215. *Phthalocyanines. Part IV. Copper Phthalocyanines.*

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Phthalonitrile combines readily at high temperatures with metallic copper and many of its compounds to yield phthalocyanines. The reaction with the metal begins at 190°, and proceeds vigorously at 210° with evolution of heat to give *copper phthalocyanine* in excellent yield as a bright blue compound with a purple lustre. There is no apparent side reaction and the uncombined nitrile may be recovered. The reagents are used up in the ratio of 1 atom of metal to 4 molecules of nitrile, in agreement with which the product gives analyses corresponding to $(C_8H_4N_2)_4Cu$.

The tendency to form this compound is great and the readiness with which the various compounds of copper react appears to be determined by the ease with which they can supply the metal. This is clearly illustrated by the reaction between phthalonitrile and the two chlorides of copper. When cuprous chloride (1 equivalent of CuCl) and 4 molecules of the nitrile were heated together without special precautions, a copper phthalocyanine was obtained which contained chlorine. To determine the fate of the chlorine, the reaction was repeated under carefully controlled conditions in a stream of nitrogen, the issuing gas being passed through silver nitrate solution. Pigment formation commenced at 150°, but hydrogen chloride was not eliminated below 200°. Much heat was then evolved and hydrogen chloride came off in quantity. The pigment formed contained chlorine but the uncombined phthalonitrile did not, and the recovered copper chloride was mainly in the cupric state. The quantities of the products and their content of chlorine and copper suggested that the reaction was a combination of the two processes :

$$\text{(A) at 150—180°}: 4C_8H_4N_2 + Cu_2Cl_2 = (C_8H_4N_2)_4Cu + CuCl_2$$
$$\text{(B) above 200°}: 4C_8H_4N_2 + CuCl_2 = (C_8H_4N_2)_3Cu(C_8H_3N_2Cl) + HCl.$$

This was proved to be correct by the experimental realisation of the two isolated reactions (A) and (B). Cuprous chloride combined smoothly with phthalonitrile at about 170° in the ratio $2CuCl : 4C_8H_4N_2$ and one half of the copper remained behind as cupric chloride. The pigment formed was copper phthalocyanine, practically free from chlorine and identical with that prepared from metallic copper. Cupric chloride reacted only above

200° with the evolution of one half of the chlorine as hydrogen chloride and the formation of *copper monochlorophthalocyanine*, $C_{32}H_{15}N_8ClCu$.

In the second process the chlorine undoubtedly enters one of the benzene nuclei in the phthalocyanine complex and cannot be removed without complete disruption of the molecule. Fission with nitric acid yields a mixture of phthalimide and a chlorophthalimide but no chloride ion, showing the independence of the chlorine from the copper. The chlorine is probably in the 4-position.

The readiness with which cuprous chloride combines with phthalonitrile is due without doubt to the ease with which it can supply metallic copper, whereas the only way in which cupric chloride can act as a source of copper is by losing chlorine simultaneously. It is a clear indication of the great tendency for the formation of the phthalocyanine complex that so unlikely a reaction as nuclear halogenation should take place in this way. The almost explosively exothermic nature of the reaction also illustrates the tendency for the production of the phthalocyanine.

The formation of copper phthalocyanine from copper oxides, acetate, sulphide, and sulphate does not call for special comment, but it is worthy of note that copper sulphide appeared to provide copper for the reaction by liberating sulphur, there being no nuclear substitution. Similarly, the use of the sulphate did not give any nuclear sulphonation. None of these substances was as satisfactory in practice as the metal or the chlorides.

The relationship between copper phthalocyanine and the other members of the group, which is indicated by their general resemblance in physical properties and mode of formation, is proved by the following facts: (1) Free phthalocyanine, when heated with metallic copper in boiling quinoline, yields a copper compound identical with that prepared from phthalonitrile. (2) Nitric acid decomposes copper phthalocyanine to give phthalimide in good yield, together with copper and ammonium nitrates. (3) A similar decomposition is effected by dilute acid permanganate.

Copper phthalocyanine is even more stable than the other compounds of this series and in this respect must be classed among the most remarkable of organic compounds. It resists the action of molten potash and of boiling hydrochloric acid. It dissolves in concentrated sulphuric acid and is precipitated unchanged and in almost quantitative amount by dilution with water. It is exceptionally resistant to heat and at about 580° it may be sublimed at low pressure in an atmosphere of nitrogen or carbon dioxide. The sublimate is beautifully crystalline and analytically pure. The substance also sublimes with some decomposition in air at atmospheric pressure. It is an indication of the remarkable nature of the compound that an apparatus of hard glass or silica is necessary for these operations. In contrast with this, the monochloro-copper compound cannot be sublimed, but is decomposed with the evolution of hydrogen chloride. This supports the formula assigned to the substance and renders it improbable that it is an inseparable mixture of one part of a fully chlorinated copper phthalocyanine with three parts of unsubstituted copper phthalocyanine.

EXPERIMENTAL.

Preparation of Copper Phthalocyanine from Phthalonitrile and Copper.—A mixture of the nitrile (4 g.-mols.) and copper-bronze (1 g.-atom) was heated (oil-bath) with stirring in a wide glass tube. A green colour first formed at 190°, the mass became pasty at 220° and was too stiff to be stirred at 270° (10 minutes). At a bath temperature of about 220°, the internal temperature began to mount rapidly and at times exceeded that of the bath by 45°. The mass was left for another 5 minutes in the bath, cooled slightly, and ground with alcohol. The finely powdered product was repeatedly boiled with alcohol until the washings were colourless and contained no phthalonitrile; it was then dried. Yield, 75—90% of the weight of nitrile. The product still contained uncombined copper-bronze, which could be removed by means of sulphuric acid.

The finely ground pigment (*w* g.) was dusted into concentrated sulphuric acid (10*w* g.) at room temperature with mechanical stirring. After an hour, the solution was filtered through sintered glass, the funnel washed with more acid, and the filtrate and washings poured in a thin stream with thorough stirring on ice (100*w* g.). The flocculent blue precipitate was allowed to coalesce for 2—3 hours, collected, washed with boiling water (about 100*w* g.), drained (pump), boiled with alcohol, and dried at 100°, 90—95% of the original crude pigment being recovered (Sample I). The solution in sulphuric acid was stable; a sample kept for 2 days at room temperature gave a 92% recovery of *copper phthalocyanine.*

The reaction between the nitrile and copper also proceeded well in boiling quinoline or α-methylnaphthalene. The pigment was precipitated as fast as formed as a crystalline product with a beautiful reflex. It could be separated from the excess of copper by shaking it with alcohol; the metal sank and the pigment, which remained in suspension, could be poured off. Repetition of this process gave analytically pure material (Sample II).

The following comments may be made on the analysis of this and similar products: *Carbon and hydrogen*: Owing to sublimation the substance can be burnt completely within ½ hour. *Nitrogen*: Macro-Kjeldahl. *Copper*: The pigment (0·3 g.) was heated with concentrated nitric acid (5 c.c.) until a clear solution was obtained. 10 C.c. of water were then added and the solution was boiled to expel nitrous fumes, the complete removal of which was ensured by the addition of bromine water (5 c.c.), followed by the removal of the bromine by boiling. The solution was cooled, treated with an excess of ammonia, boiled to remove most of this, and then acidified with acetic acid. To the cold solution an excess of saturated potassium iodide solution was added and the liberated iodine was titrated with $N/20$-sodium thiosulphate (with starch as an external indicator). Phthalic acid separated during the titration, if not before, but did not interfere with the result. The percentage of copper was calculated in the usual way. Direct ashing gave results about 1% low owing to loss by sublimation and the presence of cuprous oxide in the ash. *Chlorine*: Reaction for 6 hours by the Carius method gave somewhat divergent results, but the values obtained by the following application of Liebig's method were concordant. The pigment (0·4 g.) was heated with lime for 1½ hours with the usual precautions. The contents of the tube were washed into water and completely neutralised with an excess of nitric acid. The solution was filtered from a dark green, insoluble product, and the soluble chloride estimated gravimetrically in the filtrate and washings. The precipitation of silver chloride followed the removal of the green product fairly rapidly, as there was a tendency for the solution to deposit finely divided phthalic acid on standing, which was difficult to eliminate.

Copper phthalocyanine yielded the following results. Sample I: C, 66·9; H, 2·8; N, 19·1; Cu, 11·0. Sample II: C, 67·1; H, 3·0; N, 18·9; Cu, 11·15 ($C_{32}H_{16}N_8Cu$ requires C, 66·7; H, 2·8; N, 19·5; Cu, 11·0%).

Phthalocyanines from Copper Chlorides and Phthalonitrile.—(a) *Cuprous chloride and phthalonitrile in the ratio* 1CuCl : $4C_8H_4N_2$. An intimate mixture of 12·8 g. of the nitrile and 2·5 g. of dry cuprous chloride was heated in a flask fitted with an air-condenser, a thermometer, and an inlet-tube for nitrogen, the last two reaching to the bottom. The flask was slowly heated in a bath while nitrogen was passed through it into a solution of silver nitrate. The course of the reaction has been described on p. 1027. At its conclusion the flask was swept free from hydrogen chloride and the residue was broken up and boiled successively with alcohol, dilute sulphuric acid, alcohol, and ether. Yield of pigment, 9·95 g. The total chloride in the combined washings was precipitated as silver chloride. The liberated hydrogen chloride yielded 0·84 g. of silver chloride (equiv. to 0·21 g. of chlorine) and the residual chloride in the flask yielded 1·94 g. of silver chloride (equiv. to 0·48 g. of chlorine). Therefore the chlorine combined in the pigment = original chlorine less 0·69 g. = 0·21 g. This is exactly equivalent to that evolved as hydrogen chloride; hence there has been simple substitution. The chlorine combined in the pigment is $100 \times 0{\cdot}21/9{\cdot}95 = 2{\cdot}11\%$. A fully chlorinated pigment with 1 atom of chlorine to $4C_8$ units would contain 5·83% of chlorine. The pigment being taken to contain 11% of copper, the uncombined copper and chlorine remaining are in the atomic ratio 1 : 1·7 (see equations A and B, p. 1027).

(b) *Cuprous chloride and phthalonitrile in the ratio* 2CuCl : $4C_8H_4N_2$. Reaction was effected exactly as before and proceeded smoothly below 200° without appreciable elimination of hydrogen chloride. The weight of pigment obtained was 105·5% of that of the nitrile taken, representing a 94% yield on equation A. It was practically free from chlorine.

(c) *Cupric chloride and phthalonitrile in the ratio* $CuCl_2 : 4C_8H_4N_2$. The chloride (dried at 100°) showed no sign of reaction with phthalonitrile below about 200° Hydrogen chloride was first evolved at an internal temperature of 200° and a bath-temperature of 215°; the temperature of the melt then rose very rapidly to 280° and the reaction was complete in 5—10 minutes. The product was isolated, by the same method as was used in the case of cuprous chloride, in yields of 80—90% (equation B). It could be purified by precipitation from a sulphuric acid solution in the manner already described, the recovery being 91—92% (Found: N, 18·0; Cl, 5·7; 6·1; Cu, 10·5. $C_{32}H_{15}N_8ClCu$ requires N, 18·4; Cl, 5·8; Cu, 10·4%).

Reaction of Other Copper Compounds with Phthalonitrile.—Cuprous oxide gave a 21% yield of copper pigment after 30 minutes' heating at 150—215°. The product was crystalline and had all the general properties of copper phthalocyanine.

Cupric sulphide reacted rapidly at 200—215° to give a 61% yield of a blue pigment with the properties of a phthalocyanine but containing sulphur even after purification with sulphuric acid (Found : Cu, 22·4; S, 6·1%). After a second treatment with sulphuric acid the substance contained Cu, 19·0; S, 4·1, 4·1%. (Analyses for sulphur were carried out by decomposing the compound with nitric acid and estimating the sulphur as sulphate. The same result was obtained by fusion with sodium peroxide.) If the copper content of pure copper phthalocyanine (11·04%) is deducted from the two sets of figures given above, the copper : sulphur ratios are 11·4 : 6·1 and 8·0 : 4·1, respectively, and the atomic ratios are 1Cu : 1·06S and 1Cu : 1·04S. It therefore appears very probable that the product is ordinary copper phthalocyanine contaminated with copper sulphide which is unexpectedly difficult to remove. In agreement with this, both samples evolved hydrogen sulphide on treatment with boiling hydrochloric acid.

Cupric acetate (dried at 100°) reacted readily at 150—195° to give 65% of crude copper phthalocyanine of rather dull appearance. This contained a brown impurity which yielded a brown solution in alkali.

Copper sulphate (dried at 150°) reacted at 175—185°. The product after being washed with alcohol dissolved partially in boiling water. The insoluble residue (32%) contained a trace of sulphur and had the properties of copper phthalocyanine. The clear blue aqueous solution was colloidal. It deposited a flocculent blue precipitate on the addition of salt or alkali and exhibited Tyndall's effect.

Conversion of Phthalocyanine into the Copper Derivative.—Phthalocyanine was treated for 30 hours with an excess of copper-bronze in boiling quinoline. The beautifully crystalline product was washed free from quinoline and the excess of copper was removed by treatment with sulphuric acid in the manner already described (Found : C, 66·2; H, 2·9; N, 19·4; Cu, 11·2. Calc. for $C_{32}H_{16}N_8Cu$: C, 66·7; H, 2·8; N, 19·5; Cu, 11·0%).

Properties of Copper Phthalocyanine.—The finely powdered or dispersed compound is bright blue, free from a green shade. It is less soluble in boiling quinoline than other phthalocyanines and cannot be conveniently crystallised from this solvent. When, however, it is prepared in the presence of quinoline, it is microcrystalline and has a fine purple lustre. The solution in concentrated sulphuric acid is dark green.

Action of heat. Copper phthalocyanine can be heated under reduced pressure to 500° without change. Sublimation commences at 550° and is rapid at 580° (Whipple platinum resistance thermometer). The vapour is deep pure blue and the crystals, which have the usual purple lustre, may be obtained up to 1 cm. in length. Similar results are obtained in an atmosphere of nitrogen or carbon dioxide at ordinary pressure (Found : C, 66·7; H, 2·9; N, 19·6; Cu, 11·1. Calc. for $C_{32}H_{16}N_8Cu$: C, 66·7; H, 2·8; N, 19·5; Cu, 11·0%). The process is tedious and only small quantities can be collected at a time. When the copper pigment is heated in air, some sublimes apparently unchanged, but the major part is burnt. The compound is also decomposed by heating it fiercely in an evacuated silica tube; a mirror of copper is sometimes obtained on the side of the vessel.

Fission. The compound (1 g.) was heated rapidly with concentrated nitric acid (4 c.c.). Nitrous fumes were evolved and an intermediate compound with a strong purple colour was transitorily formed. As soon as solution was complete, the mixture was diluted with four parts of water and filtered hot from a little resin. Pure phthalimide separated in needles from the cold solution (m. p. and mixed m. p. 228°). The yield after 45 minutes' standing of the solution was only 50% of that calculated on the assumption that phthalimide was the sole organic product, but after 24 hours an 80% yield could be isolated. An even better recovery was obtained from the substituted analogue (below). This fission is also readily effected by acid permanganate and by ceric sulphate (p. 1038).

Copper monochlorophthalocyanine resembles the unsubstituted copper compound in general properties, but is very slightly greener in shade. When heated under reduced pressure, the substance decomposed with evolution of hydrogen chloride. On treatment with nitric acid in the manner already described, a yield of over 90% of a mixture of phthalimide and a chlorophthalimide was obtained and the mother-liquor contained no chloride. The mixed imides melted at about 204° and were inseparable by fractional crystallisation from water, chloroform, or benzene; or by fractional acidification of their solutions in alkali.

The mixture was hydrolysed with boiling alkali to the mixed acids, which were converted into the methyl esters. The mixed esters were carefully fractionated, but the chlorine content of the highest fraction only rose to 4·8, 4·9% ($C_{10}H_9O_4Cl$ requires Cl, 15·4. $C_{10}H_9O_4Cl + 3C_{10}H_{10}O_4$ requires Cl, 3·85%). Fractional sublimation of the mixed anhydrides was also attempted, and a small amount of a more volatile anhydride, m. p. 96°, was obtained. This was not pure 4-chlorophthalic anhydride (m. p. 98°), as it depressed the melting point of an authentic specimen. Nevertheless, in view of the fact that the esterification proceeded as readily as that of unsubstituted phthalic acid, the 4-position for the chlorine atom seems more probable than the 3.

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[*Received, May* 22*nd*, 1934.]