945. *Conjugated Macrocycles. Part XXIII.* Tetracyclohexenotetrazaporphin.*

By G. E. Ficken and R. P. Linstead.

3 : 4 : 5 : 6-Tetrahydrophthalonitrile (I) reacts with various magnesium-containing reagents to give magnesium tetra*cyclo*hexenotetrazaporphin (III; M = Mg). The optimum yield is 66%. Various solvated forms have been obtained. Boiling glacial acetic acid removes the metal, to give tetra*cyclo*hexenotetrazaporphin (II) (hexadecahydrophthalocyanine). Copper and nickel derivatives of this compound have been prepared by metal-exchange and by reaction of the metal-free compound with suitable reagents. The azaporphin (II) is dehydrogenated to phthalocyanine thermally at 300—320°, or by treatment with sulphur; use of palladium leads to a mixture of phthalocyanine and its palladium derivative. The colour, fluorescence, light absorption, and chemiluminescence of these substances are described.

The structure (II) has been conclusively established from the analytical results, dehydrogenation, and oxidative fission to 3 : 4 : 5 : 6-tetrahydrophthalimide and ammonia. 4 Mols. of ammonia can be eliminated under controlled conditions, one atom of oxygen being taken up. These results parallel closely those obtained with phthalocyanine.

The synthesis of tetrazaporphin (Linstead and Whalley, preceding paper) has opened up the possibility of making analogous substances from substituted maleic nitriles. 3 : 4 : 5 : 6-Tetrahydrophthalonitrile (I) was selected for study because the series acts as a link between the tetrazaporphins and the phthalocyanines, there are no complications from geometrical isomerism, and the parent compounds are comparatively accessible. H. France of Imperial Chemical Industries Limited, Dyestuffs Division (personal communication, 1950 †), prepared metallic pigments by heating this nitrile with a metallic compound, urea, and ammonium molybdate. The same compounds were prepared from 3 : 4 : 5 : 6-tetrahydrophthalic anhydride, whilst a metal-free compound was obtained from the sodium derivative, itself prepared from the nitrile and sodium amyloxide. The macrocyclic compounds which are to be expected are of the general types (II) and (III) and can be considered as tetra*cyclo*hexenotetrazaporphins or as hexadecahydrophthalocyanines.

Intermediates.—The parent anhydride (IV), obtained by sodium amalgam reduction of phthalic acid (von Baeyer, *Annalen*, 1890, **258**, 199), was converted into the imide (V) by Küster (*Z. physiol. Chem.*, 1908, **55**, 519). Fusion with urea is however a preferable method. Treatment of the imide with aqueous ammonia yielded the diamide (VI), the structure of which was confirmed by its reconversion into the imide above its melting point

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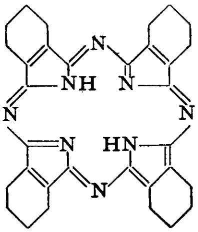
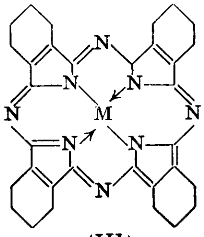
* Part XXII, preceding paper. † Patent application pending.

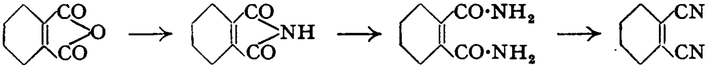
and into the anhydride with nitrous acid. A by-product in the formation of the diamide was the ammonium salt (VII) of the amic acid. Dehydration of the diamide with boiling acetic anhydride for a short period gave mainly 2-cyano-3 : 4 : 5 : 6-tetrahydrobenzamide (VIII) and for a longer time some of the required dinitrile (I), contaminated with the imide (V). These reactions resemble the preparative methods for the corresponding derivatives of phthalic acid used by Byrne, Linstead, and Lowe (*J.*, 1934, 1017, 1022). A much better process for the dinitrile was dehydration of the diamide with phosphoric oxide in the presence of triethylamine (cf. McElvain and Clarke, *J. Amer. Chem. Soc.*, 1947, **69**, 2657); the yield of pure dinitrile was 38%, the main contaminant being the imide which could be removed by taking advantage of its easy hydrolysis by alkali.



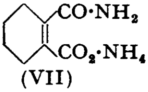
(II)



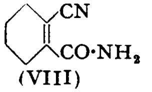
(III)



(IV) (V) (VI) (I)



(VII)



(VIII)

Macrocyclic Pigments.—3 : 4 : 5 : 6-Tetrahydrophthalonitrile was found to give macrocyclic pigments less readily than does phthalonitrile but rather more easily than maleic dinitrile. As with the latter, the best yield of tetrazaporphin derivatives was obtained by the use of reagents containing magnesium. Reaction with magnesium amyloxide was much slower than in the case of maleic dinitrile, but useful reagents were found in the solutions obtained by decomposing methylmagnesium iodide by alcohols (ROH) and which are equivalent to RO·MgI (Tschelinzew, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 844, 1917; *Chem. Zentr.*, 1914, I, 622, 1827). Comparative reactions with various alcohols indicated that the best results were given when R was *iso*amyl, and by the interaction of 3 : 4 : 5 : 6-tetrahydrophthalonitrile with a decomposed Grignard reagent in boiling amyl alcohol, magnesium tetra*cyclo*hexenotetrazaporphin (III; M = Mg) was obtained in 66% yield. The superiority of this yield over that of magnesium tetrazaporphin reflects the increased stability of both the intermediates and the pigments of the substituted series.

Like other magnesium derivatives of macrocycles, this magnesium compound could be obtained in a number of solvated forms; a mono- and a di-hydrate and a substance analysing as a pyridine-hydrate have been isolated. The preparation of the latter was surprising as it separated from a pyridine solution of the magnesium pigment after drying over phosphoric oxide.

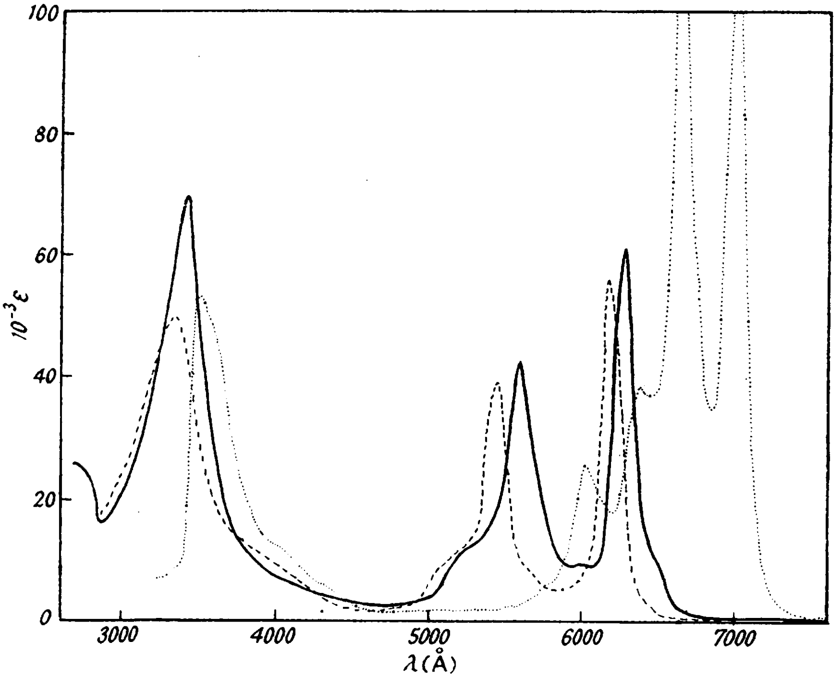
Removal of metal from the magnesium compound was best accomplished by boiling glacial acetic acid. Mineral acids gave more or less degradation of the macrocycle. The product crystallised from chlorobenzene as blue needles, much less green than phthalocyanine, and analysing as unsolvated tetra*cyclo*hexenotetrazaporphin, $C_{32}H_{34}N_8$.

Phthalonitrile gives an excellent yield of sodium pigment on treatment with sodium amyloxide (Linstead and Lowe, *J.*, 1934, 1024), and maleic dinitrile none at all (Linstead and Whalley, preceding paper). 3 : 4 : 5 : 6-Tetrahydrophthalonitrile was intermediate. A blue sodium pigment was rapidly formed, which lost metal on treatment with acid, to yield tetra*cyclo*hexenotetrazaporphin identical with that described above. The yield of sodium pigment was, however, small, the bulk of the nitrile being converted into a brown polymer. Indications of the formation of metallic tetrazaporphin derivatives were also obtained when the tetrahydrophthalonitrile was treated with lithium *iso*amyloxide in boiling *iso*amyl alcohol, lead *iso*amyloxide (Chablay, *Ann. Chim.*, 1917, **8**, 167), or aluminium *iso*propoxide in urea.

Copper tetra*cyclo*hexenotetrazaporphin (III; M = Cu) was readily prepared from the magnesium pigment by direct metal exchange, with copper bronze in boiling pyridine. This falls into line with the results in the naphthalocyanine and tetrazaporphin series. We have also found that magnesium phthalocyanine gives copper phthalocyanine by the same process.

Treatment of the metal-free compound with nickel chloride or palladous chloride in boiling chlorobenzene led to considerable fixation of metal. The reactions, were, however, incomplete and the metal-free compound formed mixed crystals with the metallic derivatives. The components could not be separated by solvent extraction or crystallisation. Attempts to prepare palladium phthalocyanine had led to similar mixtures (Barrett, Frye, and Linstead, *J.*, 1938, 1157). When boiling *o*-dichlorobenzene was used as solvent the formation of nickel and cobalt derivatives from the metal-free compound and nickel chloride and cobalt acetate respectively went to completion, the products being of the usual type (III; M = Ni and Co). Under these conditions, however, the reaction between tetra*cyclo*hexenotetrazaporphin and palladous chloride led not only to fixation of metal but also to dehydrogenation, a considerable amount of palladium phthalocyanine, $C_{32}H_{16}N_8Pd$, being formed. This compound has now been obtained by direct interaction of palladium black and boiling phthalonitrile :

FIG. 1.



——— *Tetra*cyclo*hexenotetrazaporphin (in chlorobenzene).*
– – – – *Tetrazaporphin (in chlorobenzene).*
. . . . *Phthalocyanine (in chloronaphthalene).*

$$4C_8H_4N_2 + Pd = C_{32}H_{16}N_8Pd$$

The dissolution of a noble metal by a neutral organic compound is remarkable.

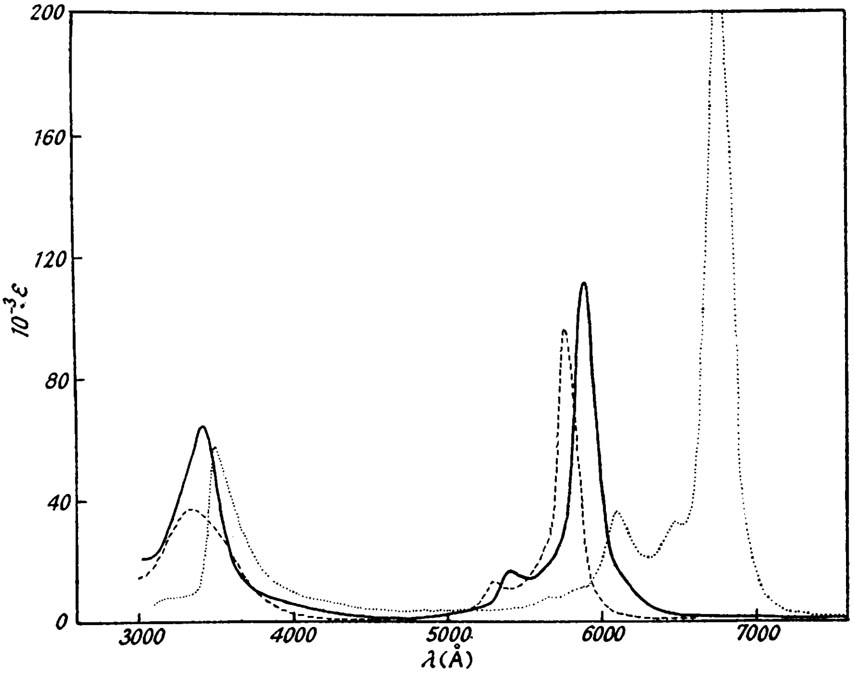
When 3 : 4 : 5 : 6-tetrahydrophthalonitrile was heated with urea, nickel chloride, and a trace of ammonium molybdate, a coloured product was obtained from which boiling chlorobenzene extracted a blue pigment spectroscopically identical with nickel tetra*cyclo*hexenotetrazaporphin. The yield was about 8%.

Properties.—As hexadecahydrophthalocyanines, the new azaporphins bear a general resemblance to the corresponding phthalocyanines. They are sparingly soluble blue solids which crystallise in small needles generally with a purple reflex. They are less stable to heat and to acids than are phthalocyanines but more stable than the corresponding unsubstituted tetrazaporphins. The solids do not melt but can be sublimed at low pressures, although large crystals have not been obtained in this way. The temperature must be kept below 300° in sublimations; otherwise dehydrogenation to the corresponding phthalocyanine occurs. Dehydrogenation of the metal-free compound to phthalocyanine :

$$C_{32}H_{34}N_8 \longrightarrow C_{32}H_{18}N_8 + 8H_2$$

occurs thermally at 300—320°, also on treatment with sulphur, or with palladium in boiling naphthalene. In the last-named process some palladium phthalocyanine is also produced.

FIG. 2.



—— *Copper tetra*cyclo*hexenotetrazaporphin (in dichlorobenzene).*
– – – – *Copper tetrazaporphin (in dichlorobenzene).*
. . . . *Copper phthalocyanine (in chloronaphthalene).*

The solubility of the tetra*cyclo*hexenotetrazaporphins in organic solvents is very low, but greater than that of the corresponding phthalocyanines. Thus, the parent compound is appreciably soluble in chlorobenzene to give a pure blue solution, and the solubilities of the copper, the nickel, and the cobalt derivative are lower. As usual, the magnesium compound has the greatest solubility, being soluble in cold pyridine (*ca.* 1%) and even slightly in dioxan, alcohol, and acetone. Its solutions are slowly decolorised, probably by photodecomposition. The solutions in pyridine, dioxan, and hydroxylic solvents show a fine crimson fluorescence in daylight and a brilliant vermilion in ultra-violet light. These fluorescences are comparable with those of magnesium tetrazaporphin and greater than those of magnesium phthalocyanine and of chlorophyll. Solutions of metal-free tetra*cyclo*hexenotetrazaporphin fluoresce rose-red in ultra-violet light.

Magnesium tetra*cyclo*hexenotetrazaporphin, like analogous magnesium compounds, gives a vivid red chemiluminescence when added to hot peroxide-containing hydrocarbons.

Light absorption of the metal-free and of some metallic pigments has been measured over the approximate range 300—1000 mμ. The main bands are tabulated on p. **4854.** The spectral curves for metal-free and copper tetra*cyclo*hexenotetrazaporphins are in Figs. 1 and 2, where data for the corresponding tetrazaporphins and phthalocyanines are given. A comparison makes clear the following points: (i) There is a very close resemblance in both the metal-free and the copper compound to the unsubstituted tetrazaporphin (Linstead and Whalley, preceding paper). There is a bathochromic shift of the long-wave bands by the substitution of the pyrrole β-carbon atoms. (ii) A substantial difference exists between the phthalocyanines and their hexadecahydro-derivatives; the main absorption bands in the red of the aromatic compounds are considerably higher in wave-length and intensity, corresponding to the enlarging of the conjugated systems. (iii) All these azaporphins (including the phthalocyanines) show a rather broad band in the ultra-violet spectrum. The position of this, at about 340 mμ, is apparently little affected by β-substitution or by the introduction of metal. This band is more intense with metal-free compounds. Other bands undoubtedly exist at shorter wave-lengths but information about them is rather fragmentary owing to solubility difficulties.

Our main bands for metal-free and magnesium tetra*cyclo*hexenotetrazaporphins are, as expected, very close to those reported by Fischer and Endermann for the corresponding " tetraimidoætioporphins " (tetramethyltetraethyltetrazaporphins):

Metal-free	mμ	Magnesium (in pyridine)	mμ
F. and E. (in pyridine–ether)	624, 553	F. and E.	599, 548
Present work (in chlorobenzene)	628, 560	Present work	599, 550

Structure.—Apart from the strong arguments based on analogy with the phthalocyanines, the structure of the tetra*cyclo*hexenotetrazaporphins has been conclusively established as (II) and (III) by two lines of evidence, *viz.*: dehydrogenation to phthalocyanines already referred to, and the evidence of oxidative fission. Tetra*cyclo*hexenotetrazaporphin was readily oxidised by hydrogen peroxide in concentrated sulphuric acid (cf. Fischer and Baümler, *Annalen*, 1928, **468**, 91), or preferably chromic acid (cf. Fischer and Walach, *ibid.*, 1926, **450**, 180; Muir and Neuberger, *Biochem. J.*, 1949, **45**, 163), to 3 : 4 : 5 : 6-tetrahydrophthalimide (V). The oxidation thus follows the same course as that of phthalocyanine, and it is clear that no new carbon–carbon bonds have been formed in the pigment formation. Four atoms of nitrogen are eliminated as ammonia by chromic acid oxidation at 0° and tetrahydrophthalimide can be isolated in 75% yield. Oxidation with ceric sulphate, by the method used for phthalocyanine (Dent, Linstead, and Lowe, *J.*, 1934, 1036), gave figures considerably higher than those required for the theoretical uptake of 1 atom of oxygen per molecule. This excess corresponds with the oxidation of the imide, which was found to be rapid under the conditions necessary to break the great ring. A rough correction for the oxidation of the imide gave a value of 1·2 atoms of oxygen taken up per molecule of tetra*cyclo*hexenotetrazaporphin.

The structures(II) and (III) represent, of course, only one state of the resonance hybrid.

EXPERIMENTAL

Continuous extractions were done following Barrett, Dent, and Linstead (*J.*, 1936, 1726).

3 : 4 : 5 : 6-*Tetrahydrophthalimide.*—3 : 4 : 5 : 6-Tetrahydrophthalic anhydride (61·0 g.) and urea (12·5 g.) were heated together at 155—160° until effervescence ceased and the mixture had almost completely solidified (45 minutes). The product was cooled and crystallised from benzene, giving 50·8 g. (83%) of the imide, which after sublimation had m. p. 170·5° (Küster, *loc. cit.*, found m. p. 169—170°) (Found: C, 63·3; H, 6·0; N, 9·0. Calc. for $C_8H_9O_2N$: C, 63·6; H, 6·0; N, 9·3%).

3 : 4 : 5 : 6-*Tetrahydrophthalamide.*—The finely-powdered imide (41·0 g.) was mixed with aqueous ammonia (120 ml., saturated with ammonia at 0°) and set aside at 0° for 15 hours. The precipitated solid was filtered off and washed with cold water. Methanol removed 2·2 g. of unchanged imide, leaving 35·5 g. (83%) of 3 : 4 : 5 : 6-*tetrahydrophthalamide*, m. p. 208° (decomp.) (Found: C, 57·0; H, 7·3; N, 16·4. $C_8H_{12}O_2N_2$ requires C, 57·2; H, 7·1; N, 16·7%). The aqueous filtrate and washings were evaporated almost to dryness in a vacuum-desiccator over concentrated sulphuric acid, and alcohol was added. Decomposition of the

precipitated solid (4·4 g., 9%) commenced at 142° (cf. Küster's figure of 145° for ammonium 3 : 4 : 5 : 6-tetrahydrophthalamate). Hydrolysis with concentrated hydrochloric acid converted it into 3 : 4 : 5 : 6-tetrahydrophthalic anhydride in 97% yield.

The diamide (2·5 g.) was dissolved in concentrated sulphuric acid (10 ml.), the solution cooled in a freezing mixture, and a saturated solution of sodium nitrite (5·0 g.) added in drops. The mixture was warmed on the steam-bath for ½ hour, then cooled, and ice was added. Ether extracted 1·77 g. of material which after crystallisation from light petroleum (b. p. 60—80°) had m. p. 67—68° and mixed m. p. 68—69° with 3 : 4 : 5 : 6-tetrahydrophthalic anhydride.

2-Cyano-3 : 4 : 5 : 6-tetrahydrobenzamide.—The diamide (21·0 g.), acetic anhydride (25·5 ml.), and acetic acid (22·5 ml.) were refluxed together until a clear solution was obtained (1 minute; cf. 1 hour required for phthalamide, Byrne, Linstead, and Lowe, *loc. cit.*). The solution was cooled and diluted with an equal volume of water, and the precipitated solid was filtered off and washed with cold water. Benzene extracted 5·6 g. of imide, leaving 4·4 g. (24%) of *2-cyano-3 : 4 : 5 : 6-tetrahydrophthalamide* which, recrystallised from acetone, had m. p. 169—170° (decomp.) (Found : C, 63·8; H, 6·6; N, 18·6. $C_8H_{10}ON_2$ requires C, 64·0; H, 6·7; N, 18·7%), $\lambda_{max.}$ 2270 Å (ε 12,300) in ethanol.

3 : 4 : 5 : 6-Tetrahydrophthalonitrile.—(a) *Acetic anhydride*. The diamide (4·5 g.) and acetic anhydride (20·0 ml.) were refluxed together vigorously for 5 hours, after which the acetic acid and anhydride were distilled off under reduced pressure. The residue was extracted several times with hot light petroleum (b. p. 60—80°), and the extracts were evaporated to dryness, yielding 0·73 g. (21%) of a product, m. p. 75—85°. This was warmed with 0·5N-sodium hydroxide solution (10 ml.), then cooled in ice, and the solid was filtered off, washed with water and dried. Pure *3 : 4 : 5 : 6-tetrahydrophthalonitrile*, m. p. 96°, was obtained by recrystallisation from light petroleum (b. p. 60—80°) (Found : C, 73·0; H, 6·2; N, 20·9. $C_8H_8N_2$ requires C, 72·7; H, 6·1; N, 21·2%), $\lambda_{max.}$ 2290 Å (ε 18,500) in ethanol.

(b) *Phosphoric oxide*. To a mixture of diamide (43·7 g.), triethylamine (106 g.; dried over phosphoric oxide), and benzene (200 ml.; similarly dried), phosphoric oxide (100 g.) was added as rapidly as possible and the mixture gently refluxed with stirring and protection from moisture. After 1·5 hours the benzene and excess of triethylamine were distilled out, finally under reduced pressure. Ice and water (300 g.) were added to the cold residue, and the mixture was left overnight. Some crude nitrile was filtered off and a further quantity was obtained by continuous ether-extraction of the filtrate for a few days. The combined products were boiled with N-sodium hydroxide (200 ml.) for 1 minute, and after cooling in ice the solid was filtered off, washed with cold water, and dried over sulphuric acid in a vacuum-desiccator. The yield of tetrahydrophthalonitrile was 12·8 g. (37%), m. p. 92—93°, and after one recrystallisation from light petroleum the m. p. was raised to 96°, not depressed by material made by method (a).

The filtrate from the sodium hydroxide treatment was strongly acidified with hydrochloric acid and continuously extracted with ether. Removal of the ether yielded 20·6 g. (52%) of anhydride which after crystallisation from light petroleum (b. p. 60—80°) had m. p. and mixed m. p. 72°.

*Sodium and Metal-free Tetra*cyclo*hexenotetrazaporphins*.—3 : 4 : 5 : 6-Tetrahydrophthalonitrile (520 mg.) was boiled with a solution of sodium (90 mg.) in *iso*amyl alcohol (5 ml.). The solution immediately became brown and then a blue solid was precipitated. After 15 minutes the solution was cooled and diluted with absolute ethanol, and the solid was filtered off and washed with ethanol and then ether. The yield of *sodium tetra*cyclo*hexenotetrazaporphin* was 33·3 mg. (5·9%), the product being a blue powder (Found : Na, 8·8. $C_{32}H_{32}N_8Na_2$ requires Na, 8·0%). Treatment with cold, dry pyridine extracted a small amount of metal-free pigment, identified spectroscopically.

The sodium pigment prepared from 5·28 g. of nitrile was warmed on the steam-bath with 2N-hydrochloric acid for 2 hours. The solid product was separated and washed successively with boiling water, alcohol, and ether, giving a deep blue solid (305 mg., 5·8%). *Tetra*cyclo*hexenotetrazaporphin* crystallised from chlorobenzene in blue, microscopic needles with a purple reflex (Found : C, 71·9; H, 6·3; N, 20·9. $C_{32}H_{34}N_8$ requires C, 72·4; H, 6·5; N, 21·1%).

After 16 hours' heating with hydrochloric acid the yield was only 2·5%.

*Magnesium Tetra*cyclo*hexenotetrazaporphin*.—Dry *iso*amyl alcohol (100 ml.) was added slowly to ethereal methylmagnesium iodide (prepared from 1·92 g. of magnesium, 5·0 ml. of methyl iodide, and 50 ml. of ether), the ether being allowed to boil off. Tetrahydrophthalonitrile (10·0 g.) was added, the solution immediately becoming yellow. When the solution was boiled gently the colour rapidly deepened, being green after 5 minutes and pure blue after

20 minutes. Boiling was continued for 9 hours and the amyl alcohol was distilled out, eventually under reduced pressure. The residue was washed thoroughly with light petroleum and then treated with glacial acetic acid (100 ml.) and ice (100 g.) for 30 minutes. The solid was filtered off and washed with cold dilute acetic acid and then with boiling water until no further brown material was removed. The product was extracted with acetone, the extracts at first being almost black, owing to the presence of impurities. The latter were very rapidly removed, however, and the extracts were soon pure blue with a red fluorescence. Extraction was stopped at this stage, and the extracts on evaporation to dryness yielded 3·50 g. of an almost black solid containing only 14·3% of magnesium pigment (estimated spectrometrically).

The residue from the acetone extraction was extracted exhaustively with chlorobenzene, there being very little final insoluble residue. The cold extract was diluted with an equal volume of light petroleum, and the solid was filtered off, and washed with benzene and then alcohol. The yield of magnesium pigment (of about 97% purity) was 6·88 g. (62%).

In another experiment, the crude material from the acetic acid treatment was thoroughly extracted with acetone and then with benzene. The latter extract was cooled, and the precipitated solid was filtered off, washed with benzene and then acetone, and dried, giving *magnesium tetra*cyclo*hexenotetrazaporphin dihydrate* (Found : C, 65·1; H, 7·0; N, 19·3; Mg, 4·2. $C_{32}H_{32}N_8Mg,2H_2O$ requires C, 65·3; H, 6·1; N, 19·0; Mg, 4·1%). When dried over phosphoric oxide in a vacuum-desiccator for 24 hours this gave the *monohydrate* (Found : C, 67·0; H, 5·8; N, 19·95. $C_{32}H_{32}N_8Mg,H_2O$ requires C, 67·3; H, 6·0; N, 19·6%). The dihydrate was boiled with pyridine, then filtered hot, and the filtrate was cooled. The precipitate was separated, washed with ether and light petroleum, and dried in a vacuum-desiccator. The hydrated pyridine *complex* crystallised in clusters of needles, blue by transmitted light but showing a pronounced purple reflex (Found : C, 68·9, 68·8; H, 6·1, 5·9; N, 19·0, 18·7; Mg, 3·5, 3·4. $C_{32}H_{32}N_8Mg,C_5H_5N,H_2O$ requires C, 68·4; H, 6·1; N, 19·4; Mg, 3·8%). A solution of the pyridine complex in pyridine was dried for several hours with phosphoric oxide, then filtered into light petroleum (previously dried with phosphoric oxide), and the microcrystalline solid was filtered off and washed as above with anhydrous solvents. The product so formed had the same composition (Found : C, 68·6; H, 6·4; N, 19·1; Mg, 3·7%).

Removal of metal from the magnesium pigment. The magnesium pigment (dihydrate) (2·33 g.) was boiled with glacial acetic acid (50 ml.) for 15 minutes, water (100 ml.) was added, and the solid separated and washed with boiling water and with alcohol. The product was extracted with acetone for 1 hour, to remove impurities, and was then extracted exhaustively with chlorobenzene. The latter extract was cooled, and the solid was filtered off, and washed with benzene and then alcohol. The yield of metal-free pigment was 1·90 g. (90%) (Found : C, 72·3; H, 6·6; N, 21·0%).

Other Metal Derivatives.—The metal-free pigment (167 mg.) was boiled in *o*-dichlorobenzene (50 ml.) with anhydrous nickel chloride (1·45 g.) for 3·5 hours, the solution was cooled, and the solid was filtered off and washed with alcohol, dilute hydrochloric acid, and finally alcohol. Recrystallisation from chlorobenzene yielded 156 mg. (85%) of *nickel tetra*cyclo*hexenotetrazaporphin* (Found : C, 65·1; H, 5·3; N, 18·8; Ni, 8·9. $C_{32}H_{32}N_8Ni$ requires C, 65·45; H, 5·5; N, 19·1; Ni, 10·0%).

The *cobalt* pigment (100 mg., 75%) was prepared similarly from the metal-free pigment (121 mg.) and cobalt acetate (1·0 g.), in boiling dichlorobenzene (50 ml.) for 40 minutes (Found : Co, 10·2. $C_{32}H_{32}N_8Co$ requires Co, 10·0%).

The magnesium pigment (dihydrate; 112 mg.) was boiled in pyridine (20 ml.) for 12 hours with copper bronze (100 mg.), and the solid was filtered off and washed with alcohol. The pigment was separated from unchanged copper bronze by extraction with chlorobenzene, the pigment crystallising almost completely from the extract. It was filtered off and washed with benzene and then with ethanol, giving *copper tetra*cyclo*hexenotetrazaporphin* (98 mg., 87%) (Found : C, 64·9; H, 5·3; N, 18·7; Cu, 10·8. $C_{32}H_{32}N_8Cu$ requires C, 64·9; H, 5·5; N, 18·9; Cu, 10·7%).

Preparation of Copper Phthalocyanine from Magnesium Phthalocyanine.—Magnesium phthalocyanine dihydrate (695 mg.) and copper bronze (440 mg.) were boiled together in quinoline (20 ml.) for 2 hours, alcohol was added, and the solid was filtered off. The crude pigment was separated from unchanged copper by dissolution in concentrated sulphuric acid and precipitation by ice in the usual manner, the yield of copper phthalocyanine being 534 mg. (76%) (Found, on sublimed material : N, 19·0; Cu, 10·9. Calc. for $C_{32}H_{16}N_8Cu$: N, 19·45; Cu 11·0%).

Palladium Phthalocyanine.—(*a*) Phthalonitrile (110 g.) and palladium black (5·8 g.) were refluxed together; blue pigment was formed almost immediately. After 48 hours the product was cooled and freed from excess of nitrile by extraction with chloroform and from unchanged palladium by flotation in chloroform. The product was then filtered off, washed with boiling ethanol, and dried (yield, 21·2 g.). It was shown spectroscopically to contain a little metal-free phthalocyanine, and was also still contaminated by traces of other solid impurity. The crude pigment (5·0 g.) was dissolved in concentrated sulphuric acid (50 ml.), the solution was filtered to remove insoluble impurities, and the filtrate poured on ice. The finely divided solid was boiled with nitric acid (20%; 50 ml.) for 5 minutes, the metal-free phthalocyanine being preferentially oxidised. The residual solid was filtered off, well washed with water and then with ethanol, dried, and crystallised from chloronaphthalene. The product showed no light absorption corresponding to metal-free phthalocyanine, the main bands in the visible region (in chloronaphthalene) being: I, 6605; II, 6335; III, 5955; IV, 5765; V, 5580 Å. I > III > II > IV > V. This *product* however had a high palladium content (Found: C, 60·3; H, 2·7; N, 17·7; Pd, 20·1. $C_{32}H_{16}N_8Pd$ requires C, 62·1; H, 2·6; N, 18·1; Pd, 17·2%). The analytical figures were little altered by further crystallisation (Found: C, 60·4, 60·3; H, 3·0, 2·9; N, 17·5; Pd, 18·8%), but after sublimation in a silica tube (compare Barrett, Dent, and Linstead, *loc. cit.*) were close to the correct values (Found: C, 61·7; H, 2·8; Pd, 17·0%). Crystallisation thus appears to give a material containing excess of palladium (? colloidal) which is only lost by sublimation.

(*b*) Metal-free tetra*cyclo*hexenotetrazaporphin (400 mg.) was refluxed in dichlorobenzene (50 ml.) with palladous chloride (2 g.) for 33 hours. The solid was filtered off and washed with ethanol, then with boiling dilute hydrochloric acid until free from palladous chloride, and finally with ethanol. The product was extracted with chlorobenzene until no further blue material was extracted. The extract from spectroscopic examination consisted of approximately equal amounts of palladium tetra*cyclo*hexenotetrazaporphin and palladium phthalocyanine. The residue was extracted with chloronaphthalene and gave 131 mg. of a pigment shown spectroscopically to be identical with palladium phthalocyanine, prepared from phthalonitrile.

*Oxidation of Tetra*cyclo*hexenotetrazaporphin.*—(a) *Hydrogen peroxide.* Tetra*cyclo*hexenotetrazaporphin (91 mg.) was dusted into concentrated sulphuric acid (2·0 ml.), the solution was cooled in ice, and hydrogen peroxide (30% solution, 10 drops) was added. When the solution was allowed to warm to room temperature the colour became green immediately and then faded, until after 10 minutes the solution was only pale brown. The solution was poured on ice and extracted continuously with ether, the extracts were dried (Na_2SO_4), and the solvent was distilled off. Light petroleum (b. p. 60—80°) extracted from the residue 46 mg. (44%) of tetrahydrophthalimide, which after recrystallisation from light petroleum had m. p. 167—168° and mixed m. p. 168—169°.

(b) *Chromic acid.* A solution of metal-free pigment (104 mg.) in sulphuric acid (2·0 ml.) was cooled in a freezing mixture and poured on ice (3 g.). Chromium trioxide (80 mg.), dissolved in the minimum amount of water, was added. The mixture was kept at room temperature for 6 minutes, by which time the pigment was completely oxidised. The solution was extracted with ether, and the imide isolated from the extracts was sublimed at 90°/14 mm. The yield of tetrahydrophthalimide was 90 mg. (75%) of m. p. 166—168° and mixed m. p. 169—170°.

A known weight (approx. 100 mg.) of metal-free pigment was dissolved in the minimum (0·5 ml.) of cold concentrated sulphuric acid and oxidised with chromium trioxide (80 mg.) as described above. The imide was removed by extraction with ether, and the ammonium salts in the residual aqueous solution were determined as in the Kjeldahl estimation (Found: 3·8, 4·15 moles of ammonia per mole of pigment).

(c) *Ceric sulphate.* 10—15 Mg. of the metal-free pigment were dissolved in concentrated sulphuric acid (5 ml.), the solution was cooled in a freezing mixture, and pure ice (20 g.) was added. A known volume of 0·01N-ceric sulphate solution was added immediately and the mixture was warmed on the steam-bath until all of the pigment was oxidised. The solution was treated at 0° with a known excess of standard ferrous ammonium sulphate solution and titrated with ceric sulphate solution, *o*-phenanthroline being used as indicator. A correction for the oxidation of tetrahydrophthalimide was made by carrying out the above operations on pure imide. Found: observed oxygen uptake (g.-atom/mole of pigment), 1·34, 1·35; corrected, 1·16, 1·23.

Absorption Spectra.—For the control of preparative work, absorption spectra in the visible region were measured on a Hilger-Nutting spectrometer. For the measurement of intensities a Unicam spectrophotometer (SP500) was used, a hydrogen lamp being employed for readings below 4000 Å and a tungsten lamp for higher wave-lengths. Solutions were prepared by boiling an accurately weighed amount (0·5—1·0 mg.) of the pigment with the solvent, cooling, and diluting to 100 ml. For the accurate measurement of the main band it was sometimes necessary to dilute the solution 4 times.

Pigment	Solvent	Absorption maxima (Å) and log $\epsilon_{max.}$			
Metal-free	PhCl	3425	5600	6000	6280
		4·84	4·63	3·99	4·79
Magnesium	C_5H_5N	3470	5505	5995	
		5·00	4·26	5·12	
	Dioxan	2750	3440	5485	5970
		4·09	4·96	4·21	5·01

Pigment	Solvent	Absorption maxima (Å) and log $\epsilon_{max.}$		
Cobalt ...	PhCl	3505	5425	5910
		4·67	4·17	4·91
Nickel ...	PhCl	3215	3400	5915
		4·55	4·54	4·77
Copper ...	$C_6H_4Cl_2$	3430	5410	5905
		4·81	4·24	5·05

Analyses were carried out in the microanalytical laboratory of the department (Mr. F. H. Oliver). For Dumas nitrogen determinations it was advisable to mix the compound with chromium trioxide to ensure complete combustion. We thank the Department of Scientific and Industrial Research for a maintenance grant (to G. E. F.) and Imperial Chemical Industries Limited, Dyestuffs Group, for gifts of chemicals.

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