroscopy," J. H. Beynon and A. E. Williams, Ed., Elsevier Publishing Co., New York, N. Y., 1963.

from methanol afforded 72 mg (84%) of octaethyl *cis*-bacteriochlorin, mp 130–133° (lit.[42] mp 138°). Its uv-visible spectrum agreed with that reported.

Diimide Reduction of *meso*-Tetraphenylporphyrin. A mixture of 2 g (3.2 mmoles) of *meso*-tetraphenylporphyrin, 1.2 g of *p*-toluenesulfonylhydrazine, 4.0 g of anhydrous potassium carbonate, and 150 ml of dry pyridine was heated with stirring at 105° under nitrogen. After 2 hr, a solution of 1.29 g of toluenesulfonylhydrazine in 4 ml of pyridine was added. This was repeated at the end of 4 hr. After heating a total of 6.5 hr the reaction mixture was added to a mixture of 1 l. of benzene and 500 ml of water and the mixture was digested for 1 hr on a steam bath, and cooled, and the separated benzene layer was washed with cold 3 *N* hydrochloric acid, water, and saturated sodium bicarbonate solution. Analysis of the visible spectrum of the benzene solution showed it to be a mixture of *meso*-tetraphenylchlorin, 62%, and *meso*-tetraphenylbacteriochlorin, 38%. To the benzene solution was added in one portion 400 mg (1.64 mmoles) of tetrachloro-*o*-quinone and the mixture was stirred at room temperature for 1 hr. The benzene to solution was then washed with 5% aqueous sodium bisulfite solution, 5% aqueous sodium hydroxide solution, 500 ml of 68% (w/w) phosphoric acid (to remove residual tetraphenylporphyrin), water, and saturated aqueous sodium bicarbonate solution, and was dried over anhydrous sodium sulfate. Removal of solvent gave 1.8 g of a residue that was recrystallized from 200 ml of benzene to afford 1.45 g (72% yield) of tetraphenylchlorin: $\lambda_{\max}^{C_6H_6}$ 419 mμ (ε 190,000), 517 (16,000), 542 (12,000), 598 (6100), 652 (42,000) [lit.[45,46] $\lambda_{\max}$ 419 (ε 190,000), 517 (16,000), 542 (11,000), 598 (6000), 652 (42,000)]; nmr ($CDCl_3$) δ 1.3 (broad, 2 H, NH), 4.10 (singlet, 4 H, $-CH_2CH_2-$), 7.6–8.5 (multiplet, 26 H). This latter band could be resolved into a singlet, area 2 H at δ 8.34 and AB quartet of area 4 H (δ_A 8.10, δ_B 8.49, $J_{AB} = 4.5$ Hz) assigned to the chlorin ring protons.

***meso*-Tetraphenylbacteriochlorin.** A mixture of 1 g (1.63 mmoles) of tetraphenylporphyrin, 0.60 g (3.2 mmoles) of toluensulfonylhydrazine, 2.0 g of anhydrous potassium carbonate, and 75 ml of dry pyridine were heated at 100° with stirring under nitrogen for 12 hr. Every 1.5 hr 0.6 g of toluenesulfonylhydrazine was added. The cooled reaction mixture was diluted with 1 l. of benzene and 500 ml of water and digested on a steam bath for 1 hr. The cooled benzene layer was washed with 500 ml of cold 3 *N* hydrochloric acid and was then extracted with four 500-ml portions of 82% (w/w) phosphoric acid (to remove the porphyrin and chlorin), aqueous sodium bicarbonate solution, and water, and evaporated. Recrystallization of the residue from benzene afforded 0.50 g (50% yield) of tetraphenylbacteriochlorin: $\lambda_{\max}^{C_6H_6}$ 356 (ε 130,000), 378 (160,000), 520 (60,000), 742 (130,000) [lit.[47] $\lambda_{\max}$ 742 (120,000), 520 (60,000)]; nmr ($CDCl_3$) δ 1.3 (singlet, NH, 2 H), 3.92 (singlet, 8 H, $-CH_2CH_2-$), 7.52 (multiplet, ArH, 12 H), 7.85 (doublet, $\Delta v = 2$ Hz, 4 H, bacteriochlorin HC=CH).

Anal. Calcd for $CH_4H_{38}N_4$: C, 85.39; H, 5.55; N, 8.92. Found: C, 85.06; H, 5.87; N, 8.92.

***meso*-Tetraphenylisobacteriochlorin.** Zinc *meso*-tetraphenylchlorin was prepared by refluxing with stirring under nitrogen a mixture of 1 g of the chlorin and 1 g of zinc acetate dihydrate in 75 ml of pyridine for 15 min. To the reaction flask was then added 6 g of potassium carbonate and 0.3 g of toluenesulfonylhydrazine. Heating and stirring was continued for 26 hr, 0.3 g of toluenesulfonylhydrazine being added every hour (the reaction mixture was allowed to stand under nitrogen at room temperature for 8 hr after the first 12 hr of heating). The cooled reaction mixture was partitioned between 200 ml of chloroform and 200 ml of water, and the chloroform layer was washed first with cold 3 *N* hydrochloric acid and then with concentrated hydrochloric acid until the acid washes were almost colorless (three 200-ml washes). The chloroform layer was then washed with a 200-ml portion of aqueous sodium bicarbonate solution and then with 500 ml of 85% (w/w) phosphoric acid. The deeply colored acid layer was separated and the faintly colored chloroform layer was discarded. The cooled phosphoric acid layer was washed with chloroform, diluted with water to 50% (w/w) concentration, and extracted with chloroform, and the colored chloroform extracts were washed, dried, and concentrated to a volume of 30 ml. Methanol, 10 ml, was added to the hot chloroform and the solution was cooled to −10° for 2 hr. Filtration afforded 575 mg (57% yield) of dark red needles: $\lambda_{\max}^{C_6H_6}$ 390 mμ (ε 100,000), 408 (sh, 79,000), 516 (10,000), 552 (19,000), 594 (28,000) [lit.[39] $\lambda_{\max}^{C_6H_6}$ 594 (ε 29,000), 552 (22,000), 516 (12,000)].

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(44) At this stage the material was contaminated by 5% octaethylchlorin and 2% octaethylbacteriochlorin.

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