189. *Phthalocyanines. Part XI. The Preparation of Octaphenylporphyrazines from Diphenylmaleinitrile.*

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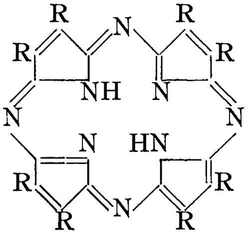
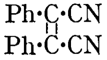
We have been engaged for some years in these laboratories on attempts to synthesise compounds containing the simple porphyrazine system (I). The general method of attack has been to treat the nitrogenous derivatives of acids of the maleic series with metallic reagents, under conditions which result in the formation of phthalocyanines from the corresponding derivatives of phthalic acid. Experiments on various maleic acids of the aliphatic and alicyclic series are still in progress; in the present paper we describe the first successful syntheses.

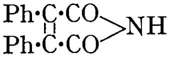
(I.)*





$$\begin{matrix}\mathrm{Ph\cdot C\cdot CN}\\ \|\\ \mathrm{Ph\cdot C\cdot CN}\end{matrix}$$

(II.)



$$\begin{matrix}\mathrm{Ph\cdot C\cdot CO}\\ \|\\ \mathrm{Ph\cdot C\cdot CO}\end{matrix}\!\!>\!\mathrm{NH}$$

(III.)

Diphenylmaleinitrile (II) is especially suitable for the preparation of porphyrazines because it is comparatively easily obtained, is stable in the *cis*-form, and has a high thermal stability (even at 300° there is no detectable conversion into the *trans*-form). The *cis*-configuration follows from the ease of conversion into the imide (III) or, *via* the acid, into the corresponding anhydride.

When the nitrile is heated with metallic derivatives such as cuprous chloride, stannous chloride, or litharge at about 250° or with metallic magnesium or copper at 270—275°, vigorous exothermic reactions occur with the production in excellent yield of intensely green metallic octaphenylporphyrazines. The reactions are parallel to those of phthalonitrile (Dent and Linstead, J., 1934, 1027; Barrett, Dent, and Linstead, J., 1936, 1719), but a higher temperature is required for their inception. The reaction with the bivalent metals is the simple one: $4C_{16}H_{10}N_2 + \text{Met.} \longrightarrow (C_{16}H_{10}N_2)_4\text{Met.}$ Cuprous chloride gives a monochlorinated porphyrazine by the reaction $4C_{16}H_{10}N_2 + Cu_2Cl_2 \longrightarrow (C_{16}H_{10}N_2)_3Cu(C_{16}H_9N_2Cl) + Cu + HCl$ even when it is used in excess. Phthalonitrile gives an almost entirely *unchlorinated* pigment under these conditions, and nuclear chlorination appears to be more easily effected in the present series.

The parent octaphenylporphyrazine could not be easily prepared through the sodium compound, as in the phthalocyanine series (Linstead and Lowe, J., 1934, 1022), for example, by heating the nitrile with sodium amyloxide, owing to the facility of hydrolysis to diphenylmaleinimide (III). On the other hand, the series resembles the phthalocyanine and porphyrin in that the metal is eliminated by the action of suitable acids on the *magnesium* derivative to yield the parent *octaphenylporphyrazine* (I, R = Ph). This reaction is not

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* In the metallic derivatives a bivalent metal, as usual, takes the place of the two imino-hydrogen atoms inside the great ring.

always straightforward. The use of sulphuric acid leads to sulphonation of the phenyl groups, and the best results are obtained with boiling dilute hydrochloric acid. Formic acid has a considerable solvent action, the metal is quickly removed, and the free porphyrazine is isolated as a *diformate*, which yields the parent compound on treatment with alkali. If acetic or oxalic acid is used in place of formic acid, magnesium octaphenylporphyrazine yields a salt without elimination of the metal. This property of forming a salt with an organic acid has not been so far observed in the phthalocyanine group, although zinc phthalocyanine yields a hydrochloride (Barrett, Dent, and Linstead, *loc. cit.*). We do not know which of the two types of nitrogen atom is concerned in these salt formations.

Octaphenylporphyrazine and its metallic derivatives are purplish-black microcrystalline solids, yielding green amorphous powders. Of the compounds studied, the tin derivative was the dullest, the metal-free and the copper compound intermediate, and the magnesium derivative the brightest green. Unlike the corresponding phthalocyanines, these substances are appreciably soluble in cold organic solvents, such as benzene and acetone, forming emerald-green solutions. They could not be obtained in a macrocrystalline form from these solutions, or by sublimation, and were best purified by chromatographic adsorption on alumina from a benzene solution, followed by elution with pyridine. The various members of the group were not adsorbed equally easily and the magnesium and the copper derivative could be sharply separated in this way. The porphyrazines appear to be the first complex synthetic pigments to have been purified by this method. It is not applicable to phthalocyanines owing to their insolubility.

These compounds are given the porphyrazine structure, analogous to that now definitely established for phthalocyanine, for the following reasons: (i) The method of preparation is exactly analogous to that of phthalocyanines and proceeds smoothly without side reaction. (ii) Analyses correspond to the type $(C_{16}H_{10}N_2)_4H_2$ or $(C_{16}H_{10}N_2)_4Met^{II}$. (iii) Cryoscopic determinations of molecular weights (in camphor) support this formula. These were not possible in the phthalocyanine group, for which molecular weights were obtained with great difficulty in one case ebullioscopically (Linstead and Lowe, J., 1934, 1031) and, more generally, from a combination of *X*-ray measurements and elementary analysis of the metallic derivatives (Robertson, Linstead, and Dent, *Nature*, 1935, **134**, 506). (iv) There is a general resemblance in chemical properties, in the resistance to heat, alkalis, and, to some extent, acids. The metallic derivatives are comparable in stability.

A distinctive property of the octaphenylporphyrazines is their resistance towards oxidation by acid ceric sulphate, which oxidises phthalocyanines smoothly to phthalimide. The magnesium derivative, however, rapidly reduced potassium permanganate in warm acetone. Derivatives of diphenylmaleic acid could not be isolated, the oxidation product being benzoic acid. This reaction serves to show that there has been no interaction between the phenyl groups, for example, with the formation of a phenanthrene arrangement.

Solutions of magnesium octaphenylporphyrazine, but apparently not those of the copper derivative, show a beautiful rose-red fluorescence in ultra-violet light. This is paralleled in the phthalocyanine and the porphyrin group and will form the subject of a future communication.

Treatment of *p*-nitrophenylacetonitrile with sodium methoxide and iodine yielded *di*-p-*nitrophenylmaleinitrile*. This condensed with copper and with magnesium at about 300° to yield octa(nitrophenyl)porphyrazines, almost indistinguishable from the corresponding un-nitrated compounds, except that solutions of the magnesium derivative of the nitrophenylporphyrazine do not fluoresce. This is a normal result of the introduction of a nitro-group. The derived di-*p*-aminophenylmaleinitrile did not appear to yield similar pigments.

EXPERIMENTAL.

Analytical Notes.—Consistent values for the carbon and hydrogen content of octaphenylporphyrazine derivatives were obtained when the substance in the combustion boat was covered with a layer of potassium dichromate. Without this, the results were low and irregular. In macro-Dumas determinations of nitrogen, combustion had to be very prolonged to give satisfactory results; normal micro-Dumas estimations were always low. All the porphyrazine derivatives described were dried at 100° for at least 3 hours.

Diphenylmaleinitrile (II).—The method of Chalenay and Knoevenagel (*Ber.*, 1892, **25**, 288; cf. Ramart-Lucas and Hoch, *Ann. Chim.*, 1930, **13**, 385) was improved as follows: A cold solution of sodium (18·4 g.) in methanol (300 c.c.) was dropped during 30 minutes into an ice-cooled, stirred mixture of iodine (101·6 g.), phenylacetonitrile (46·8 g.), and ether (1500 c.c.). The product was washed successively with water, dilute sodium thiosulphate solution and water and dried over sodium sulphate. Removal of the solvent left an impure orange-coloured, often lachrymatory, solid. Direct crystallisation was tedious and wasteful. Rapid vacuum distillation yielded phenylacetonitrile (3 g.), a lachrymatory fraction boiling up to 150°/18 mm., probably mainly iodophenylacetonitrile (9 g.), and 20—22 g. (50%) of diphenylmaleinitrile, b. p. 230—235°/18 mm., which solidified to a faintly yellow, crystalline mass. This melted at 156—158° and was sufficiently pure for preparative purposes. Crystallisation from benzene gave pure white needles, m. p. 158°. The crude orange dinitrile could also be purified by adsorption of the impurities on alumina from a benzene solution.

Diphenylmaleinitrile exhibits some remarkable colour reactions apparently not directly related to the formation of porphyrazines described later; *e.g.*, cold sodium ethoxide in alcohol or benzene produces an intense green colour which fades after some 20 minutes to a yellow. The yellow solution in benzene becomes on acidification a magnificent blue with a red fluorescence, but this colour also fades in a few hours. The only solids isolable from these solutions were diphenylmaleinimide (III) and unchanged dinitrile. After 20 minutes at 80° mixtures of the nitrile with sodium alkoxides had become intensely green and yielded the imide contaminated with a little octaphenylporphyrazine. The yield of pigment by this process was very poor. The imide produced in these experiments was identified by m. p. 213°, alone and admixed with material prepared by the method of Reimer (*Ber.*, 1881, **14**, 1800), and by analysis (Found: C, 76·4; H, 4·6. Calc.: C, 77·1; H, 4·4%).

Magnesium and Metal-free Octaphenylporphyrazines.—A mixture of 5 g. of the nitrile and 0·5 g. of magnesium powder was heated to 275° (salt-bath temperature). The melt became intensely green and after 10 minutes had set to a crystalline mass with a fine purple sheen. The product was ground, freed from excess of metal with 25% acetic acid, and then digested with hot 10% caustic soda solution to break down the acetate of the complex (see below) and to hydrolyse unchanged nitrile. The resulting *magnesium octaphenylporphyrazine* was washed thoroughly with hot water and dried. Yield, 4·8 g. (92%) of a purplish-black powder (Found: C, 81·5; H, 4·3; N, 11·75; Mg, 2·5. $C_{64}H_{40}N_8Mg$ requires C, 81·35; H, 4·2; N, 11·9; Mg, 2·6%). The magnesium was determined as MgO after oxidation with nitric acid and ignition.

A solution of 0·6 g. of the compound in 300 c.c. of benzene was run through a 20 × 1·5 cm. column of Merck alumina (*nach Brockmann*). The chromatograph was obtained as a broad green band separating minute quantities of brown impurities. The green zone was eluted with pyridine, the solution concentrated under reduced pressure to 30 c.c. and poured into 120 c.c. of hot water, and the precipitated porphyrazine filtered off, washed, and dried; yield, 0·47 g. of a blue-black powder (Found: C, 81·5; H, 4·3; N, 11·7; *M*, in camphor, 890, 930. $C_{64}H_{40}N_8Mg$ requires *M*, 944).

Magnesium octaphenylporphyrazine is slightly soluble in alcohol, more easily in chloroform, benzene, acetone and *cyclo*hexanone, and readily in pyridine and quinoline. The solutions are emerald-green with a magnificent red fluorescence, destroyed by acids and heat. It separated from benzene as a microcrystalline powder, but could not be obtained macrocrystalline. Like other compounds of the series, it could not be sublimed in a vacuum and the m. p. was very high and indefinite. The solution in sulphuric acid was intensely violet, and on dilution with ice gave sulphonated metal-free derivatives. Attempted quantitative oxidation with acid ceric sulphate (Dent, Linstead and Lowe, J., 1934, 1038) gave no useful results.

A solution of 500 mg. of the magnesium compound in 50 c.c. of pyridine was boiled with a solution of an equal weight of anhydrous oxalic acid in a little pyridine. The colour rapidly changed through olive-green to brown and a solid was deposited. After a few minutes the solution was cooled, and the oxalate collected and washed with water; yield, 320 mg. of an insoluble black crystalline powder. Reconversion of the salt into its components is effected quantitatively by hot aqueous alkali carbonate and to a small extent by a large excess of boiling pyridine. The regenerated pigment still contains its magnesium. A similar series of reactions is effected by the use of acetic acid.

500 Mg. of magnesium octaphenylporphyrazine were boiled for 2 hours with 100 c.c. of 85% formic acid. Dilution of the brownish-green solution yielded a brown solid, which was washed thoroughly with pyridine and water and dried. *Octaphenylporphyrazine diformate* formed a brownish-black, crystalline, almost insoluble powder, which was free from magnesium (Found:

C, 77·8; H, 4·3; N, Kjeldahl, 11·7. $C_{64}H_{42}N_8,2H_2CO_2$ requires C, 77·9; H, 4·5; N, 11·1%). Treatment of the salt with caustic alkali gave the free porphyrazine, easily detected by its solubility in pyridine and its intense colour, which was more conveniently prepared as follows: 500 Mg. of the magnesium compound were boiled for 3 hours with 100 c.c. of 15% hydrochloric acid; the greenish solid was filtered off and treated similarly for a further 3 hours. The solid was dried and dissolved in 250 c.c. of benzene, and a small amount of unchanged magnesium derivative separated by chromatographic adsorption on alumina. The magnesium compound was preferentially adsorbed. The main band was eluted with warm pyridine, the extract concentrated, and free *octaphenylporphyrazine* (I, R = Ph) precipitated by the addition of water (Found: C, 83·3; H, 4·65; N, 12·5. $C_{64}H_{42}N_8$ requires C, 83·3; H, 4·6; N, 12·2%). It resembles the magnesium compound in solubility and appearance, but the colour is less bright and the solutions do not appear to be fluorescent. Vacuum sublimation was impossible.

Copper Derivatives.—5·0 G. of diphenylmaleinitrile were heated at 275° with 0·5 g. of copper-bronze (more reactive than reduced copper) for 15 minutes. The solidification of the melt and the development of a purple reflex were similar to but less marked than those observed in the reaction with magnesium. The product was finely ground and extracted from unreacted metal with boiling pyridine. The pyridine solution was concentrated to 60 c.c. and poured into 200 c.c. of boiling water, and the precipitated *copper octaphenylporphyrazine* was filtered off, washed and dried (4·2 g.). Subsequent analyses showed this product to be pure, but as a precaution it was subjected to chromatographic adsorption. A solution of 0·5 g. in 300 c.c. of benzene gave a broad green band when passed through a 1·5 × 20 cm. column of alumina. This was eluted with pyridine, and the pigment precipitated as before and crystallised from benzene, yielding a greenish-black crystalline powder (Found: C, 78·2; H, 4·2; N, 11·1; Cu, 6·9, 6·5; *M*, in camphor, 950. $C_{64}H_{40}N_8Cu$ requires C, 78·1; H, 4·1; N, 11·4; Cu, 6·5%; *M*, 983). Copper was determined by oxidation with a mixture of nitric and sulphuric acids, followed by iodometric titration.

The metal in this compound and that described below was very firmly bound, and not removed by the methods used for the magnesium compound. The colour was comparatively dull and the solution did not fluoresce. The compound was remarkably stable to acids and withstood fusion with caustic potash in the air.

4·0 G. of diphenylmaleinitrile reacted vigorously with cuprous chloride (1·0 g.) at 250°. Hydrogen chloride was evolved and the melt became red, then greenish-black, and finally solidified. After 15 minutes the product was isolated in the same way as the simple copper compound, except that the solid was finally isolated by evaporation of a chloroform solution, instead of by crystallisation from benzene. *Copper monochloro-octaphenylporphyrazine* formed shining black scales, giving green solutions, and was practically indistinguishable from the unchlorinated compound (Found: C, 75·5; H, 3·9; N, 10·8; Cl, 3·6; Cu, 6·6; *M*, in camphor, 1050, 970. $C_{64}H_{39}N_8ClCu$ requires C, 75·4; H, 3·8; N, 11·0; Cl, 3·5; Cu, 6·3%; *M*, 1018).

Nuclear-substituted Compounds.—Di-*p*-nitrophenylmaleinitrile, m. p. 268°, was prepared in 56% yield by Heller's method (*Annalen*, 1904, **332**, 258) from *p*-nitrophenylacetonitrile ("Organic Syntheses," **2**, 57).

The nitro-nitrile reacted with explosive violence with metallic copper at 280°. On the small scale a product was isolated showing the typical properties of the compounds already described and a colour and absorption spectrum almost identical with those of the unsubstituted pigment. 4·0 G. of dinitrophenylmaleinitrile were heated with 1 g. of magnesium for 3 hours at 280° and a further 3 hours at 300°. The finely ground product was freed from metal with dilute acetic acid, and precipitated from a pyridine solution with boiling water; yield, 1·8 g. It was purified by the chromatographic method in the manner already described. *Magnesium octa*-p-*nitrophenylporphyrazine* was finally isolated by evaporation of a benzene solution as a dark green powder, with a similar colour and spectrum to those of the un-nitrated magnesium compound. The solutions were not fluorescent (Found: C, 59·1; H, 2·7; N, 17·6; Mg, 1·7. $C_{64}H_{32}O_{16}N_{16}Mg$ requires C, 58·9; H, 2·5; N, 17·2; Mg, 1·8%).

Di-*p*-aminophenylmaleinitrile was prepared by Heller's method (*loc. cit.*). This compound is not very suitable for porphyrazine formation, as it sublimes without melting above 300°. Qualitative experiments with cuprous chloride, zinc chloride, litharge, magnesium and copper both alone and in the presence of inert solvents have so far given no evidence of the formation of a porphyrazine.

Oxidation of Magnesium Octaphenylporphyrazine.—To a solution of 500 mg. of the compound in 500 c.c. of warm acetone, finely powdered potassium permanganate was added with shaking. The first portions were quickly reduced and much more of the reagent was decomposed than that required for a simple oxidative fission. The solution was left at room temperature with an excess of permanganate for 3 days, by which time the characteristic fluorescence in ultra-violet light had disappeared. The product was filtered off and decolorised with sulphur dioxide, and the solvent removed under reduced pressure. The acidic portion was separated by means of sodium bicarbonate as usual and purified by sublimation, benzoic acid being identified by m. p. and mixed m. p.

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