214. *Phthalocyanines. Part III. Preliminary Experiments on the Preparation of Phthalocyanines from Phthalonitrile.*

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As has been indicated (Part II), *o*-phthalonitrile was not at first thoroughly investigated as a source of phthalocyanines because preliminary experiments with magnesium oxide, which yields a pigment with great facility when heated with *o*-cyanobenzamide, had shown no comparable reaction. Moreover, it was at first believed that the formation of pigment proceeded through the fixation of metal by an acidic hydrogen atom.

In 1931, Heilbron and Irving directed our attention to the reaction between *o*-dibromobenzene, cuprous cyanide, and pyridine, first studied by de Diesbach and van der Weid (*Helv. Chim. Acta*, 1927, **10**, 886), who formulated the intensely blue, insoluble product as a complex pyridine salt, $[C_6H_4(CN)_2,C_5H_5N]_2Cu$. The same substance was also formed from phthalonitrile, cuprous bromide, and pyridine, and Heilbron and Irving suggested that it might in reality be a copper phthalocyanine. Furthermore, they showed that sodamide reacted with phthalonitrile in quinoline at 150° to yield some 15% of a substance resembling metal-free phthalocyanine in properties. We are greatly indebted to Professor Heilbron for communicating these facts to us.

We find that many metals and metallic derivatives react with phthalonitrile to yield compounds of the phthalocyanine type. The reaction is generally more ready with the nitrile than with *o*-cyanobenzamide, but magnesium oxide and antimony are exceptions in this respect. In the most favourable cases the reaction proceeds with considerable evolution of heat: it may become uncontrollable when large quantities of reagents are used. The temperature necessary to start the reaction varies from 135° to the boiling point of the nitrile (294°) according to the nature of the metal and its availability (see p. 1027). A general examination of the capacity of metals for combination with phthalonitrile is in progress, but the results of preliminary work may be classified as follows:

(A) *The following react readily*: Sodium, sodium amyloxide; magnesium; copper, cuprous chloride, cupric chloride; ferric chloride; nickel, nickel chloride.

(B) *The following react less readily or give poorer yields*: Sodamide, sodium methoxide, sodium ethoxide, sodium *cyclo*hexyloxide; potassium amyloxide; calcium amyloxide; magnesium oxide; antimony; cuprous and cupric oxides, cupric acetate.

(C) *The following do not appear to react*: Sodium hydroxide, sodium phenoxide, sodium chloride, potassium hydroxide; magnesium chloride; antimony chlorides; phosphorus chlorides; manganese and its salts; iodine.

The reactions which were studied in more detail are described below.

Copper. The product of the reaction between cuprous chloride, phthalonitrile, and pyridine resembled that isolated by de Diesbach and van der Weid, but yielded no pyridine on fusion with alkali, and could indeed be more easily prepared from the nitrile and cuprous chloride in the absence of this base. It cannot, therefore, have the structure assigned to it by these workers and is in fact crude copper phthalocyanine. The copper compounds presented many features of interest and were made the subject of a separate study by Mr. C. E. Dent (Part IV).

Magnesium. The pure metal reacted only slowly below the boiling point of the nitrile. The product was magnesium phthalocyanine identical with that already prepared. It yielded the same free phthalocyanine on treatment with sulphuric acid. The yields of the magnesium pigment were variable and there was an indication of the formation of a by-product (p. 1025).

Forms of Magnesium Phthalocyanine.—This compound has been prepared by the action of magnesium on (i) phthalimide and ammonia, (ii) *o*-cyanobenzamide, (iii) phthalonitrile, and (iv) phthalocyanine. The products of the four reactions, after being exhaustively extracted with organic solvents and crystallised from quinoline, are of constant composition (the percentages tabulated below were found each for a different preparation) :

Magnesium phthalocyanine (dihydrate).

	C.	H.	N.†	Mg.
From phthalimide	67·3, 67·8, 67·7 *	3·7, 3·4, 3·7 *	19·5 19·4	4·5, 4·4
,, cyanobenzamide	67·7, 67·7 *	3·7, 3·7 *	—	4·3, 4·2
,, phthalonitrile	67·3, 67·1, 67·7 *	3·7, 3·7, 3·6 *	19·5	4·1, 4·0
,, phthalocyanine	67·8	3·6	—	4·5
Calc. for $C_{32}H_{16}N_8Mg,2H_2O$	67·1	3·5	19·6	4·2
,, ,, $C_{32}H_{16}N_8Mg,H_2O$	69·3	3·3	20·2	4·4
,, ,, $C_{32}H_{16}N_8Mg$	71·6	3·0	20·9	4·5

* Schoeller. † Kjeldahl method.

The most carefully purified samples gave the figures in best agreement with the dihydrate formula. Two atoms of oxygen are therefore present in the molecule for each atom of magnesium. They must be very loosely held, because the compound readily yields oxygen-free phthalocyanine and is easily formed from this and from phthalonitrile. The most reasonable ways in which they can be combined are as water, taken up from the aqueous solvents during purification, or as oxygen, taken up from the air during the preparation. That the oxygen is present as water is proved by the following facts :

(i) No oxygen is liberated when the magnesium compound is converted by sulphuric acid into phthalocyanine, neither is a persulphuric acid formed.

(ii) The quantitative oxidation of the magnesium compound with ceric sulphate (p. 1036) proves that there is no oxygen available for oxidation in the molecule.

(iii) When magnesium phthalocyanine is heated, as, for example, by boiling a suspension in decalin, water is slowly eliminated. It is difficult to obtain a completely anhydrous compound, $(C_8H_4N_2)_4Mg$, as there is a tendency for gross decomposition of the complex. On one occasion a sample was obtained which gave analytical figures corresponding closely to those required for anhydrous magnesium phthalocyanine, but usually only partly dehydrated products were obtained even after prolonged heating.

This partly dehydrated magnesium compound was less stable than the original dihydrate. It was considerably more soluble in boiling quinoline and pyridine than all other phthalocyanines, and from these solutions it separated with base of crystallisation (B) as a complex of the general composition $(C_8H_4N_2)_4Mg,H_2O,B$. The heterocyclic base was readily eliminated by heating the complex or by treating it with dilute acid, the dihydrate being regenerated. The dehydrated substances present an instructive contrast with the stable dihydrate, which shows no tendency to take up quinoline on crystallisation, and it would appear that the unit $(C_8H_4N_2)_4Mg$ shows a general tendency to co-ordinate with two, but not more than two, " solvent " molecules.

The view that water is present in ordinary magnesium phthalocyanine finds additional support in the results of special preparative experiments. The preparation from phthalonitrile and magnesium was first carried out in an atmosphere of nitrogen, the excess of metal removed with dilute acid in the usual way, and the product finally crystallised from quinoline in an atmosphere of nitrogen (in other words, the compound was allowed to take up water but no oxygen) : the product was the ordinary magnesium compound (the dihydrate). In a second experiment, the reverse conditions obtained; free access of air was permitted, but the washing with dilute acid was omitted : the product was unstable and absorbed quinoline during the crystallisation. Another sample of crude magnesium phthalocyanine was purified in two ways. A portion was treated with dilute acid and crystallised from quinoline; this gave the dihydrate. The remainder was crystallised from quinoline direct and gave a complex containing the base.

Alkali Metals.—During experiments on the direct reduction of phthalonitrile to phthalocyanine, it was noticed that a solution of sodium amyloxide in amyl alcohol reacted rapidly with the nitrile at 140° to give, ultimately, a product containing a small amount of sodium (*ca.* 1%) which could be eliminated by acid. The yield is good and the process constitutes a convenient method for the laboratory preparation of phthalocyanine. It appears to be immaterial whether the sodium amyloxide is pre-formed or whether the metal is added to a solution of the nitrile in amyl alcohol.

Potassium reacted similarly to sodium but less readily. The product contained a small amount of metal, which was removed by sulphuric acid to yield free phthalocyanine. The reaction with calcium appeared to yield a product intermediate in properties between that from magnesium and those from the alkali metals; zinc chloride reacted in the same manner as cupric chloride. The investigation of these reactions and those with other metals is being continued.

Mechanism of the Formation of the Phthalocyanines.—No intermediate products have been isolated during the formation of phthalocyanines from phthalonitrile or cyanobenzamide and the mechanism of the reactions is only partly understood. The combination of phthalonitrile and copper and similar reactions appear to be simple additions, but when cyanobenzamide is used dehydration must also occur and some at least of the water is used up in the hydrolysis of the cyanoamide into phthalimide and ammonia. Alkalis such as sodium amyloxide do not produce phthalocyanines from cyanobenzamide, because the amide group is rapidly hydrolysed. On the other hand, magnesium oxide reacts only very slowly with phthalonitrile (because of the difficulty of breaking the metal–oxygen link), but readily produces magnesium phthalocyanine from cyanobenzamide. It is probable that in this case preliminary salt formation occurs with the cyanoamide. The formation of free phthalocyanine from phthalonitrile and sodium amyloxide and similar reagents probably occurs through the preliminary production of a sodium phthalocyanine. This must be accompanied by the oxidation of some organic material—(?) of amyl alcohol to valeric acid. The manner in which antimony produces phthalocyanine from cyanobenzamide is obscure and we have not yet observed the formation of the metal-free compound in the complete absence of mineral matter.

EXPERIMENTAL.

Phthalonitrile prepared by prolonged boiling of phthalamide with an excess of acetic anhydride is contaminated with phthalimide and other products (Braun and Tcherniac, *loc. cit.*). The conditions necessary for obtaining it in consistently good yields are not yet known. In the most successful preparation, 330 g. of the pure diamide were boiled vigorously under reflux for 5 hours with 1140 c.c. of acetic anhydride. The bulk of the acetic acid and anhydride was neutralised while hot with aqueous caustic alkali, and the solution was made alkaline when cold. The nitrile was washed with water, dried (235 g.), and distilled under reduced pressure from a flask with a wide-mouthed receiver sealed to the neck, a tube leading to the pump being sealed to the receiving flask. This apparatus prevented choking by solidification of the distilled nitrile. The distillate (190 g.) had m. p. 136—137°, and 141° after one crystallisation from benzene.

Reaction with Magnesium.—Dry recrystallised phthalonitrile (m. p. 141°), pure magnesium turnings (Grignard), and carefully dried solvents were used in the following typical experiments.

(i) 32 G. of the nitrile were boiled with 2 g. of magnesium for 5 hours. The unchanged nitrile was extracted with benzene, and the residue washed with hydrochloric acid, water, alcohol, and ether (yield, 12·6 g.). After being dried at 100° for 15 hours, 10 g. were boiled with 150 c.c. of quinoline; the solution, filtered from 4·5 g. of undissolved pigment and allowed to crystallise over phosphoric oxide in a desiccator, deposited the pure dihydrate (Found: C, 67·25; H, 3·7%).

(ii) As in (i). Benzene extracted 25 g. of nitrile and left 5 g. of pigment. This was boiled with concentrated hydrochloric acid for 5 minutes and crystallised twice from pyridine [Found: (once crystallised) C, 67·8; H, 3·7; (twice crystallised) C, 67·1; H, 3·7; N, 19·5; Mg, 4·1%].

(iii) A suitably fitted flask containing 23 g. of the nitrile and 1·5 g. of magnesium was evacuated and filled with nitrogen, the operation being repeated twice. The mixture was then boiled for 6 hours and cooled in a current of the gas. Excess of nitrile (19 g.) was removed with benzene, and excess of metal with dilute acid. The pigment (3·5 g.) was finally crystallised from quinoline in an atmosphere of nitrogen in a special apparatus which permitted the complete exclusion of air during dissolution, filtration, and crystallisation. The crystals contained C, 67·3; H, 3·7; Mg, 4·0%.

(iv) Exactly as in (i). Time of boiling, $\frac{3}{4}$ hour. The product was extracted with boiling benzene and crystallised from quinoline without preliminary extraction with hydrochloric acid. The product (Found: C, 69·8; H, 3·4; Mg, 4·0%) contained quinoline, which was evolved on gentle warming.

(v) The nitrile (30 g.) was boiled with 2·5 g. of magnesium for 4 hours in a flask fitted with a calcium chloride tube. Boiling benzene removed 10 g. of unchanged nitrile. The residue (22 g.) of pigment and metal was divided into two parts: one part contained quinoline after crystallisation from dry quinoline (Found: C, 71·0; H, 3·9; N, 18·5, 18·5; Mg, 3·75%); the other part was treated with dilute acid, boiled with water, dried, and crystallised from quinoline (Found: C, 67·95; H, 3·7%).

(vi) (Formation of by-product). 95·6 G. of the nitrile and 4 g. of magnesium were boiled for 4 hours. During the last 30 minutes the mixture became almost solid. The product was washed with alcohol and hydrochloric acid and extracted with acetone (Soxhlet). The residue (80 g.) was much duller than previous products, owing to the presence of a *polymeride* of phthalonitrile, which was removed by prolonged extraction with acetic acid (Soxhlet) and crystallised from this solvent in straw-coloured needles, m. p. 296° [Found: C, 75·0 *; H, 3·1 *; N, 21·3; ash, 1·1. $(C_8H_4N_2)_x$ requires C, 75·0; H, 3·1; N, 21·9%]. This substance gave a yellow solution in sulphuric acid, yielded no ammonia when boiled with caustic soda, and gave no phthalocyanine pigment when heated alone or with sodium amyloxide or with fresh magnesium metal. It is therefore undoubtedly a by-product and not an intermediate in the formation of the phthalocyanine. The residue (67 g.) after the removal of this substance had the usual bright blue colour of magnesium phthalocyanine.

Conversion into Phthalocyanine.—The magnesium compound prepared from the nitrile was treated with sulphuric acid in the manner already described. The product after careful removal of the acid was crystallised from quinoline [Found: C, 74·6; H, 3·6. Calc. for $(C_8H_4N_2)_4H_2$: C, 74·7; H, 3·5%].

*Action of Heat on Magnesium Phthalocyanine (Dihydrate *).*—Analytically pure material was used for the typical experiments described below.

(1) A sample was heated at 116° for 358 hours [Found: loss, 3·2. Calc. for loss of $1H_2O$, 3·15%. Found in the residue: C, 68·2; H, 3·7; N, 20·2; Mg, 4·2. Calc. for $(C_8H_4N_2)_4Mg,H_2O$: C, 69·3; H, 3·3; N, 20·2; Mg, 4·4%] (Sample I).

(2) 2 G. of the magnesium compound were suspended in 200 c.c. of sodium-dried decalin, which was slowly distilled at 180°, a constant level of liquid being maintained by addition from a dropping-funnel; 460 c.c. of decalin were distilled during 25 hours. The residue was washed with light petroleum and dried in an oven ($\frac{1}{2}$ hour) and in a vacuum desiccator (Found: C, 68·4; H, 3·6%).

(3) 22·5 G. were heated as before for 20 hours in boiling decalin (original volume, 160 c.c.; total distillate, 775 c.c.). The distillate, particularly at first, coloured anhydrous copper sulphate, unlike the original decalin (Found in the residue: C, 71·1; H, 3·5; N, 20·8; Mg, 4·3%).

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* The presence of water in this compound was first suspected from the fact that during estimations of carbon and hydrogen water collected at the end of the combustion tube almost immediately after the substance was first heated and well before any actual burning could be observed.

Magnesium Compounds containing a Base [*compare also preparations* (*iv*) *and* (*v*) *above*].—(*a*) Partly dehydrated magnesium phthalocyanine (sample I above) was crystallised from dry quinoline, dissolution and crystallisation being unusually easy (Found: C, 72·2; H, 3·7; N, 18·6; Mg, 3·5%).

(*b*) A partly dehydrated product (2) prepared by the decalin method (Found: C, 70·2; H, 3·5; N, 19·5; Mg, 4·5%) was unaffected by boiling benzene, the extract containing neither phthalimide nor phthalonitrile. This shows that there was no gross decomposition during the dehydration. 10 G. of this product were crystallised from 100 c.c. of redistilled dry quinoline. There was a gain in total weight; 5·9 g. remained undissolved and 5·0 g. (carefully washed and dried) crystallised from the filtrate. The undissolved portion was dissolved in the boiling mother-liquor; 5·5 g. crystallised on cooling. The united crystals were recrystallised twice from boiling quinoline and the product was freed from adhering base by extraction of the finely ground material with hot light petroleum for 7 hours (Soxhlet). The sample was analysed after being left for some time in a vacuum at room temperature. It tended to lose quinoline in the steam-oven {Found: C, 71·8 *; H, 4·0 *; N, 18·6; Mg, 3·3; compare the product from (*a*) above. The magnesium compound containing one molecule of quinoline and one molecule of water " of crystallisation," *i.e.*, [$(C_8H_4N_2)_4Mg,H_2O,C_9H_7N$], requires C, 72·0; H, 3·9; N, 18·5; Mg, 3·5%}.

(*c*) 2 G. of sample (2) were boiled with dry pyridine (50 c.c.), and the filtered solution allowed to crystallise. The crystals were washed with ether, extracted for 22 hours with light petroleum, and freed from petroleum in a vacuum desiccator (yield, 1·8 g.) [Found: C, 69·4*; H, 3·8 *; N, 19·7; Mg, 4·0. $(C_8H_4N_2)_4Mg,H_2O,C_5H_5N$ requires C, 70·2; H, 3·6; N, 19·9; Mg, 3·8%].

Both the *quinoline* and the *pyridine* compound resemble the ordinary dihydrate in general appearance, but show an even stronger purple lustre in the crystalline form. They are more soluble in the respective bases than is the dihydrate. When the solids are gently warmed, the base is eliminated. For instance, the quinoline compound prepared in experiment (*b*) above was heated for 4 hours at 140°; the loss in weight corresponded to the elimination of two-thirds of the theoretical amount of quinoline. The expelled quinoline was identified as the dichromate.

Reaction with Sodium.—(1) Phthalonitrile (1 g.-mol.), either alone or as a saturated solution in amyl alcohol, was added to sodium (1 g.-atom) dissolved in the minimum quantity of boiling amyl alcohol. An immediate yellow colour formed, which rapidly changed to an intense green when the solution was boiled. On continued boiling, the solution darkened and the walls of the flask became coated with a lustrous film of phthalocyanine. After 1 hour at 135—140° the mixture was diluted with alcohol and the liquid was filtered. The residue was boiled several times with more alcohol to remove a brown impurity and was finally washed with dilute acid and boiling water. The lustrous powder obtained left about 1% of ash on ignition. After careful dissolution in sulphuric acid and reprecipitation with ice in the manner described for the magnesium compound, pure phthalocyanine was obtained free from mineral matter. The yield varied from 50 to 75%; too prolonged boiling produced more of the brown impurity. The material had the properties of phthalocyanine and crystallised from quinoline in bronze needles which appeared translucent and blue under a microscope [Found: C, 74·5; H, 3·8; N, 21·5. Calc. for $(C_8H_4N_2)_4H_2$: C, 74·7; H, 3·5; N, 21·8%].

(2) 0·2 G. of sodium was added to a boiling solution of phthalonitrile (10 g.) in amyl alcohol (10 c.c.). The mixture was boiled for $\frac{1}{4}$ hour and worked up as before. The yield was variable (40—50%). The product after treatment with sulphuric acid gave a good yield of phthalocyanine. A similar experiment with 2 g. of sodium yielded 8 g. of product, 6·9 g. of which with sulphuric acid gave 5·3 g. of phthalocyanine.

(3) Sodium (1 g.) was dropped in small portions into the molten nitrile (10 g.) at 150°, a semi-solid mass being obtained. The mixture was cooled, treated with 100 c.c. of ethyl alcohol, boiled, and filtered, and the residue washed thoroughly with alcohol to remove the brown impurity. Yield, 4 g. of a blue solid.

(4) To 10 g. of phthalonitrile, dissolved in 30 c.c. of boiling amyl alcohol, 3·5 g. of sodamide were added in small portions. The heat of reaction was sufficient to keep the alcohol boiling. The mixture after the usual treatment yielded 3·3 g. of crude phthalocyanine.

(5) Phthalonitrile (5 g.) was added to 0·2 g. of sodium in 20 c.c. of absolute alcohol. A yellow colour developed, but there was no formation of phthalocyanine after 20 minutes' boiling. The alcohol was removed; the residue, when " baked " at about 200° with a free flame, rapidly developed the colour of phthalocyanine. When the mass had become hard, it was worked up in the usual way and yielded 3 g. of crude phthalocyanine.

Sodium methoxide reacted similarly to the ethoxide. A solution of sodium in boiling *cyclo*hexanol gave a poor yield of phthalocyanine, and sodium phenoxide gave only resinous products.

Reaction with Other Metals.—(1) Potassium (0·5 g.) was dissolved in amyl alcohol (30 c.c.) and 10 g. of phthalonitrile were added to the cold solution. The solution became bright green when warmed, but after a few minutes' boiling the colour changed to a dirty brown. After 30 minutes' boiling, the mixture was worked up in the manner described for the reaction with sodium amyloxide, 6·5 g. of a dull-looking pigment being obtained which left a slight ash containing potassium. 5 G. of this material after the sulphuric acid treatment gave 1·7 g. of phthalocyanine free from mineral matter.

(2) A mixture of calcium turnings (0·5 g.), amyl alcohol (30 c.c.), and phthalonitrile (10 g.) was boiled under reflux for 5 hours. The development of colour was slow. Worked up in the usual manner, the product yielded 2·2 g. of impure calcium phthalocyanine as a dark blue, lustrous powder (Found: Ca, 4·7%). 2 G. of this on treatment with sulphuric acid gave 1·8 g. of calcium-free phthalocyanine.

(3) Phthalonitrile (20 g.) was gently refluxed over a stick of zinc chloride (10 g.) suspended from the neck of the flask by a spiral of platinum wire. An intense green colour formed instantaneously as the fused zinc chloride dripped into the nitrile. After 30 minutes, the semi-solid mass was extracted with boiling alcohol and boiling water. 14·5 G. of a dark blue powder were obtained which contained chlorine and 10·2% of zinc. The metal was not eliminated by treatment with sulphuric acid.

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