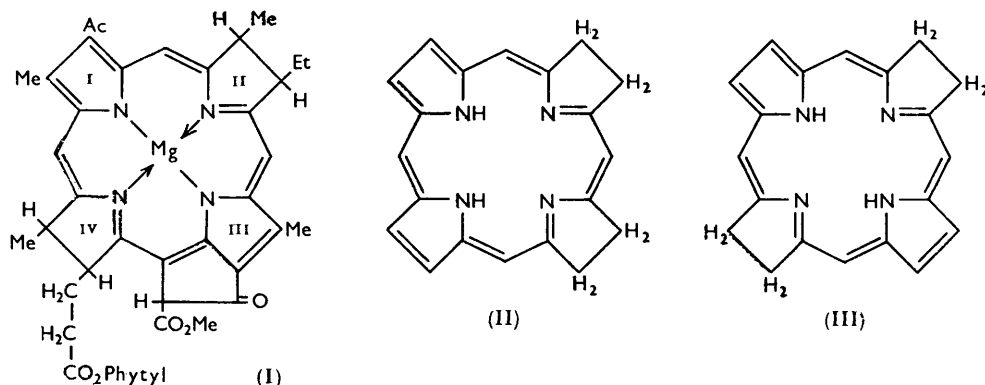


690. *Some Novel Hydroporphyrins.*

By ULLI EISNER.

The two isomeric octaethyltetrahydroporphyrins have been prepared by the reduction of octaethylporphyrin with sodium and *isopentyl* alcohol. Reduction of the corresponding chlorin afforded, in addition to the tetrahydro-derivatives, the octaethylhexa- and an octaethylocta-hydroporphyrin. Light-absorption properties are discussed, and quantitative stepwise dehydrogenation of the hydro-pigments has been studied.

COMPARATIVELY little is known about porphyrins at a higher hydrogenation level than the dihydro-derivatives or chlorins. Bacteriochlorophyll (I), the naturally occurring dihydrochlorophyll derivative, is the only compound which has been extensively studied. Its constitution was elucidated by Fischer¹ and by Mittenzwei² and its formulation as a tetrahydroporphyrin is now generally accepted. The position of the two pairs of "extra" hydrogen atoms has never been established unequivocally. Fischer¹ assigned them to the pyrrole nuclei II and IV. Seely,³ however, suggested that the alternative I-IV or III-IV structures were not excluded by the chemical evidence. Recent molecular-orbital calculations⁴ have shown that the two isomeric tetrahydroporphyrins, the "adjacent"



(II) and "opposite" (III) types,* would differ considerably in their light-absorption properties. The long-wave bands of (II) and (III) have been predicted to lie below and above that of the corresponding chlorin respectively. These calculations place Fischer's structure of bacteriochlorophyll on a sound basis.

Even less is known about synthetic hydroporphyrins. Dorough and Miller⁵ obtained

* Throughout this work the "adjacent" and "opposite" types will be referred to as *a*- and *b*-tetrahydroporphyrins respectively.

¹ Fischer-Orth, "Die Chemie des Pyrrols," Springer Verlag, Leipzig, 1940, II/2, p. 305.

² Mittenzwei, *Z. physiol. Chem.*, 1942, **275**, 93.

³ Seely, U.S. Atomic Energy Comm., U.C.R.L. 2417, 1953.

⁴ Barnard and Jackman, *J.*, 1956, 1172.

⁵ Dorough and Miller, *J. Amer. Chem. Soc.*, 1952, **74**, 6106.

two compounds, "α" and "β," in very low yield by the catalytic hydrogenation of mesotetraphenylchlorin. Compound "α" was tentatively formulated as a tetrahydroporphyrin. The sole evidence was the similarity of its spectrum to that of bacteriochlorophyll and its photo-oxidation to the chlorin with 1:2-naphthaquinone. No structure was proposed for the "β" compound although photo-oxidation to the chlorin with 1:2-naphthaquinone was observed. Seely *et al.*^{3,6} reduced zinc mesotetraphenylporphin photochemically with benzoin and obtained, apart from some of the corresponding zinc chlorin, a new compound to which they assigned a tetrahydro-structure on the basis of its dehydrogenation to the zinc porphin or chlorin. It was subsequently shown to be identical with Dorrough and Miller's "β" compound. Under certain conditions a second pigment was obtained which could be converted into the tetrahydro-compound and was therefore formulated as a hexahydro-derivative.

The reduction, by sodium and higher alcohols, of the iron complex of ætioporphyrin was first examined by Fischer *et al.*⁷ who claimed to have obtained the corresponding chlorin

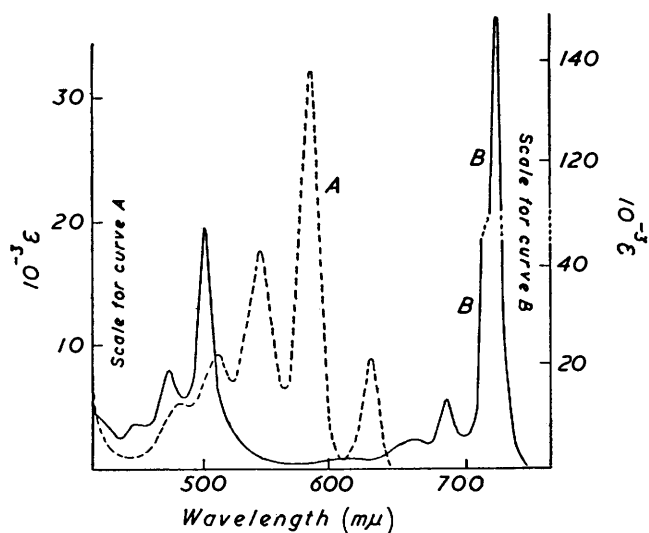


FIG. 1. A, *a*-Octaethyltetrahydroporphin. B, *b*-Octaethyltetrahydroporphin.

and a red "perhydro"-derivative which could readily be converted into the chlorin. These results were confirmed by Corwin and his co-workers⁸ who isolated the pure "perhydro"-derivative. This was formulated as a tetrahydroætioporphyrin on the basis of its quantitative dehydrogenation to ætiochlorin by potassium molybdicyanide. Neither analytical nor light absorption data were recorded.

It was decided to re-investigate the above reduction and to establish, if possible, the nature of the products, starting from the readily available octaethylporphin.⁹ Reduction of the iron complex with sodium in boiling *isopentyl* alcohol (cf. ref. 9) afforded a complex mixture of pigments which were separated by chromatography on magnesium oxide. The bands, in order of elution, were: a yellow band containing traces of *b*-octaethyltetrahydroporphin (IV); a pink band of *a*-octaethyltetrahydroporphin (V); a green band of octaethylchlorin (VI); and a red band of unchanged starting material. Traces of three other pigments were also observed: a red and a green pigment (both unidentified) whose light

⁶ Seely and Calvin, *J. Chem. Phys.*, 1955, **23**, 1068.

⁷ Fischer, Platz, Helberger, and Niemer, *Annalen*, 1930, **479**, 49.

⁸ Schlesinger, Corwin, and Sargent, *J. Amer. Chem. Soc.*, 1950, **72**, 2867.

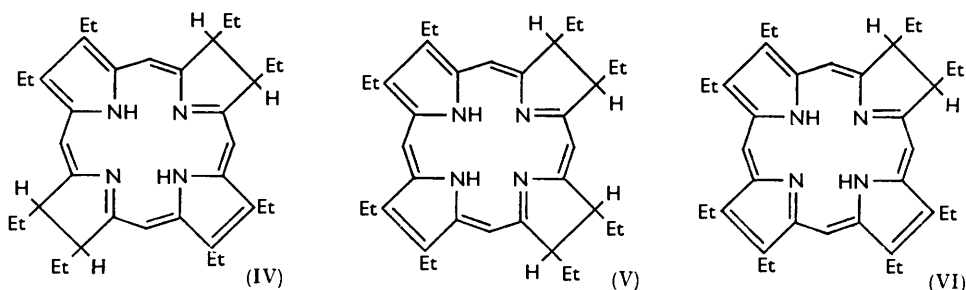
⁹ Eisner, Lichtarowicz, and Linstead, *J.*, 1957, 733.

absorptions were very similar to those of the *a*-tetrahydroporphin (V) and the chlorin (VI) respectively; and a purple material which is discussed below.

a-Octaethyltetrahydroporphin.—This pigment (V), together with the chlorin (VI) which was formed in about 30% yield, constituted the bulk of the product. It was extremely soluble in all organic solvents and crystallised only with difficulty and considerable loss. Its solutions are magenta with an intense characteristic orange fluorescence. They are stable in the absence of light. It has a typical four-banded spectrum of porphyrin type and a Soret band (see Table 1 and Fig. 1). Fischer and Helberger¹⁰ recorded light-absorption maxima at 583 and 543 $m\mu$ for the "perhydro"-derivative of a porphinmonocarboxylic acid, in good agreement with the spectral properties of our material. Its spectrum is also in good agreement with the predicted light-absorption⁴ of a tetrahydroporphin in which the two pairs of "extra" hydrogen atoms are placed on adjacent pyrrole nuclei, and with Dorough and Miller's " β " compound.

This pigment (V) forms a blue solution in the presence of mineral acids. It is not stable under these conditions but is converted into the corresponding chlorin (VI) almost instantaneously. Treatment with methanolic cupric acetate afforded a purple copper derivative, the light-absorption maxima of which are recorded in Table 1. In presence of ammonia this derivative is partially dehydrogenated to copper octaethylchlorin.

The structure of the *a*-octaethyltetrahydroporphin is confirmed by spectroscopic and analytical data, and by the quantitative dehydrogenation (see below) of the metal-free pigment and of its copper complex to the corresponding chlorin derivatives.



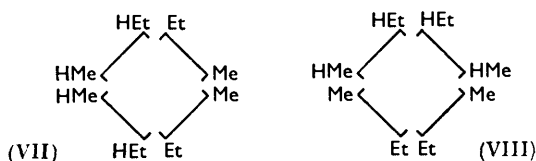
b-Octaethyltetrahydroporphin.—The yellow fraction from the chromatogram showed an intense peak at 720 $m\mu$ indicating the presence of a pigment of "bacterio"-type. It was not pure, however, and when it was re-chromatographed on magnesium oxide in hexane traces of a yellow material of unknown constitution were separated from it. A purified *b*-octaethyltetrahydroporphin (IV) concentrate was obtained which was used in subsequent experiments. It exhibited a faint orange fluorescence which may have been due to traces of impurities. The yield of the pigment was less than 1% and no attempts were made to isolate it in the solid state. Its light-absorption properties are given in Table 1 and in Fig. 1. They bear a striking resemblance to those of bacteriochlorin e_6 ;¹¹ the spectrum of the latter compound shows a bathochromic shift of about 20–30 $m\mu$, presumably due to the presence of a nuclear acetyl group in the 2-position. This fact, together with the quantitative dehydrogenation to octaethylchlorin (see below), are compelling evidence for the structure proposed.

In order to determine whether the reaction was general, the iron complexes of octa-methyl- and α -porphin II were reduced under the same conditions. From the former, poor yields were obtained, chiefly owing to the low solubility of the pigment. *a*-Tetrahydro-octamethylporphin was, however, identified spectroscopically and by its characteristic orange fluorescence. In the case of the α -porphyrin II it was possible to separate

¹⁰ Fischer and Helberger, *Annalen*, 1929, **471**, 293.

¹¹ Golden and Linstead, unpublished results.

the products chromatographically. *Ætiochlorin* II and *a*-tetrahydro α etioporphen II were isolated in good yield and identified spectroscopically. Traces of the *b*-tetrahydro-derivative were also present. The behaviour of the pigments on chromatography differed somewhat from those of the octaethyl series: the order of elution was the same but the pigments were adsorbed more strongly. It is interesting that the *a*-tetrahydro α etioporphen II separated into two zones on chromatography. They were spectroscopically



identical and furnished the same chlorin on dehydrogenation. Two positional isomers (VII) and (VIII) of *a*-tetrahydro α etioporphen are theoretically possible and the two fractions may correspond to these.

During the preparation of unsubstituted chlorin¹² a red pigment with an orange fluorescence was obtained which was not further investigated at the time. In the light of the present results it seemed likely that it was *a*-tetrahydroporphen. In attempts to isolate it in a pure state, chromatography on magnesium oxide proved very slow and the pigment tended to be dehydrogenated on prolonged contact with the adsorbent. By developing the column with benzene for a short time and separating the bands mechanically the pigment was obtained pure. Its light absorption is included in Table 1: it corresponds to that of *a*-octaethyltetrahydroporphen (V) but the whole spectrum, with the exception of the long-wavelength band, exhibits a hypsochromic shift of about 5 $m\mu$ with respect to the latter compound. This is probably due to the lack of alkyl substituents since chlorin shows a similar shift with respect to the octaethyl derivative. The 637.5 $m\mu$ band of *a*-tetrahydroporphen, which is apparently chromatographically pure, is in the same position as the main peak of chlorin and it is difficult to determine whether it is genuine or due to traces of chlorin formed during the isolation of the pigment. Reaction of *a*-tetrahydroporphen with excess of tetrachloro-1:2-benzoquinone was very slow in the cold but, on warming, a mixture of chlorin and porphen was produced. When treated with methanolic cupric acetate, *a*-tetrahydroporphen afforded a copper derivative with absorption maxima at 547, 589, and 602.5 $m\mu$. The last peak is presumably due to copper chlorin which may have been formed during the preparation of the copper derivative or from chlorin originally present in the *a*-tetrahydroporphen. Treatment of the above mixture of copper derivatives with tetrachloro-1:2-benzoquinone afforded copper chlorin which was identified spectroscopically.

Reduction of octaethylchlorin (VI) was next investigated. The first stage involved the preparation of the unknown iron complex of the chlorin (VI). Treatment of the pigment (VI) with ferric chloride and sodium acetate in boiling benzene, dioxan, pyridine, or acetic acid afforded only unchanged starting material, but ferrous chloride and sodium acetate in boiling acetic acid in an inert atmosphere afforded the desired product. It could not readily be crystallised and was used without purification. It and the corresponding iron octaethylporphen complex have broad and ill-defined maxima of low intensity (see Table 1) in contrast to the corresponding metal-free and copper derivatives.

Reduction of the iron octaethylchlorin in the usual manner and subsequent chromatography afforded unchanged starting material, *a*-octaethyltetrahydroporphen, traces (<1%) of the *b*-tetrahydro-derivative, and two new substances, namely octaethylhexa-(IX) and octaethylocta-hydroporphen (X).

Octaethylhexahydroporphen.—This material, a purple pigment, was separated from the

¹² Eisner and Linstead, *J.*, 1955, 3742.

a-tetrahydro-derivative (formed in roughly equal amount) on deactivated alumina but not on magnesium oxide. The purple pigment produced in the reduction of octaethylporphin was shown to be identical with octaethylhexahydroporphin. The pure hexahydro-derivative does not fluoresce although its solutions generally show a faint orange fluorescence due, presumably, to traces of the *a*-tetrahydro-derivative. It is very soluble in all organic solvents except methanol and acetone, and attempts at crystallisation failed. Its solutions are stable in the absence of light. Its absorption bands (Table 1; Fig. 2) are broad and

FIG. 2. A, Octaethylhexahydroporphin.
B, Octaethyloctahydroporphin.

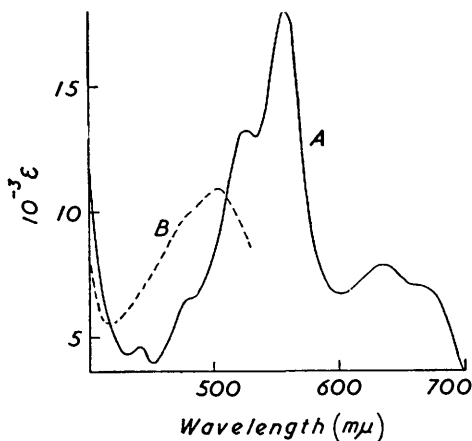


TABLE I. Light absorptions (in benzene).

λ_{\max} (m μ)	ϵ	λ_{\max} (m μ)	ϵ	λ_{\max} (m μ)	ϵ	λ_{\max} (m μ)	ϵ
<i>a</i> -Octaethyltetrahydroporphin				Bacteriochlorin e_8 ¹¹			
370 ^a	103,500	511	9,300	387 ^a	112,000	631	3,700
379.5 ^a	92,700	546	17,600	457	3,500	691	7,200
401	52,300	586	32,100	493	5,000	754	93,300
482	5,300	634	9,000	525	27,600		
Cu <i>a</i> -octaethyltetrahydroporphin				Octaethylhexahydroporphin			
391 ^a	208,000	550.5	12,800	355—357 ^c	43,600	527 ^c	13,100
532 ^b	8,800	594	60,000	436—440	4,600	557.5 ^c	18,100
				480 ^b	6,500	636	7,800
α -Tetrahydroporphin				Octaethyloctahydroporphin			
378 ^a	1.927 ^e	583	0.569	339—349 ^a	38,400	500—505 ^d	10,900
500	0.194	637.5	0.285				
541	0.326						
<i>b</i> -Octaethyltetrahydroporphin				Fe octaethylchlorin			
374 ^a	180,700	604	2,500	380 ^a	98,400	604	12,400
434	9,200	661.5	6,200	525—529	7,600	655—658	18,200
463	20,300	685	14,100				
491	49,300	721	150,000				
				Fe octaethylporphin			
				375 ^a	90,000	534.5	10,500
				395—398 ^b	71,800	632.5	5,500
				517	9,200		
				Cu octaethylporphin			
				399 ^a	364,000	562.5	30,600
				525.5	14,200		

^a Soret band. ^b Infection. ^c λ_{\max} 519—522 m μ and 552—554 m μ in cyclohexane; 518—520 m μ and 552 m μ in *n*-hexane. ^d λ_{\max} at 491 m μ in light petroleum. ^e Arbitrary *E* values.

ill-defined, particularly in benzene, with relatively low intensities, and are subject to considerable solvent influence. The whole spectrum in benzene is bathochromically shifted by about 5 m μ from that observed in *n*-hexane or cyclohexane. Calvin and Seely⁶ pointed out that although the conjugation of the macrocyclic system in a hexahydroporphin is formally interrupted, several resonance forms may be drawn; this is not possible

in the case of an octahydroporphin. Consequently we should expect the spectrum of the former, but not of the latter, to resemble that of a porphyrin, which in fact it does.

Treatment of a boiling benzene solution of octaethylhexahydroporphin with methanolic cupric acetate afforded copper *a*-octaethyltetrahydroporphin quantitatively. When a warm solution of octaethylhexahydroporphin was treated with methanolic zinc acetate, a colour change to bluish-green took place with the appearance of a broad absorption peak at 652 $m\mu$. Almost instantaneously, however, this began to disappear and its place was taken by a new peak at 598 $m\mu$. The latter is due to the *a*-tetrahydro-derivative, as shown by its occurrence with an authentic specimen. The qualitative absorption data of the zinc complexes of octaethyl- and *meso*tetraphenyl-porphin and their hydro-derivatives are given in Table 2.

Octaethyloctahydroporphin.—The first fraction in the chromatographic separation of the reduction product was a pink pigment with a single absorption peak at 491 $m\mu$ (in light petroleum). It was not very stable and could not be obtained free from traces of the *a*- and *b*-tetrahydroporphins. This was not due to imperfect separation as the bands were well-defined and completely separated from each other. On spontaneous evaporation of the concentrated solution in light petroleum at 0° and in the absence of light, the corresponding di-, tetra-, and hexahydro-derivatives, separable by chromatography, were formed. The spectrum of the purified concentrate of octaethyloctahydroporphin (which still contained traces of the two tetrahydro-derivatives) is given in Table I and Fig. 2. The single peak in the visible region is in agreement with the interrupted conjugation of structure (X). The solvent effect is even more pronounced than for the hexahydro-derivative. The Soret band shows a hypsochromic shift with respect to the other hydro-derivatives; the wavelengths of the Soret bands in the series decrease in the order porphin > chlorin > *b*-tetrahydro > *a*-tetrahydro > hexahydro > octahydro. The number of "extra" hydrogen atoms is confirmed by quantitative dehydrogenation (see below). Their position cannot at present be determined. Hydrogen may be added to the 2 : 3-positions of a pyrrole nucleus as in (Xa) or to the 2 : 5-positions as in (Xb). The addition of hydrogen to the *meso*-positions of the porphyrin system is also a possibility.

TABLE 2. Absorption maxima ($m\mu$) of zinc complexes (in benzene).

Series	Porphin	Chlorin	<i>a</i> -Tetrahydro	Hexahydro
Octaethyl	536, 573	617	598, 553	652
<i>meso</i> Tetraphenyl	549, 587	618	602	642

Determination of Hydrogenation Level by Quantitative Dehydrogenation.—An excess of tetrachloro-1 : 2-benzoquinone converts *a*-octaethyltetrahydroporphin in benzene into the chlorin. When carried out quantitatively (cf. Eisner and Linstead¹³), the reaction was relatively slow at room temperature, being complete only after about 70 hr. The chlorin (VI) was not dehydrogenated under these conditions. When 1 mol. of freshly sublimed quinone in carefully dried benzene was used a 90% yield of chlorin was obtained. With 0.5 mol. of quinone the yield was about 50%.

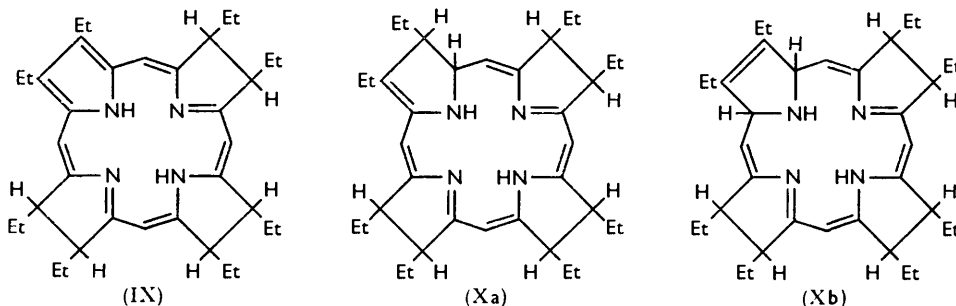
The copper derivative of *a*-octaethyltetrahydroporphin was dehydrogenated almost instantaneously to the copper chlorin complex under the same conditions and the yield of the latter was quantitative with 1 mol. of quinone. When 2 mols. of quinone were used, slow dehydrogenation to the copper porphin took place. The yield of the latter was 57% after 71 hr. and reached a limiting value of 76% after 428 hr. The light absorption of the known copper octaethylporphin, which was prepared by standard methods, is given in Table I.

b-Octaethyltetrahydroporphin with a slight excess of the quinone afforded octaethylchlorin. The concentration of the pigment, and hence its ϵ values, was calculated from the amount of chlorin produced. *b*-Octaethyltetrahydroporphin with 1 mol. of quinone

¹³ Eisner and Linstead, *J.*, 1955, 3749.

afforded 78.2% of chlorin after 70 min., and 96.6% after 18 hr., whereas the figures for the *a*-tetrahydro-compound were 55.3% after 3 hr. and 67.4% after 20 hr.

It was not possible to obtain quantitative data for the dehydrogenation of octaethylhexahydroporphin. It could be shown qualitatively that a deficiency of the quinone gave only *a*-octaethyltetrahydroporphin, with traces of the chlorin. The main absorption peaks



of the hexahydro- and *a*-tetrahydro-pigments overlap in such a way that it is very difficult to calculate their concentrations in presence of each other. Further, dehydrogenation was very slow and excess of the quinone did not afford the chlorin quantitatively. The action of 2 : 3-dichloro-5 : 6-dicyanobenzoquinone was next investigated. With a slight excess, chlorin was produced quantitatively and the concentration and ϵ values of octaethylhexahydroporphin could be calculated. Dehydrogenation with this quinone was instantaneous and the addition of 2 mols. afforded the chlorin (VI) in 100% yield. An excess (3 mols.) gave about 80% octaethylporphyrin whereas a deficiency (0.5 and 1 mol.) afforded mixtures of the chlorin (VI), the *a*-tetrahydroporphin (V), and, presumably, unchanged starting material. No *b*-octaethyl-tetrahydroporphin could be detected at any stage. The purity of the quinone used was determined by dehydrogenation of a solution of octaethylchlorin of known concentration under standard conditions.

The dehydrogenation of octaethyloctahydroporphin with the dichlorodicyanoquinone was carried out in the same way as for the hexahydro-derivative and results were comparable : 3 mols. of quinone afforded the chlorin (VI) quantitatively; 4 mols. afforded octaethylporphyrin (80%), and 1 and 2 mols. produced a complex mixture in which octaethylchlorin and the *a*-tetrahydro-derivative were identified.

EXPERIMENTAL

Unless otherwise stated, light petroleum had b. p. 60—80°.

Reduction of Octaethylporphyrin.—The procedure has been described previously.⁹ Chromatography of the product on heavy magnesium oxide with light petroleum eluted a yellow band of crude *b*-octaethyltetrahydroporphin followed by a pink band of *a*-octaethyltetrahydroporphin. The first runnings of the latter band contained traces of octaethylhexahydroporphin. Benzene-light petroleum (1 : 1) eluted octaethylchlorin (32.5%) preceded by a pink fraction which was spectroscopically identical with *a*-octaethyltetrahydroporphin. The pink fraction could not be obtained free from the chlorin. Ether-chloroform (1 : 1) eluted a green band which was spectroscopically similar to octaethylchlorin. Chloroform removed some unchanged starting material.

a-Octaethyltetrahydroporphin.—The pigment was dissolved in dry methanol and the solution was concentrated to ~1 c.c. in a current of nitrogen. On cooling to -80° or storage at 0° deep red needles of *a*-octaethyltetrahydroporphin, m. p. 138°, separated (Found : C, 80.3, 80.5; H, 9.2, 9.5; N, 9.8, 9.7. $C_{38}H_{50}N_4$ requires C, 80.25; H, 9.35; N, 10.4%).

Copper a-Octaethyltetrahydroporphin.—A solution of *a*-octaethyltetrahydroporphin in boiling

benzene was treated with a slight excess of cupric acetate in methanol in a current of nitrogen. The purple solution was cooled, washed with water, and concentrated under reduced pressure, and its light absorption was determined immediately. When the solution was washed with dilute ammonia solution instead of water, a mixture of copper *a*-octaethyltetrahydroporphin and copper octaethylchlorin was produced.

b-Octaethyltetrahydroporphin.—The crude pigment was chromatographed in *n*-hexane on heavy magnesium oxide. The following fractions were collected: (i) a pale pink solution with a faint greenish fluorescence containing traces of pigment (λ_{max} , 380, 509, 727.5 $\text{m}\mu$); (ii) a yellow solution with a faint orange fluorescence containing traces of pigment (λ_{max} , 379.5, 435, 470—475, 501, 659.5, 680, 721 $\text{m}\mu$); (iii) yellowish-green solution with a weak orange fluorescence containing the bulk of the *b*-octaethyltetrahydroporphin. This last fraction was used in subsequent experiments.

Reduction of Ætioporphyrin II.—The reduction was carried out as before. Chromatography of the product on heavy magnesium oxide afforded the following fractions: (1) with light petroleum, a yellow band of *b*-tetrahydroætioporphin; (2, 3) with light petroleum–benzene (10–40%), pink bands of *a*-tetrahydroætioporphin (spectroscopically identical with *a*-octaethyltetrahydroporphin); (4) with benzene, first a pink band similar to (2, 3), then a green band of ætiochlorin; (5) with ether–chloroform a green band similar to the preceding one; (6) with chloroform a red band of ætioporphyrin. On treatment with tetrachloro-1 : 2-benzoquinone bands 2, 3 afforded ætiochlorin.

Purification of a-Tetrahydroporphin.—The crude pigment, whose preliminary purification has been described,¹² was extracted with boiling methanol, and the insoluble residue was chromatographed in benzene on heavy magnesium oxide. Elution with benzene did not completely separate the chlorin and the tetrahydroporphin. The fraction containing the bulk of the red *a*-tetrahydroporphin was evaporated to dryness under reduced pressure, dissolved in benzene, and re-chromatographed on heavy magnesium oxide. Elution with benzene was continued for 3 hr., whereby the bands of chlorin and *a*-tetrahydroporphin were separated. The column was then drained and extruded, the *a*-tetrahydroporphin fraction separated, suspended in cold chloroform, and filtered, and the filtrate evaporated to dryness under reduced pressure. The residue was dissolved in benzene and the light absorption was determined. A warm benzene solution of *a*-tetrahydroporphin with excess of tetrachloro-1 : 2-benzoquinone gave a mixture of chlorin and porphin.

Reduction of Octaethylchlorin.—Ferrous chloride (200 mg.) and anhydrous sodium acetate (400 mg.) in boiling acetic acid (8 c.c.) were treated with octaethylchlorin (90 mg.) in acetic acid (2 c.c.), boiled under nitrogen for 5 min., then cooled, and benzene (150 c.c.) was added. The solution was washed with water, ammonia solution, and water, and evaporated to dryness under reduced pressure. Attempted crystallisation from light petroleum–methanol failed. The crude iron complex was treated in boiling *isopentyl* alcohol (15 c.c.) with sodium (1.6 g.) in a current of nitrogen. The product, which was worked up in the usual manner, was chromatographed on heavy magnesium oxide. Elution with light petroleum removed successive bands of (pink) octaethyloctahydroporphin, (yellow) *b*-octaethyltetrahydroporphin, and (purple and then pink) octaethyl-hexa- and -(*a*)tetra-hydroporphin. Benzene finally eluted octaethylchlorin (green).

Octaethylhexahydroporphin. The material obtained from the purple fraction was chromatographed in *n*-hexane on alumina (Grade IV; deactivated with methanol). Elution with *n*-hexane gave good separation of the *a*-tetrahydro- (eluted first) and the hexahydro-pigment. The latter formed deep purple solutions in organic solvents. It was sparingly soluble in acetone and insoluble in methanol but did not crystallise. Its solution in boiling benzene with methanolic cupric acetate gave copper *a*-octaethyltetrahydroporphin quantitatively. Zinc octaethylhexahydroporphin was formed from a hot benzene solution of the metal-free pigment by methanolic zinc acetate; it reverted almost immediately to the corresponding *a*-tetrahydro-derivative.

Octaethyloctahydroporphin. A solution of the pigment obtained in the first pink fraction was kept in the dark at 0° for several weeks, then rechromatographed on magnesium oxide with *n*-hexane as eluant; the first fraction consisted of octaethyloctahydroporphin containing traces of the two tetrahydro-derivatives. Octaethylhexahydroporphin and octaethylchlorin were eluted separately from the column and were identified spectroscopically.

Copper Octaethylporphin.—Octaethylporphin was extracted from a thimble into boiling

acetic acid containing excess of cupric acetate. The extract was cooled, and the copper derivative filtered off and chromatographed on alumina with benzene as eluant. After two crystallisations from benzene, copper octaethylporphin was obtained in red needles (Found : C, 72.2; H, 7.7; Cu, 10.4. Calc. for $C_{36}H_{44}N_4Cu$: C, 72.5; H, 7.4; Cu, 10.7%).

Quantitative Dehydrogenation.—The method has been described.¹³ Experiments were carried out in benzene in the dark in 5 c.c. volumetric flasks. Spectroscopic measurements were made in 1 cm. stoppered cells. 2 : 3-Dichloro-5 : 6-dicyanobenzoquinone was standardised by allowing a benzene solution of known concentration to react with an excess of a benzene solution of octaethylchlorin of known concentration. Its purity was thus found to be 84.5%. Unless otherwise stated the yields of a pigment calculated from the intensities at a certain wavelength have not been corrected for the presence of other pigments since the spectral regions chosen were such as to minimise any interference.

Freshly sublimed tetrachloro-1 : 2-benzoquinone and benzene distilled from sodium were used. The following results were obtained :

a-Octaethyltetrahydroporphin.

Time (hr.)	Quinone (mols.)			Quinone (mols.)		
	0.5	1	2	0.5	1	2
	Chlorin formed (%)			Unchanged tetrahydro (%)		
3	32	52	83.5	67	45	15
72	49	91	94	53	10	5
116	48	90	90	53	10	5

Copper a-octaethyltetrahydroporphin.

Time (hr.)	Quinone (mols.)			2 mols. of quinone	
	0.5 mol. of quinone	0.5	1	2	Cu porphin formed (%)
	Unchanged Cu <i>a</i> -tetrahydro		Cu chlorin formed (%)		527 m μ 563 m μ
0.25	47	56 *	100	99	—
71	46	59 *	96	48	53
116	45	61 *	96.5	37	57.5
284	—	—	98	26	66
428	—	—	—	23	67

* Corr. for Cu *a*-octaethyltetrahydroporphin.

b-Octaethyltetrahydroporphin.

Time (hr.)	Quinone (mols.)			Quinone (mols.)		
	0.5	1	2	0.5	1	2
	Chlorin formed (%)			Unchanged <i>b</i> -tetrahydro (%)		
1.2	45.6	78.2	99.0	57.2	24.0	1.2
18	49.1	96.6	100	51.1	2.2	—

Octaethylhexahydroporphin. Quantitative results could not be obtained with tetrachloro-1 : 2-benzoquinone. When an insufficiency of quinone was added, *a*-octaethyltetrahydroporphin with only traces of the corresponding chlorin were produced. The reaction required 3 days for completion. Using 2 : 3-dichloro-5 : 6-dicyanobenzoquinone and making measurements immediately after mixing showed 43, 100, and 18% of chlorin formed with 1, 2, and 3 mols., respectively, of quinone : and with 3 mols. of quinone, 83.5% (532 m μ) or 79% (568 m μ) of porphin was formed.

Octaethyloctahydroporphin. The procedure was that used for the hexahydro-derivative. With 1, 2, 3, and 4 mols. of quinone the amount of chlorin formed was 25, 61, 100, and 31% respectively. With 4 mols. of quinone, 80.5% (532 m μ) or 73% (568 m μ) of porphin was formed.

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