

142. Chlorophyll and Related Compounds. Part VI.* The Synthesis of Octaethylchlorin.

By ULLI EISNER, ALEKSANDRA LICHTAROWICZ, and R. P. LINSTAD.

A five-stage synthesis of 3 : 4-diethylpyrrole has been developed. From it, octaethyl-chlorin (IX) and -porphin (X) have been prepared in good yield by way of the Mannich base (VIII). The interconversion of these pigments is described.

WE have continued our study of fully substituted porphyrins and chlorins by examining octaethylchlorin (IX). The main reasons were two: although the corresponding octamethylchlorin could be synthesised¹ the preparation of the pyrrolic intermediates was complicated and tedious; secondly, octamethylporphin had a very low solubility which made it difficult to use in reactions. It seemed reasonable to expect that the octaethyl series might be more convenient in both respects and this has proved to be true.

Our starting material for the synthesis was ethyl 4-acetyl-3-ethyl-5-methylpyrrole-2-carboxylate (II). This had previously been prepared² in four stages from dipropionylmethane, the preparation of which is itself tedious. However, we have obtained it directly by a reverse type of Knorr reaction (cf. Corwin and Quattlebaum³) of acetylacetone and ethyl 3-oxopentanoate (I) (as its 2-hydroxyimino-derivative) in 55% yield. Fischer and Bäuml² appear to have tried this method although they do not record experimental details. It was rejected on account of a supposed difficulty in the preparation of ethyl 3-oxopentanoate. The keto-ester (I) can, however, be readily and consistently obtained in up to 67% yield by the method of Anderson *et al.*⁴ (action of ethylmagnesium iodide on ethyl cyanoacetate). Substitution of ethylmagnesium bromide for the iodide caused the yield to drop to 22%. Catalytic hydrogenation of the pyrrole (II) afforded the known ethyl 3 : 4-diethyl-5-methylpyrrole-2-carboxylate (III) in 82% yield.

Conversion of the pyrrole (III) into the acid ester (IV) presented some difficulty. Fischer *et al.*⁵ reported that the action of sulphuryl chloride on the pyrrole (III) afforded this substance. It was described as having m. p. 264°. In our preliminary experiments, when this method was followed exactly, we obtained a small amount of a material of m. p. 264°, but in subsequent experiments an acidic product of m. p. 196° was consistently obtained. Elementary analysis, ethoxyl content, and molecular and equivalent weights confirmed the structure of this material as being the half-ester, 3 : 4-diethyl-5-ethoxycarbonylpyrrole-2-carboxylic acid (IV). On alkaline hydrolysis it afforded the diacid (V) which had m. p. 264° and may well be identical with the product obtained by Fischer.†

The structure of our diacid (V) was confirmed by conversion into its dimethyl ester, m. p. 82°. The esterification of our material of m. p. 264°, obtained directly in the sulphuryl chloride reaction, afforded a crude diester, m. p. 77°, the melting point of which was not depressed in admixture with the authentic diester. We attempted to decarboxylate our half-ester, m. p. 196°, to the monoester (VI; R = OEt) by direct heat and by boiling 2-aminoethanol (cf. Chu and Chu⁶) but the only product was a high-boiling intractable oil which was produced in poor yield. In one experiment where excess of 2-aminoethanol was employed we isolated a crystalline 2-hydroxyethylamide (VI; R = NH·CH₂·CH₂·OH). Corwin *et al.*⁷ record a similar example of a pyrrolic acid which was not decarboxylated smoothly.

* Part V, *J.*, 1956, 2280.

† Nevertheless, Fischer records elementary analyses and an ethoxyl figure for his 264° compound which agree with the values required by the half-ester (IV).

¹ Eisner, Linstead, Parks, and Stephen, *J.*, 1956, 1655.

² Fischer and Bäuml, *Annalen*, 1928, 468, 58.

³ Corwin and Quattlebaum, *J. Amer. Chem. Soc.*, 1936, 58, 1083.

⁴ Anderson, Halverstadt, Müller, and Roblin, *ibid.*, 1945, 67, 2197.

⁵ Fischer, Guggemos, and Schäfer, *Annalen*, 1939, 540, 30.

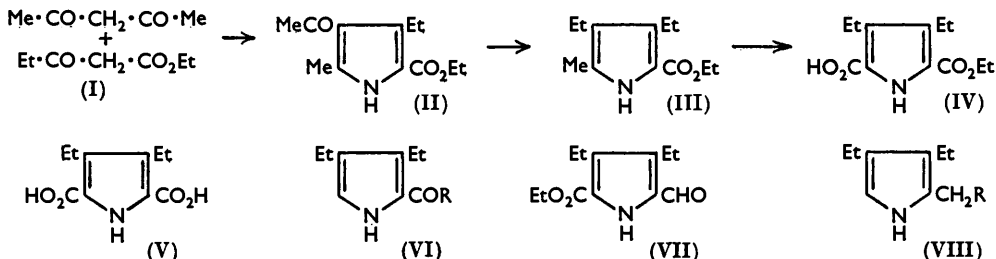
⁶ Chu and Chu, *J. Org. Chem.*, 1954, 19, 266.

⁷ Corwin, Bailey, and Viohl, *J. Amer. Chem. Soc.*, 1942, 64, 1267.

The same half-ester (IV) was obtained consistently in 70% yield by MacDonald and MacDonald's ⁸ modification of Fischer's method, with the aldehyde (VII) isolated as a by-product. Corwin's modification ⁷ of Fischer's method resulted in a 24% yield of the pyrrole (IV).

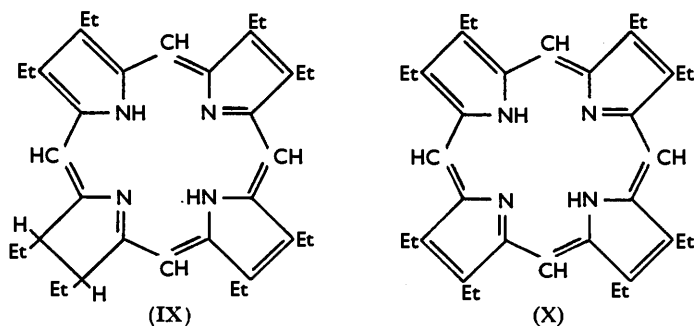
3:4-Diethylpyrrole was prepared from the half-ester (IV) in 72% yield by an adaptation of Fischer's procedure, and in 49% yield by the indirect route ¹ which involved decarboxylation of the intermediate diacid (V) with 2-aminoethanol. 3:4-Diethylpyrrole had m. p. 13°; Fischer *et al.* reported an oil.

The Mannich base (VIII; R = NMe₂) was prepared, by the method employed in our previous work,¹ in up to 79% yield, as an oil which decomposed on attempted distillation. We were not able to purify it but characterised it as the picrate. A much more stable



base and a better intermediate for the formation of pigments is the allied piperidine compound (VIII; R = NC₅H₁₀) prepared from 3:4-diethylpyrrole, piperidine, and formaldehyde. This proved to be a solid which, although it could not be distilled, crystallised from acetone at -80°.

Octaethylchlorin (IX) was prepared by the method previously employed.^{1,9} When the crude base (VIII; R = NMe₂) was used, variable yields of the chlorin (IX) and the known octaethylporphin (X) were obtained: in one case, 13% of the chlorin (IX) with only traces of the porphin (X), in others, 0—2% of the chlorin with up to 40% of the porphin. Although the conditions governing the reaction were closely investigated, it was not possible to get reproducible results. The base (VIII; R = NC₅H₁₀) was next studied. The chlorin (IX) was formed from it readily at room temperature in about 2% yield, in contrast to unsubstituted chlorin ⁹ where under the same conditions only traces of the



pigment were produced. From this observation we were able to determine the optimum conditions as being a reaction time of 16 hr. at room temperature, followed by 4 hr. at 140°. That these conditions are very specific is shown by the fact that when the reaction time at room temperature was increased to 30 hr., the total yield of the chlorin (IX) was only 3—4% as opposed to 10—15% under optimum conditions. The yields of the chlorin

⁸ MacDonald and MacDonald, *Canad. J. Chem.*, 1955, **33**, 573.

⁹ Eisner and Linstead, *J.*, 1955, 3742.

(IX), although not completely reproducible, did not vary as much as when the base (VIII; R = NMe₂) was used. A considerable amount of the porphin (X) was usually formed in the reaction.

The pigments (IX) and (X) were readily separated and purified by chromatography on alumina (cf. ref. 1) or magnesium oxide. The light absorptions of the pigments as well as that of the copper derivative of the chlorin (IX), prepared in the usual manner, are given in the Table.

Octaethylchlorin was readily dehydrogenated by 2:3-dichloro-5:6-dicyano-1:4-benzoquinone at room temperature (cf. Eisner and Linstead¹⁰); the crystalline octa-

Light absorption data (in benzene).

Octaethylchlorin		Octaethylporphin		Copper octaethylchlorin	
λ_{\max} (m μ)	ϵ	λ_{\max} (m μ)	ϵ	λ_{\max} (m μ)	ϵ
392 *	182,300	400 *	159,000	399 *	146,000
489	14,400	498	14,500	494	5,900
496	13,300	532	10,800	531	5,000
522	5,300	568	6,800	569	8,400
545	2,500	596	1,500	613	53,000
591	5,100	622	5,800		
618	5,500				
645.5	68,600				

* Soret band.

ethylporphin (X) was isolated in 64% yield. Quantitative dehydrogenation gave similar results to those obtained in our earlier work.

Reduction of the porphin (X) by the method of Schlesinger *et al.*¹¹ afforded the chlorin (IX) in about 30% yield, accompanied by a red tetrahydro-pigment with an intense orange fluorescence.¹² Traces of this pigment were occasionally formed in the preparation of the chlorin (IX).

The interconvertibility of a chlorin and a porphin has thus been demonstrated for the first time. This provides further evidence of the relations between the two pigments.

EXPERIMENTAL

Ethyl 3-oxopentanoate (I) was prepared by the method of Anderson *et al.*⁴ in 58% yield and had b. p. 80°/10 mm., n_D^{20} 1.4228. By allowing the Grignard complex to stand for 90 hr. instead of the 60 hr. reported the yield was raised to 67%. When ethylmagnesium bromide was used instead of the iodide the yield was 22%.

Ethyl 4-Acetyl-3-ethyl-5-methylpyrrole-2-carboxylate (II).—Ethyl 3-oxopentanoate (118 g., 1 mol.) in acetic acid (350 ml.) was treated with sodium nitrite (70 g., 1.2 mols.) in water (170 ml.) at 0° to 5°. The cooled solution was stirred for 4 hr. at 0° and kept overnight at room temperature. The solution was added to a well-stirred mixture of acetylacetone (96 g., 2.4 mols.), zinc dust (135 g., 2.4 mols.), and sodium acetate (100 g., 1.5 mols.), so that the mixture refluxed gently. After the initial reaction had ceased, the mixture was boiled under reflux for 4 hr. and poured while hot into ice-water (15 l.). The crude product (II), m. p. 115°, was filtered off, washed with water, and crystallised from ethanol, affording white crystals (98 g., 55%), m. p. 118.5° (lit., m. p. 115°).

Ethyl 3:4-Diethyl-5-methylpyrrole-2-carboxylate (III).—The pyrrole (II) (50 g.) in ethanol (350 ml.) was hydrogenated for 2 hr. at 160°/150 atm. in presence of Raney nickel (~4 g.). Removal of the solvent under reduced pressure and crystallisation from light petroleum (b. p. 60—80°) afforded the pyrrole (III) (38 g., 83%), m. p. 77° (lit., m. p. 75°).

3:4-Diethyl-5-ethoxycarbonylpyrrole-2-carboxylic Acid (IV).—(a) Freshly distilled sulphuryl chloride (21 ml., 3 mols.) was added dropwise to a stirred solution of the pyrrole (III) (18 g., 1 mol.) in anhydrous ether (150 ml.) at > 0°. The mixture was stirred for 2 hr. and kept at 0° for 30 hr. Excess of sulphuryl chloride was decomposed by slow addition of ice-cold water (25 ml.), and the solvent removed under reduced pressure. Sodium acetate (20 g.) in boiling

¹⁰ Eisner and Linstead, *J.*, 1953, 3749.

¹¹ Schlesinger, Corwin, and Sargent, *J. Amer. Chem. Soc.*, 1950, **72**, 2867.

¹² Result to be published later.

water (400 ml.) was added to the residual oil and the mixture was boiled with vigorous stirring until the oil *A* solidified (about 5 min.). The product was cooled and filtered. The aqueous filtrate *C* was extracted twice with ether, and the extracts *B* were washed with 10% sodium hydroxide solution (30 ml.). The residue *A* was dissolved in 10% sodium hydroxide solution (150 ml.) and washed thrice with ether. The combined alkaline solutions were acidified with concentrated hydrochloric acid in the cold, affording 3 : 4-diethyl-5-ethoxycarbonylpyrrole-2-carboxylic acid (IV) (16.8 g., 70%) which separated from aqueous ethanol as a white powder, m. p. 196° (decomp.) [Found : C, 60.2; H, 7.2; N, 5.7; OEt, 19.4%; equiv., 234; *M* (Rast), 195. $C_{12}H_{17}O_4N$ requires C, 60.2; H, 7.2; N, 5.85; OEt, 18.8%; equiv., 239; *M*, 239]. Evaporation of the combined ether extracts *B* + *C* afforded ethyl 3 : 4-diethyl-5-formylpyrrole-2-carboxylate (VII) which was purified by crystallisation from aqueous alcohol and sublimation at 100°/20 mm. It then had m. p. 53° (Found : C, 64.5; H, 7.7; N, 6.2. $C_{12}H_{17}O_3N$ requires C, 64.55; H, 7.7; N, 6.3%).

(b) Bromine (0.7 ml., 1.2 mols.) in anhydrous ether (10 ml.) was added slowly to a stirred, cooled solution of the pyrrole (III) (1.8 g., 1 mol.) in ether (10 ml.). Scratching precipitated the crude bromo-derivative, m. p. 88°. It was filtered off, washed with anhydrous ether (20 ml.), dried, suspended in anhydrous ether (40 ml.), and treated with sulphuryl chloride (2.1 ml., 3 mols.) at $\gt 3^\circ$. Working up the product as under (a) afforded the acid ester (IV) (0.52 g., 24%).

(c) The pyrrole (III) (1.8 g.) in anhydrous ether (5 ml.) was treated dropwise with sulphuryl chloride (3.5 g., 2.4 ml.) at 0°. The solution was kept overnight at 0° and washed with cold water. The solvent was removed under reduced pressure and the oily residue boiled with water (10 ml.) for 0.5 hr. The resulting mixture was extracted with ether, and the extracts were shaken with 20% sodium hydroxide solution 4 times. The diacid (V) (0.8 g., 40%) was precipitated in the cold by 50% acetic acid and crystallised from aqueous ethanol, then having m. p. 264° (decomp.). Its dimethyl ester, prepared with diazomethane, had m. p. 77°.

Decarboxylation of 3 : 4-Diethyl-5-ethoxycarbonylpyrrole-2-carboxylic Acid (IV).—The acid ester (IV) was boiled under reflux with 2-aminoethanol (2.5 ml.) for 1 hr. The solution was poured into water and extracted with ether. The ethereal extracts were dried, the solvent was removed, and the residue washed with light petroleum. Crystallisation from light petroleum (b. p. 60—80°) and sublimation at 100°/20 mm. afforded 3 : 4-diethyl-2'-hydroxyethylcarbamoypyrrole (VI; R = $NH \cdot CH_2 \cdot CH_2 \cdot OH$), m. p. 114° (Found : C, 63.1; H, 8.25; N, 13.0. $C_{11}H_{18}O_2N_2$ requires C, 62.9; H, 8.6; N, 13.3%).

3 : 4-Diethylpyrrole-2 : 5-dicarboxylic Acid (V).—The acid ester (IV) (0.664 g.) in 10% sodium hydroxide solution (10 ml.) was boiled under reflux for 1.5 hr. Acidification of the cooled solution with 2*N*-hydrochloric acid afforded the diacid (V) (0.568 g., 96%). It was dissolved in 10% sodium hydroxide solution (10 ml.), treated with charcoal, reprecipitated, and crystallised from aqueous ethanol, to give 3 : 4-diethylpyrrole-2 : 5-dicarboxylic acid (V), m. p. 264° (decomp.) (Found : C, 56.9; H, 6.3; N, 6.5%; equiv., 107. $C_{10}H_{13}O_4N$ requires C, 56.9; H, 6.2; N, 6.6%; equiv., 106). A solution of the diacid (0.20 g.) in methanol (5 ml.) was treated with excess of ethereal diazomethane. Removal of the solvent, crystallisation from light petroleum (b. p. 40—60°), and sublimation at 100°/20 mm. afforded dimethyl 3 : 4-diethylpyrrole-2 : 5-dicarboxylate, m. p. 82° (Found : C, 60.2; H, 7.1; N, 5.9. $C_{12}H_{17}O_4N$ requires C, 60.2; H, 7.2; N, 5.85%). Its mixed m. p. with the dimethyl ester, m. p. 77°, of the acid obtained under (c) was 81°.

3 : 4-Diethylpyrrole.—(a) The acid ester (IV) (62 g.) and sodium hydroxide (100 g.) in water (660 ml.) were heated in an autoclave for 2.5 hr. at 180° in nitrogen. The solution was saturated with sodium chloride and extracted with ether (15 times). The ethereal extracts were dried (K_2CO_3), the solvent was removed, and the residue distilled, affording 3 : 4-diethylpyrrole, m. p. 13°, b. p. 82°/9 mm., n_D^{20} 1.4912 (Found : C, 77.5; H, 10.9; N, 11.3. Calc. for $C_8H_{13}N$: C, 77.9; H, 10.6; N, 11.4%). The yield was 23 g. (72%); overall yield from (III), 51% [lit., b. p. 82°/10 mm., yield 54%; overall yield from (III), 38%].

(b) The acid ester (IV) was prepared as under (a) from the pyrrole (III) (30 g.) but was not isolated. Its alkaline solution was kept for 3 days, sodium hydroxide (15 g.) was added, and the solution boiled under reflux for 2 hr., cooled, and acidified. The precipitated diacid (V) was filtered off, dried, and boiled under reflux with 2-aminoethanol (15 g.) for 1 hr. After cooling and acidification with 2*N*-hydrochloric acid the solution was repeatedly extracted with ether. The ethereal extracts were washed with sodium hydrogen carbonate solution till neutral

and dried (K_2CO_3). Removal of the solvent and distillation under reduced pressure afforded 3 : 4-diethylpyrrole [4.85 g., 49%; overall yield from (III), 28%].

2-Dimethylaminomethyl-3 : 4-diethylpyrrole (VIII; $R = NMe_2$).—3 : 4-Diethylpyrrole (2.6 g., 1 mol.) in methanol (20 ml.) was treated dropwise with a solution of dry dimethylammonium chloride (1.8 g., 1.05 mol.), potassium acetate (2.1 g., 1.05 mol.), and 40% aqueous formaldehyde (1.6 g., 1.05 mol.) in water (8 ml.) at -10° to 0° in an inert atmosphere. The solution was stirred for 1 hr. and kept at 0° for 9 hr. under nitrogen in an all-glass apparatus. It was acidified with dilute hydrochloric acid and extracted with ether. The aqueous layer was basified with 2*N*-sodium hydroxide solution and extracted with ether. The extracts were washed with water and dried ($MgSO_4$). Removal of the solvent under reduced pressure afforded the crude Mannich base (VIII; $R = NMe_2$) (3.0 g., 79%). Its *picrate*, prepared in moist ether, crystallised from aqueous methanol and had m. p. 118° (decomp.) (Found: C, 49.7; H, 5.95; N, 16.9. $C_{11}H_{20}N_2, C_6H_5O_7N_3$ requires C, 49.9; H, 5.65; N, 17.1%). In preparing the base the following precautions should be taken in order to obtain the maximum yield: (a) the reaction temperature should be -10° to 0° ; (b) the reaction mixture should be kept for 6–9 hr. at 0° ; (c) all operations should be carried out under nitrogen; (d) all-glass apparatus should be used.

3 : 4-Diethyl-2-piperidinomethylpyrrole (VIII; $R = NC_5H_{10}$).—3 : 4-Diethylpyrrole (4.32 g., 1 mol.) in methanol (50 ml.) was treated dropwise with a solution of piperidine (3.14 g., 1.05 mol.) and 40% aqueous formaldehyde (2.71 g., 1.05 mol.) in methanol (10 ml.) at $>5^\circ$ in an inert atmosphere. The product was worked up as above. Crude 3 : 4-diethyl-2-piperidinomethylpyrrole (5.55 g., 72%) was obtained with m. p. 77° by removal of the solvent under reduced pressure. Crystallisation from acetone at -80° afforded the pure base (2.9 g., 37%), m. p. 80° (Found: C, 76.6; H, 10.9; N, 12.7. $C_{14}H_{24}N_2$ requires C, 76.3; H, 11.0; N, 12.7%). Its *picrate* was formed in methanol and had m. p. 124° after crystallisation from methanol (Found: C, 53.7; H, 6.3; N, 15.4. $C_{14}H_{24}N_2, C_6H_5O_7N_3$ requires C, 53.4; H, 6.1; N, 15.6%).

Preparation of Octaethylchlorin.—The chlorin (IX) was prepared essentially by the same method as chlorin⁹ and octamethylchlorin¹ except that stronger acid (2 : 1) was used to decompose the magnesium complex and the solid residues were not extracted. A number of experiments were carried out in order to determine the optimum conditions for formation of octaethylchlorin from both the Mannich bases (VIII; $R = NMe_2$ and NC_5H_{10}); they are summarised in the Table below. The yields of chlorin were calculated from spectroscopic measurements. Xylene was used as solvent throughout. Ethylmagnesium bromide was added to the base in the cold.

Expt.	Time of reaction (hr.)		Yield of chlorin (%)		Remarks
	Room temp.	140°	Room temp.	140°	
<i>A. From (VIII; $R = NMe_2$).</i>					
1	—	4.5	—	2.3	} 40% crystalline porphin Some orange fluorescence } ~30% crystalline porphin
2	—	4	—	Trace	
3	—	4	—	„	
4	—	5	—	„	
5	—	8	—	13.0	
6	—	16	—	1.6	
7	—	16	—	2.0	
8	16	4	1.5	4.7	
9	17	4	—	8.6	
10	17	4	—	1.2	
<i>B. From (VIII; $R = NC_5H_{10}$).</i>					
1	—	2	—	0.5	} From crude base
	—	16	—	1.0	
2	13	2	2.9	11.3	
	—	4	—	20.6	
	—	6	—	18.6	
	—	8	—	16.5	
	—	19	—	16.1	
3	16	4	—	6.7	
4	17	4	—	14.1	
5	17	4	—	8.0	
6	31	4	3.4	3.1	
7	31	4	2.9	2.6	} From crude base
8	40	4	—	3.6	

The following precautions are desirable: All operations should be carried out under nitrogen, the magnesium pigments should be decomposed immediately, and the pigment solutions should be examined spectroscopically and chromatographed as soon as possible.

The yields of porphin were difficult to estimate spectroscopically as background absorption tended to give high results. Thus in one experiment the calculated yields were 43% and 76% from the 622 and 569 $m\mu$ bands respectively, whereas 25% of crystalline porphin were in fact isolated. However, the yields of porphin appear to be of the order of 30–40%.

The crude pigments were purified by chromatography on alumina (grade 1) with benzene as eluant. Chlorin was first eluted as a green band, followed immediately by the porphin. Alternatively, heavy magnesium oxide could be used for the purification procedure (see below). It effected better separations than alumina.

Pure *octaethylchlorin* crystallised from benzene-methanol or light petroleum-methanol in deep blue needles, m. p. 232° (Found: C, 80.6; H, 9.2; N, 10.4. $C_{36}H_{48}N_4$ requires C, 80.5; H, 9.0; N, 10.4%). It is very soluble in all organic solvents except alcohol, forming green solutions with a strong red fluorescence. It has a high acid number. Thus, when its benzene solution is treated with concentrated hydrochloric acid, the blue hydrochloride remains in the benzene layer and does not pass into the aqueous phase.

Octaethylporphin crystallises from benzene in deep red crystals, m. p. 318° (lit.,^{2,13} m. p. 292–299°; 318°; 322°) (Found: C, 81.1; H, 8.4. Calc. for $C_{36}H_{48}N_4$: C, 80.85; H, 8.7%).

Copper octaethylchlorin. Octaethylchlorin (15 mg.) in boiling benzene (30 ml.) was treated with a solution of cupric acetate (11 mg.) in boiling methanol (5 ml.) in an inert atmosphere and heated for 2 min.; the solution was cooled, and washed with dilute ammonia solution and water. Removal of the solvent under reduced pressure and crystallisation from light petroleum (b. p. 60–80°) afforded blue needles of *copper octaethylchlorin* (17.3 mg., 90%) (Found: C, 72.3; H, 7.8; Cu, 10.5. $C_{36}H_{48}N_4Cu$ requires C, 72.3; H, 7.7; Cu, 10.6%). Chromatography of a small portion on heavy magnesium oxide with light petroleum (b. p. 60–80°)-benzene (9:1) as eluant revealed the absence of copper octaethylporphin.

Dehydrogenation of Octaethylchlorin.—(a) Octaethylchlorin (5.9 mg.) in dry benzene (40 ml.) was treated with a solution of 2:3-dichloro-5:6-dicyano-1:4-benzoquinone (3.04 mg., 1.2 mol.) in benzene (10 ml.) at room temperature. The solution became red almost instantaneously and showed the characteristic porphin spectrum. It was chromatographed on alumina as before, concentrated, and crystallised (yield, 3.9 mg., 64.4%, of spectroscopically pure octaethylporphin, m. p. 312°, mixed m. p. with authentic specimen, 317°).

(b) A solution of octaethylchlorin (4×10^{-5} mole) in *o*-dichlorobenzene was treated with dichlorodicyanoquinone at room temperature for 1 hr. and the solution was examined spectroscopically. The results are summarised below. (This experiment was carried out by Miss E. Stephen.)

Quinone (mol.)	Unchanged chlorin (%)	Porphin formed (%)		
		(500 $m\mu$)	(535 $m\mu$)	(570 $m\mu$)
0.525	50	—	54	51.5
0.525	56	—	55	54
1.05	4	103	102	108
1.05	3	103	104	106

Reduction of Octaethylporphin (X).—The porphin (100 mg.) was extracted from a thimble into boiling acetic acid containing excess of anhydrous ferric chloride and sodium acetate. The solution was kept overnight at room temperature, then filtered, and the insoluble ferric complex washed with water and alcohol. It was dissolved in boiling *isopentyl* alcohol (15 ml.) in a current of oxygen-free nitrogen, and sodium (~1.5 g.) was added to the hot solution. The mixture was boiled for 40 min., then ethanol (10 ml.) was added to react with the excess of sodium, followed by concentrated hydrochloric acid (8 ml.). The cooled solution was treated with benzene, basified with ammonia solution, and washed with water. After removal of the solvent under reduced pressure the residue was dissolved in light petroleum (b. p. 60–80°) and chromatographed on magnesium oxide. Elution with the above solvent removed a red pigment whilst the chlorin (32 mg.) was eluted with light petroleum-benzene (1:1). After crystallisation from light petroleum-methanol pure octaethylchlorin of m. p. and mixed m. p. 232° was obtained which was spectroscopically identical with the synthetic material.

¹³ Fischer and Stangler, *Annalen*, 1928, **462**, 259.

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DEPARTMENT OF ORGANIC CHEMISTRY,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
S. KENSINGTON, LONDON, S.W.7.

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