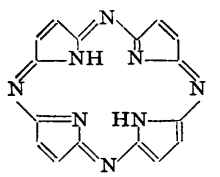
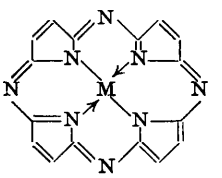
944. *Conjugated Macrocycles. Part XXII.* Tetrazaporphin and its Metallic Derivatives.*

By R. P. Linstead and Margaret Whalley.

Methods for the formation of maleic dinitrile have been studied and a routine method of preparation has been devised. Reaction of this nitrile with magnesium *n*-propoxide in *n*-propyl alcohol (and with similar reagents) leads to magnesium tetrazaporphin (II; M = Mg) in yields of up to 15%. Removal of the metal gives metal-free tetrazaporphin (I). Copper and nickel derivatives have also been prepared. The absorption spectra of these substances are given. The structure of tetrazaporphin and its relation to porphin and phthalocyanine are discussed.

The four structural cornerstones of the group of macrocyclic tetrapyrrolic pigments are porphin, tetrazaporphin, tetrabenzoporphin and phthalocyanine. Of these the last two (and compounds intermediate between them) have been described in earlier papers in this series.* Porphin has been investigated in a preliminary way by Hans Fischer and Gleim (*Annalen*, 1936, **521**, 157; cf. Rothemund, *J. Amer. Chem. Soc.*, 1936, **58**, 625). We now report the discovery of the fourth parent compound, tetrazaporphin (I) (the prefixes μ μ′ μ″ μ‴ systematically required to indicate the positions of the four entering aza-groups are omitted in this series of papers).

(I)   (II)

Many attempts to make this substance and its simple derivatives were made before the war but our only success was the preparation of its octaphenyl substitution product (A. H. Cook and Linstead, *J.*, 1937, 929). At about the same time Fischer and Endermann (*Annalen*, 1937, **531**, 245) prepared a related compound containing four methyl and four ethyl substituents in the β-positions of the pyrrole rings, which they called tetraimido-ætioporphyrin.

* Part XXI, *J.*, 1950, 2981. The earlier general title of the series (Phthalocyanines and Related Compounds) has now become too restrictive.

Our synthetic methods have throughout been based on those used in the preparation of phthalocyanines, namely, the treatment of the dinitriles or other nitrogenous derivatives of 1 : 2-dicarboxylic acids with metallic reagents. The appropriate dicarboxylic acid for the preparation of tetrazaporphin is maleic, and the obstacles to the synthesis are of three kinds: the tendency of maleic derivatives to invert to their fumaric isomerides; the intrinsic lack of stability of maleic dinitrile leading to polymerisation and other side reactions not encountered with phthalonitrile; and the lower stability of tetrazaporphin compared with phthalocyanine.

In February 1950, Mr. N. Haddock informed us privately that H. France and W. O. Jones of Imperial Chemical Industries Limited, Dyestuffs Division, had prepared metallic pigments from maleic dinitrile by the action of a metallic reagent, urea, and ammonium molybdate.* These pigments were formulated as tetrazaporphins from their general properties and method of preparation.

Our investigations, described below and in the following paper, involved different methods but gave products of the same general type as those of France and Jones.

Maleic Dinitrile.—The literature on the preparation of this compound is unsatisfactory. The nitrile reported by de Wolfe and van de Straete (*Bull. Acad. roy. Belg.*, 1935, **21**, 216) is actually the imide (Bruylants and Jennen, *ibid.*, 1936, **22**, 1141) whilst the methods of Jennen (*ibid.*, p. 1169) and of Blomquist and Winslow (*J. Org. Chem.*, 1945, **10**, 149) give small yields of impure material. We have developed a practicable method by the route: Methyl maleate ⟶ diamide ⟶ dinitrile. This process, although apparently simple, involves considerable difficulties at all stages. The published methods for the preparation of methyl maleate give products containing appreciable amounts of fumarate (de Wolfe and van de Straete, *loc. cit.*; Rinkes, *Rec. Trav. chim.*, 1927, **48**, 272; Adickes, *J. pr. Chem.*, 1943, **161**, 271). We found that if the esterification of maleic anhydride in the presence of sulphuric acid was carried out in the dark at room temperature an excellent yield of methyl maleate containing less than 1% of fumarate was obtained. This was converted into maleic diamide by passing ammonia gas into its supension in concentrated aqueous ammonia (Rinkes, *loc. cit.*). The yield was only 30%; efforts to raise it under various conditions were defeated by the tendency of the ester to invert (cf. Tanatov, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1742; Clemo and Graham, *J.*, 1930, 213). The action of liquid ammonia on methyl maleate alone or in solution in organic solvents gave an unidentified crystalline solid.

Maleic diamide was dehydrated to the dinitrile by phosphorus oxychloride in ethylene dichloride, the reagents used for the preparation of malononitrile by Surrey (*J. Amer. Chem. Soc.*, 1943, **65**, 2471). Considerable investigation of this reaction showed that maleic dinitrile could only be obtained on a routine basis if special care were paid to very thorough drying of the amide, the use of only a small excess of phosphorus oxychloride, and the final decomposition of this excess by means of bicarbonate. In this way the nitrile was not exposed to a high concentration of hot oxychloride or to aqueous hydrochloric acid. It was not possible to scale the process up satisfactorily. As a result over 70 small experiments have been carried out under the same conditions. The optimum yield of maleic dinitrile was 40%, the average 23%.

Maleic dinitrile so obtained melted at 31—32°, and had a peak at 220 mμ in the ultraviolet absorption spectrum. It was fairly rapidly isomerised by N/100-aqueous hydrochloric acid, but in comparison with maleic esters was relatively stable to light. An analytically pure sample had, however, changed completely to fumaric dinitrile, m. p. 96°, after 18 months.

A small yield of maleic dinitrile was obtained by dehydrating maleic diamide with phosphoric oxide in a mixture of triethylamine and benzene (McElvain and Clarke, *J. Amer. Chem. Soc.*, 1947, **69**, 2657, 2661). No appreciable quantity was obtained by other methods (see p. 4844).

Tetrazaporphins.—Attention was particularly directed to the preparation of derivatives containing a labile metal, such as sodium or magnesium, which could lead to the parent

* Patent application pending.

substance (cf. Barrett, Dent, and Linstead, *J.*, 1936, 1729). The main difficulty was that the nitrile was isomerised and decomposed by heat, and very rapidly decomposed under alkaline conditions. The method whereby phthalonitrile smoothly yields sodium phthalocyanine on treatment with sodium amyloxide (Linstead and Lowe, *J.*, 1934, 1022) failed when applied to maleic nitrile.

The less basic magnesium alkoxides gave positive results. Thus magnesium *iso*-amyloxide (made by an exchange reaction between magnesium ethoxide and *iso*amyl alcohol) immediately gave some blue pigment when warmed with maleic dinitrile. The yield of crystalline product, however, was low and a comparative study was therefore made of a number of alkoxides, which led to the selection of magnesium *n*-propoxide in *n*-propyl alcohol. The reaction is extremely sensitive to variations in procedure and the optimum conditions are described in detail in the Experimental section. A few illustrations may be given to show some peculiarities of the process. The magnesium is first dissolved in *n*-propyl alcohol, reaction being initiated by means of a trace of iodine. A heterogeneous dispersion of fine particles of the propoxide is thereby obtained and it appears that the pigment formation largely occurs on the surface of the solid reagent. If the nitrile is added during the reaction between the metal and alcohol the magnesium tetrazaporphin obtained is contaminated with some very similar materials. These are being further investigated and may well be more hydrogenated products. The best yields have been obtained only from small-scale experiments; scaling-up may lead to catastrophic falls in yield. In 68 experiments performed under apparently the same conditions on a 1-g. scale, the yield of magnesium pigment varied between 2 and 15%, the average being 8%. If carbon tetrachloride was used in place of iodine to activate the magnesium, the yield was decimated. No macrocyclic pigment was obtained when *iso*propyl alcohol was used in place of *n*-propyl alcohol or when maleic dinitrile was treated with *N*-methylanilino-magnesium iodide. Very little was formed when ethanol was substituted for *n*-propanol or when the magnesium reagent was amyloxymagnesium iodide in amyl alcohol (contrast Ficken and Linstead, following paper). These peculiarities arise from the complexity of the total process and the comparative instability of the radicals which may be assumed to be involved in the growth of the chain and the final cyclisation of the great ring.

Magnesium tetrazaporphin was recovered from the crude reaction product by extraction with benzene–methanol (99 : 1), followed by chromatography on alumina, elution with benzene–methanol (4 : 1) and crystallisation. Magnesium tetrazaporphin crystallises in various solvated forms, and in this respect resembles other magnesium macrocyclic pigments, *e.g.*, magnesium phthalocyanine—which forms a mono- and a di-hydrate and a pyridine-hydrate (Linstead and Lowe, *loc. cit.*; Barrett, Dent, and Linstead, *loc. cit.*)—and magnesium tetra*cyclo*hexenotetrazaporphin (Ficken and Linstead, *loc. cit.*).

The metal was best removed from magnesium tetrazaporphin by the action of glacial acetic acid at room temperature. This yielded tetrazaporphin (I) as a reddish-blue crystalline solid with a purple reflex. Analysis and spectroscopic examination showed it to be free from metal. The method used for the preparation of phthalocyanine from its magnesium derivatives—treatment with sulphuric acid and dilution with water—led to gross decomposition of the tetrazaporphin. There was also some decomposition when the reagents used were dilute hydrochloric acid or formic acid. The use of cold glacial acetic acid, however, gave a 74% yield of metal-free pigment.

Other metallic derivatives of tetrazaporphin. These have been prepared in three ways, all of which are paralleled in benzazaporphin chemistry :

(i) *From tetrazaporphin.* Copper tetrazaporphin (II; M = Cu) was readily obtained by heating the metal-free compound with copper bronze in boiling *o*-dichlorobenzene (compare the preparation of copper tetrabenzotriazaporphin, Barrett, Linstead, and Tuey, *J.*, 1939, 1810). The nickel derivative was prepared in the same way by the use of anhydrous nickel chloride. In boiling monochlorobenzene the fixation of metal was incomplete after many hours' boiling and separation of the metal-free compound from the metallic derivative proved difficult. This was probably due to the formation of mixed crystals, for which there are many precedents in this type of compound.

(ii) *By metal exchange.* When magnesium tetrazaporphin was heated with copper

bronze in boiling pyridine a direct exchange of metal occurred, to give a copper derivative identical with that already mentioned. Similar metal exchanges have been observed with magnesium naphthalocyanine (Bradbrook and Linstead, *J.*, 1936, 1748) and in the porphyrin series (Barnes and Dorough, *J. Amer. Chem. Soc.*, 1950, **72**, 4045).

(iii) *From maleic dinitrile.* Other metals form tetrazaporphin derivatives by direct reaction with maleic dinitrile, although none has been found as effective as magnesium. With nickel and copper our results confirmed those of France and Jones. Thus, when maleic dinitrile was heated with urea, anhydrous nickel chloride, ammonium molybdate, and a trace of nitrobenzene, nickel tetrazaporphin was obtained, spectroscopically and analytically identical with that recorded above. The yields in our experiments were closely dependent on the temperature and length of heating and never exceeded 2·5%. When cuprous chloride replaced nickel chloride, traces of copper tetrazaporphin, identical with that already mentioned, were obtained. Calcium *n*-propoxide in *n*-propyl alcohol gave a small amount of green product which may have contained calcium tetrazaporphin, but alkoxides of lithium, lead, and aluminium showed no evidence of the formation of metallic tetrazaporphins.

Properties. Tetrazaporphin and its magnesium, nickel, and copper derivatives are purple, crystalline solids with purple reflexes. They are considerably more soluble in organic solvents than the corresponding phthalocyanines, the magnesium compound being soluble in methanol and in pyridine, the metal-free compound in benzene, and the nickel and copper derivatives in chlorobenzene. From solutions in these solvents they crystallise in characteristic forms. The thermal stability is considerably less than that of the phthalocyanines, and good crystals have not yet been obtained by sublimation.

The solutions are intensely coloured in shades between blue and amethyst (see Table 1).

TABLE 1. *Visual colours of tetrazaporphin derivatives.*

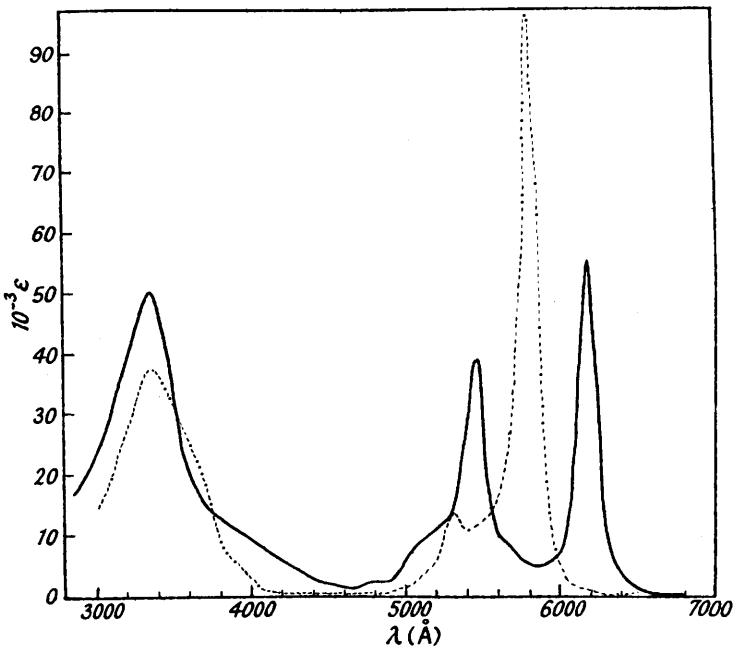
Compound	Transmitted light	Visible fluorescence	Ultra-violet fluorescence
Metal-free	Violet-blue	Red	Rose-pink
Magnesium (in hydroxylic solvents)	Blue	Red	Orange
Magnesium (in chlorobenzene)	Blue	Faint red	Faint orange
Copper	Blue	—	Pale blue
Nickel	Amethyst	—	—

Solutions of magnesium tetrazaporphin in pyridine and in hydroxylic solvents are blue to transmitted but red to reflected light and show an intense orange fluorescence in ultra-violet light. A similar but weaker visible fluorescence and a rose-red ultra-violet fluorescence are shown by solutions of metal-free tetrazaporphin in benzene or chlorobenzene. Very slight visible or ultra-violet fluorescence is shown by solutions of magnesium tetrazaporphin in hydrocarbon solvents.

The light absorption of the various pigments has been measured over the range 350—1000 mμ. Determination at lower wave-lengths was prevented by the lack of suitable solvents. There is some general resemblance in light absorption to the phthalocyanines (Anderson, Bradbrook, Cook, and Linstead, *J.*, 1938, 1151; Barrett, Linstead, Rundall, and Tuey, *J.*, 1940, 1091; see also following paper), but the spectra are simpler. Tetrazaporphin itself has two peaks of almost equal intensities at 545 and 617 mμ, whereas the metallic derivatives have an intense maximum at 580 and a smaller peak at about 540 mμ. The position of the main band is little affected by the nature of the metal but the intensities vary considerably: as with the phthalocyanines, the nickel absorbs less intensely than the copper compound. All the tetrazaporphins show a single or double maximum in the near ultra-violet region. It is proposed to review these results more fully when data from allied compounds have been accumulated. The absorption spectra are summarised in Table 2 and illustrated in the Figure.

Structure.—The structures (I) and (II) given to tetrazaporphin and its metallic derivatives (M = bivalent metal) rest upon the following evidence: (1) Elementary analyses correspond to the formulæ $C_{16}H_{10}N_8$ and $C_{16}H_8N_8M$ respectively. These are equivalent to four maleic dinitrile units ($C_4H_2N_2$) and two replaceable atoms of hydrogen. There is complete analogy with phthalocyanine, $C_{32}H_{18}N_8$, containing four phthalonitrile

units ($C_8H_4N_2$). This analogy extends to the method of preparation from the 1 : 2-dinitrile. (2) The loss and gain of metals in the tetrazaporphin molecule corresponds to that in phthalocyanine. (3) The properties of magnesium tetrazaporphin resemble closely those of magnesium derivatives of other macrocycles. In addition to the solvation already described, magnesium tetrazaporphin exhibits the striking decomposition of hot peroxide-containing hydrocarbon which gives a vivid red chemiluminescence. This is also shown by chlorophyll, and the magnesium derivatives of phthalocyanine, tetrabenzoporphin, and



——— *Metal-free tetrazaporphin (in chlorobenzene).*
– – – – *Copper tetrazaporphin (in dichlorobenzene).*

octaphenyltetrazaporphin (A. H. Cook, *J.*, 1938, 1845; Helberger and Hever, *Ber.*, 1939, **72**, 11). (4) There is an extremely close resemblance between the absorption spectra of tetrazaporphin and of tetra*cyclo*hexenotetrazaporphin. This is also shown by the corresponding metallic derivatives, and extends to even quite minor details of the absorption curves (see Fig. 1 of following paper). The only difference lies in a general slight shift to

TABLE 2.

Metal-free tetrazaporphin (in chlorobenzene).

$\lambda_{max.}$, Å	6170	5450	3330
log $\epsilon_{max.}$	4·75	4·60	4·70

Magnesium tetrazaporphin, monomethanol solvate (in methanol).

$\lambda_{max.}$, Å	5840	5360	3260	2280
log $\epsilon_{max.}$	5·03	4·17	4·79	4·26

Magnesium tetrazaporphin, dimethanol solvate (in pyridine)

$\lambda_{max.}$, Å	5870	5350	3320
log $\epsilon_{max.}$	5·07	4·14	4·70

Nickel tetrazaporphin (urea-melt) (in dichlorobenzene)

$\lambda_{max.}$, Å	5770	5300	3450	3140
log $\epsilon_{max.}$	4·85	4·20	4·57	4·44

Nickel tetrazaporphin (from metal-free) (in *o*-dichlorobenzene).

$\lambda_{max.}$, Å	5770	5300	3450	3150
log $\epsilon_{max.}$	4·77	4·14	4·50	4·38

Copper tetrazaporphin (in *o*-dichlorobenzene).

$\lambda_{max.}$, Å	5780	5310	3340
log $\epsilon_{max.}$	4·98	4·13	4·57

longer wave-lengths for the β-substituted tetrazaporphins. The close correspondence can only be explained on the basis of a near relationship in structure. The structure of tetra*cyclo*hexenotetrazaporphin has been fully established chemically (see following paper). (5) All the nitrogen atoms in tetrazaporphin are liberated as ammonia by degradation of

the pigment with chromium trioxide in sulphuric acid at 100°. It has not yet been possible to obtain significant yields of maleinimide or similar compounds by milder fission. The conditions necessary to break the great ring appear to oxidise the fission products further; traces of maleic acid [as required for formula (I)] have, however, been identified.

The formulæ (I) and (II) correspond, of course, with only one canonical state. Like the phthalocyanines, the molecules are regarded as symmetrical resonance structures. In the covalent metallic derivatives, the metal atoms are not considered as attached in some preferred manner among the four pyrrole nitrogen atoms. The extent to which the hydrogen atoms of the metal-free compound are localised must be left open at present. In terms of the molecular-orbital theory, there is an orbital of delocalised electrons corresponding to the whole of the molecule, which may be presumed to be planar. It is to this conjugated structure of the molecule as a whole, that the intense light absorption in the 600-mμ region is to be ascribed.

Experimental

Continuous extractions of macrocyclic pigments were carried out in the apparatus described by Barrett, Dent, and Linstead (*J.*, 1936, 1726), except that of magnesium tetrazaporphin which could be extracted in a normal Soxhlet apparatus.

Methyl Maleate.—Concentrated sulphuric acid (25 ml.) was added to maleic anhydride (500 g.) in methanol (1500 ml.), and the mixture left at room temperature in the dark for 2 days. Most of the methanol was removed under reduced pressure and the mixture neutralised with aqueous sodium carbonate. The organic layer was separated, washed with water, and dried (Na_2SO_4). Methyl maleate (605 g., 85%), b. p. 99—101°/18 mm., was obtained on removal of the ether. According to the data of Clemo and Graham (*J.*, 1930, 213) the proportion of methyl fumarate * appeared to be less than 1%.

Maleic Diamide.—A steady stream of ammonia was bubbled through a stirred cooled mixture of methyl maleate (300 g.) and aqueous ammonia (*d* 0·880; 900 ml.). The reaction mixture was kept in the dark. After about 0·5 hour a white solid began to separate and after 4·5 hours the reaction was complete. The solid was filtered off and dried over phosphoric oxide in a vacuum-desiccator, giving maleic diamide, m. p. 171—173° (72 g., 30%). Fumaric diamide, m. p. 267° (20 g., 8%), separated from the filtrate overnight.

Methyl Maleate and Liquid Ammonia.—Liquid ammonia (15 ml.) was added to a solution of methyl maleate (10 g.) in chloroform (50 ml.) or methanol (50 ml.). After 24 hours, the solvent was removed. The solid residual *substance* crystallised from methanol in colourless prisms, m. p. 72—74° (3·6 g.) (Found: C, 47·6; H, 6·2; N, 5·0%). Methyl fumarate (1·75 g.) was obtained on concentration of the mother-liquors.

Maleic Dinitrile.—Freshly distilled phosphorus oxychloride (34·5 g., 1·15 mol.) was added dropwise during 1 hour to a boiling stirred suspension of maleic diamide (22 g.) and sodium chloride (dried at 80° for 1 hour) (50 g.) in ethylene dichloride (redistilled from phosphoric oxide) (63 ml.). Stirring and refluxing were continued for 2 hours 50 minutes, the mixture gradually becoming black. The black solid was filtered off and washed with ethylene dichloride or chloroform, and the filtrate added slowly to a stirred saturated aqueous solution of sodium hydrogen carbonate. The organic layer was separated, washed thoroughly with water, dried (Na_2SO_4), and filtered through charcoal. After removal of the solvent, maleic dinitrile, b. p. 110—112°/20 mm., was obtained (maximum yield, 6·1 g.; average, 3·5 g.). Maleic dinitrile, purified by further distillation and crystallisation from ethanol, gave colourless prisms, m. p. 31—32° (Found: C, 61·9; H, 2·7; N, 35·6. Calc. for $C_4H_2N_2$: C, 61·6; H, 2·6; N, 35·9%).

The following methods gave little or no dinitrile: dehydration of maleic amide by phosphoric oxide alone, by phosphorus pentachloride in toluene, or by acetic anhydride or by 3 : 5-dinitrobenzoyl chloride in pyridine (Mitchell and Ashby, *J. Amer. Chem. Soc.*, 1945, **67**, 161); decomposition of diazoacetonitrile with copper bronze (Loose, *J. pr. Chem.*, 1909, **79**, 508); dehydration of maleic dialdoxime; bromination of succinonitrile, followed by dehydrobromination.

Magnesium Tetrazaporphin.—Magnesium (0·5 g.) dissolved in refluxing *n*-propanol (20 ml.) during 7 hours, the reaction being initiated by a crystal of iodine. Maleic dinitrile (1·0 g.) in

* Methyl fumarate has been reported to have an irritating effect on the skin. We observed a definite vesicant action.

n-propanol (5 ml.) was added during 5 minutes and the mixture refluxed for a further 17 minutes. The mixture became green, then ink-blue. The propanol was removed under reduced pressure and the dry solid continuously extracted with benzene containing 1% of methanol. The extract was chromatographed on alumina (Spence, type H), and the pigment, which was adsorbed in a narrow band at the top of the column, eluted with benzene–methanol (4 : 1). Concentration of the eluate gave 180—230 mg. of solid magnesium tetrazaporphin, the purity of which could be estimated spectroscopically and was generally about 75%.

Magnesium tetrazaporphin monomethanolate was obtained as purple plates by re-extraction with benzene and chromatography as before (Found : C, 55·0; H, 3·6; N, 30·7; Mg, 7·1. $C_{17}H_{12}ON_8Mg$ requires C, 55·4; H, 3·3; N, 30·4; Mg, 6·6%). Recrystallisation of this monosolvate from aqueous pyridine gave rhombohedral plates of *magnesium tetrazaporphin dimethanolate* (Found: C, 54·4; H, 4·5; N, 28·3; Mg, 6·2. $C_{18}H_{16}O_2N_8Mg$ requires C, 54·0; H, 4·0; N, 28·0; Mg, 6·1%).

Metal-free Tetrazaporphin (I).—Magnesium tetrazaporphin (110 mg.) was added in portions to glacial acetic acid (3 ml.), and the mixture set aside with occasional stirring for 1·5 hours. Ice was added, and the solid filtered off, washed with water and boiling methanol, and continuously extracted with benzene. Metal-free *tetrazaporphin* (70·5 mg., 74%) crystallised in dark purple needles (Found : C, 61·7, 60·9; H, 3·5, 3·9. $C_{16}H_{10}N_8$ requires C, 61·2; H, 3·2%). Analyses for nitrogen are given below.

Copper Tetrazaporphin.—(a) *From metal-free tetrazaporphin.* Metal-free tetrazaporphin (48·5 mg.) was dissolved in *o*-dichlorobenzene (40 ml.), and copper bronze (1·5 g.) added. The mixture was refluxed for 3 hours, cooled, and filtered. The solid was extracted with chlorobenzene, and *copper tetrazaporphin* (19 mg., 33%) crystallised from the extract (Found : C, 50·4; H, 3·0; Cu, 16·9. $C_{16}H_8N_8Cu$ requires C, 51·1; H, 2·1; Cu, 16·9%).

(b) *From magnesium tetrazaporphin.* Magnesium tetrazaporphin (20 mg.) and copper bronze (1·0 g.) in pyridine(10 ml.) was refluxed for 1 hour by which time the visible and ultra-violet fluorescence of the magnesium pigment had disappeared. The pyridine was removed under reduced pressure and the solid extracted with chlorobenzene. Copper tetrazaporphin (9 mg., 45%) crystallised from the extract.

(c) *By the urea-melt method.* A mixture of maleic dinitrile (1·0 g.), cuprous chloride (1·0 g.), urea (4·0 g.), ammonium molybdate (0·1 g.), and nitrobenzene (2 ml.) was heate drapidly to 135° and kept at that temperature for 35 minutes, with cooling when necessary. After about 3 minutes at 135° the nitrobenzene layer became olive-green and after a further 5 minutes deep purple. The black solid was cooled, broken up with hot water, and washed with water and ethanol. The dried residue was then extracted with chlorobenzene, giving copper tetrazaporphin (2 mg., 0·1%).

Nickel Tetrazaporphin.—(a) *From metal-free tetrazaporphin.* Metal-free tetrazaporphin (37 mg.) and anhydrous nickel chloride (1·5 g.) were refluxed in *o*-dichlorobenzene (25 ml.) for 1·5 hours, and the mixture was filtered hot. The solid was washed with boiling water and ethanol, and extracted with chlorobenzene. *Nickel tetrazaporphin* crystallised in small, bronze rods (27 mg., 86%) (Found : C, 52·0; H, 2·6; N, 30·1; Ni, 15·6. $C_{16}H_8N_8Ni$ requires C, 51·8; H, 2·2; N, 30·2; Ni, 15·8%).

(b) *By the urea-melt method.* Maleic dinitrile (2·0 g.), nickel chloride (2·0 g.), urea (12·0 g.), ammonium molybdate (0·4 g.), and nitrobenzene (8 drops) were heated together, with continuous stirring in the early stages, at 125° for 1·75 hours. The solid was cooled, and broken up with hot water. It was then warmed at 90° with 5N-hydrochloric acid for 1·5 hours, filtered, and washed with hot water and ethanol. The residue was extracted with ethanol for 4 hours, then chlorobenzene for 8—10 hours. Nickel tetrazaporphin (59·6 mg., 2·5%) was obtained, spectroscopically and analytically identical with the above.

Oxidation of Tetrazaporphin.—Metal-free tetrazaporphin (about 30 mg.) was dissolved in concentrated sulphuric acid (0·5 ml.), and chromium trioxide (100 mg.) added. The mixture was heated for 1 hour at 100° and diluted with a little water. The solution was made alkaline with 20% sodium hydroxide solution, and the ammonia distilled off in steam and collected in a known volume of 0·1N-hydrochloric acid. The excess of acid was titrated with 0·1N-sodium hydroxide, screened methyl-red being used as indicator (Found : N, 36·2, 34·8, 34·9. $C_{16}H_{10}N_8$ requires N, 35·7%).

Absorption Spectra.—Routine control of preparative work was carried out by means of a Hilger-Nutting visual spectrometer. Intensity measurements were made with a Unicam spectrophotometer (SP. 500), a hydrogen lamp being used for readings below 4000 Å and a tungsten lamp for the visible and near infra-red regions. Solutions containing about 0·7 mg.

of pigment in 100 ml. of solvent were used. Dilution of these to quarter strength was necessary to obtain accurate readings for the maxima of the copper and the magnesium compounds. The results are in Table 2 and graphically in the Figure.

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