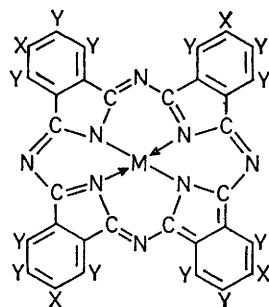# Polyfluoroarenes. Part XIV.[1] Synthesis of Halogenophthalocyanines

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Tetrafluorophthalonitrile reacts with a variety of metals and metal halides to give halogenophthalocyanines. The reaction with zinc, zinc bromide, or zinc iodide gives zinc hexadecafluorophthalocyanine in good yield, but zinc chloride, iron(III) chloride, and aluminium chloride react to give mixtures of polychloropolyfluorophthalocyanines. Copper(II) hexadecafluorophthalocyanine may be obtained from the reaction of copper, copper(I) chloride, or copper(II) chloride with tetrafluorophthalonitrile, and a similar reaction with tin(II) chloride yields dichlorotin(IV) hexadecafluorophthalocyanine. A new route to zinc phthalocyanine itself and the first syntheses of zinc hexadecachlorophthalocyanine and chloroiron(III) hexadecachlorophthalocyanine are described.

THE phthalocyanines have aroused great interest since their characterisation in 1933,[2] and their technological importance is now considerable.[3] The physical and chemical properties of the halogenated derivatives, particularly the polychloro-compounds, are often significantly different from those of the unsubstituted compounds,[3a] but few fluorine-containing phthalocyanines have hitherto been described. Fluorination of phthalocyanines or halogenophthalocyanines with elemental fluorine and anhydrous hydrogen fluoride gives low yields of mixtures of phthalocyanines containing up to seven fluorine atoms per molecule,[4] whilst trifluoromethyl-substituted phthalocyanines have been obtained from copper(II) phthalocyaninetetracarboxylic acid and sulphur tetrafluoride [5] and from the reaction of 3,4-dichlorobenzotrifluoride with copper(I) cyanide.[6] The preparation of copper(II) hexadecafluorophthalocyanine (I) has also been claimed in the patent literature,[7] and iron(II) hexadecafluorophthalocyanine has been reported recently.[8] Polyfluorophthalocyanine derivatives of zinc, copper, tin, iron, and aluminium are described here.

(I) M = Cu, X = Y = F
(II) M = Zn, X = Y = F
(III) M = Zn, X = Cl, Y = F
(IV) M = Zn, X = Y = H
(V) M = Zn, X = Y = Cl
(VI) M = SnCl$_2$, X = Y = F
(VII) M = FeCl, X = Y = Cl

Zinc Halogenophthalocyanines.—Zinc hexadecafluorophthalocyanine (II) is obtained in 87% yield from the reaction of tetrafluorophthalonitrile with zinc dust in boiling α-chloronaphthalene. The resulting purple crystals, which yield a bright blue powder when crushed, are presumed to be analogous to the product obtained by similar treatment of phthalonitrile itself. The general similarity of the absorption spectra in the visible region of zinc phthalocyanine and zinc hexadecafluorophthalocyanine in concentrated sulphuric acid (Figure) is particularly striking.

Zinc hexadecafluorophthalocyanine is extremely thermally stable and sublimes at 600° *in vacuo* to yield a blue vapour, which condenses to a sublimate of analytical purity. Oxidative degradation with boiling concentrated nitric acid or hot chromic acid gives tetrafluorophthalimide, but acidified aqueous cerium(IV) sulphate is ineffective. Like the copper derivative

$$C_{32}F_{16}N_8Zn \xrightarrow{[o]} \text{tetrafluorophthalimide}$$

(II)

(45—75%)
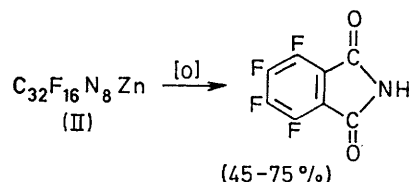
(I),[7] zinc hexadecafluorophthalocyanine is thus considerably more stable to oxidation than its hydrocarbon analogue, which is oxidised easily to phthalimide at room temperature by all three reagents.

The zinc compound (II) is soluble * in α-chloronaphthalene and in aliphatic ketones, such as acetone and pentan-2-one, to give a blue solution. It is apparent, therefore, that the sixteen fluorine atoms on the perimeter of the phthalocyanine molecule confer unique solubility on the system, since the hydrocarbon analogue, and indeed all other nonsubstituted transition-metal phthalocyanines, are completely insoluble in ketones. In common with the majority of phthalocyanines, the perfluoro-compound (II) is also soluble in concentrated sulphuric acid and may be precipitated unchanged by the addition of water.

The reaction of tetrafluorophthalonitrile with the theoretical quantity of either zinc iodide or zinc bromide in the absence of a solvent at 250° for 1½ hours also

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* The term ' soluble ' is applied here when the compound under consideration imparts a colour to the solvent.

[1] Part XIII, J. M. Birchall, R. N. Haszeldine, and J. G. Speight, *J. Chem. Soc.* (C), 1970, 2187.
[2] R. P. Linstead, *Brit. Assoc. Advance. Sci. Rep.*, 1933, 465; *J. Chem. Soc.*, 1934, 1016.
[3] F. H. Moser and A. L. Thomas, (a) ' Phthalocyanine Compounds,' Reinhold Pub. Corp., New York, 1963; (b) *J. Chem Ed.*, 1964, **41**, 245.
[4] U.S.P. 2,227,628/1941 (*Chem. Abs.*, 1941, **35**, 2738).
[5] U.S.P. 3,006,921/1961 (*Chem. Abs.*, 1962, **56**, 10,171).
[6] U.S.P. 2,225,441/1940 (*Chem. Abs.*, 1941, **35**, 2337).
[7] B.P. 1,037,657/1966 (*Chem. Abs.*, 1966, **65**, 13,854f).
[8] J. G. Jones and M. V. Twigg, *Inorg. Chem.*, 1969, **8**, 2018.

gives zinc hexadecafluorophthalocyanine [77 or 85% yield based on nitrile converted (67 or 90%), respectively]. Almost the calculated quantity of free halogen is evolved during these reactions and a substantially pure product is obtained following a simple extraction procedure.

$$4C_6F_4(CN)_2 + ZnX_2 \longrightarrow C_{32}F_{16}N_8Zn + X_2$$
$$X = I \text{ or } Br$$
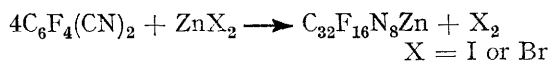
However, the reaction of tetrafluorophthalonitrile with zinc chloride (mole ratio, 4 : 1) at 250° for 7 hours leads to conversion of only 38% of the nitrile into zinc fluoride, elemental chlorine, and a mixture of zinc polychloropolyfluorophthalocyanines of the following approximate composition. Oxidative degradation of the products with hot chromic acid produces a mixture of substituted phthalimides in the yields given. This indicates that the original material is mainly zinc

$$4C_6F_4(CN)_2 + ZnCl_2 \longrightarrow C_{32}Cl_4F_{12}N_8Zn + ZnF_2 + Cl_2$$

$$\downarrow [O]$$
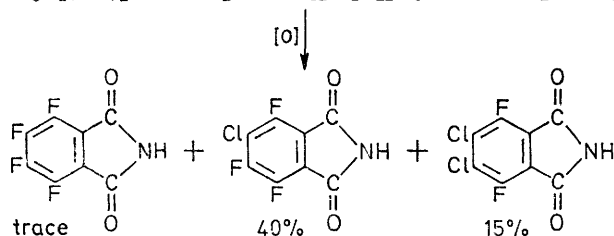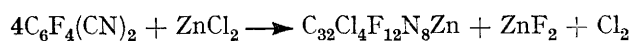
tetrachlorododecafluorophthalocyanine and one isomer is shown as compound (III).

The reaction between equimolar proportions of tetrafluorophthalonitrile and zinc chloride yields a product of approximate composition $C_{32}Cl_7F_9N_8Zn$, and it is clear that nucleophilic attack by chloride ion is taking place during these reactions, either on tetrafluorophthalonitrile or on zinc hexadecafluorophthalocyanine already formed. Since no reaction occurs between the perfluorophthalocyanine and a large excess of zinc chloride in boiling α-chloronaphthalene (b.p. 263°) during 16 hours, it is likely that the substitution occurs before phthalocyanine formation, and the ready displacement of fluoride from the 4- and 5-positions of tetrafluorophthalonitrile by lithium chloride in aprotic solvents supports this suggestion.[9] However, an attempt to effect substitution of fluoride without phthalocyanine formation by means of a reaction between tetrafluorophthalonitrile and zinc chloride at 160° led only to the isolation of zinc hexadecafluorophthalocyanine [75% yield based on nitrile consumed (32%)] and unchanged tetrafluorophthalonitrile; at this temperature, phthalocyanine formation is clearly faster than the substitution reaction.

The reason for the extensive halogen exchange during the reaction with zinc chloride and its absence from the reactions involving zinc bromide and zinc

[9] J. M. Birchall, R. N. Haszeldine, and J. O. Morley, *J. Chem. Soc. (C)*, 1970, 456.

[10] P. A. Barrett, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, 1936, 1719.

iodide is not, at present, clear. However, the much longer reaction period required to bring about effective conversion of tetrafluorophthalonitrile in the presence of zinc chloride must be a contributory factor. Complete conversion of the reactants into zinc halogenophthalocyanines has not been achieved in any of the reactions described here, probably because the finely powdered halide gradually becomes coated with a film of product, which prevents further reaction.

Barrett, Dent, and Linstead have shown that the reaction between zinc chloride and the parent phthalonitrile yields a mixture of zinc phthalocyanines of approximate composition $C_{32}H_{15\cdot2}Cl_{0\cdot8}N_8Zn$,[10] but the
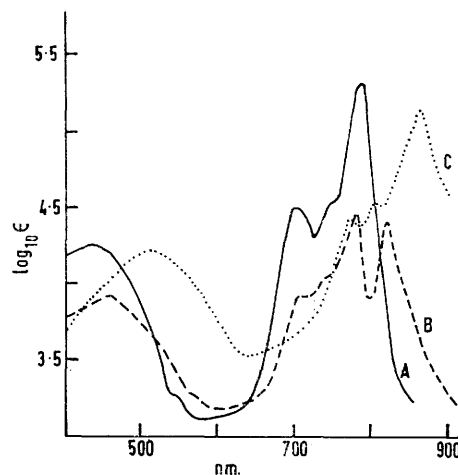
U.v. spectra of the zinc phthalocyanines in sulphuric acid:
$A = ZnC_{32}H_{16}N_8$, $B = ZnC_{32}F_{16}N_8$, $C = ZnC_{32}Cl_{16}N_8$

corresponding reactions of zinc bromide and zinc iodide have not been investigated. We have now shown that halogenation also occurs during the reaction of phthalonitrile with zinc bromide (mole ratio, 4 : 1) at 280°, which gives a phthalocyanine mixture of composition $C_{32}H_{15\cdot1}Br_{0\cdot9}N_8Zn$ in 78% yield; the corresponding reaction with zinc iodide is faster and yields only zinc phthalocyanine (IV) (87%) and almost the calculated quantity of iodine. The halogenations occurring in this series are most probably electrophilic substitutions, brought about by the free halogen liberated in the presence of the zinc halide (acting as a Lewis acid). The introduction of halogen is likely to occur after phthalocyanine formation, since phthalocyanines are easily halogenated (usually in the 4-position) in the presence of Lewis acids, whilst phthalonitrile is reluctant to undergo electrophilic substitution.[3a] The failure of a large number of aromatic compounds to react with iodine in the presence of a Lewis acid is usually attributed to weak co-ordination with the catalyst.[11]

$$4C_6H_4(CN)_2 + ZnX_2 \longrightarrow$$
$$C_{32}H_{16}N_8Zn + X_2 \longrightarrow C_{32}H_{15}XN_8Zn$$
$$(IV)$$
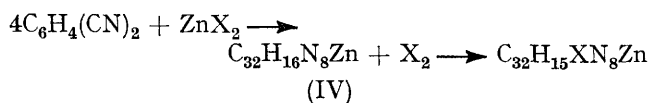
[11] See, for example, E. S. Gould, 'Mechanism and Structure in Organic Chemistry,' Holt, Rinehart, and Winston, New York, 1959, p. 443.

The hitherto unreported zinc hexadecachlorophthalocyanine (V) may be synthesised by the reaction of tetrachlorophthalonitrile with zinc chloride or zinc iodide at 290°. The latter reaction gives the phthalocyanine in 86% yield and provides both the better route and a purer product. The bright green perchlorophthalocyanine is insoluble in common organic solvents, but its solution in concentrated sulphuric acid shows absorption in the visible region which is similar in shape to that of zinc phthalocyanine itself (Figure). The pronounced bathochromic shift has been observed previously in chlorinated phthalocyanines.[3a] Oxidation of the perchloro-compound with boiling nitric acid gives tetrachlorophthalimide (78% yield).

In most of the reactions described above, acetone- or ethanol-soluble by-products are produced in 1—5% yield. These are green amorphous solids of unknown structure, but spectroscopic analysis suggests that the conjugation of the phthalocyanine system has been destroyed or markedly reduced, possibly by addition of halogen to the central ring system.

Copper(II) *Hexadecafluorophthalocyanine.*—The patented preparation of this compound involves the reaction of tetrafluorophthalonitrile with copper(I) chloride in *N*-methyl-2-pyrrolidone.[7] We have found that the phthalocyanine (I) may also be obtained (87% yield) from the same reactants in the absence of a solvent at 220° and also from the reaction of metallic copper with tetrafluorophthalonitrile in boiling α-chloronaphthalene (78% yield). The former reaction is presumably one of disproportionation, the copper(I) chloride acting as a source of metallic copper and copper(II) chloride.[12] Oxidative degradation of the product with hot chromic acid or concentrated nitric acid gives tetrafluorophthalimide in good yield.

Copper(II) chloride also reacts with tetrafluorophthalonitrile to give the perflourophthalocyanine (I) (68% yield) and chlorine, but this reaction is slower than either of those described above, 82% of the nitrile being unaffected after 7 hours at 250°.

Other Polyhalogenophthalocyanines.—The reaction of tin(II) chloride with tetrafluorophthalonitrile at 250° yields purple crystals of dichlorotin(IV) hexadecafluorophthalocyanine (VI) in 79% yield based on nitrile consumed (89%). The product is extremely resistant to oxidation, but reacts with hot fuming nitric acid to give tetrafluorophthalimide in 40% yield. A small

$$4C_6H_4(CN)_2 + SnCl_2 \longrightarrow C_{32}F_{16}N_8SnCl_2$$
$$(VI)$$
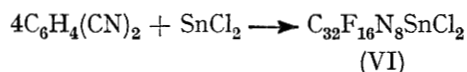
amount of tin(IV) chloride is evolved during the course of the phthalocyanine reaction, suggesting that a disproportionation reaction is also occurring ($2SnCl_2 \rightleftharpoons Sn + SnCl_4$). This implies that the product may contain traces of tin(II) hexadecafluorophthalocyanine ($C_{32}F_{16}N_8Sn$).

However, iron(III) chloride reacts with tetrafluorophthalonitrile (mole ratio, 1 : 4) to give what is believed to be a mixture of chloroiron(III) polychloropolyfluorophthalocyanines, of the composition indicated, in 74% yield based on nitrile consumed (44%). The chlorine content of the product increases, as in the zinc chloride

$$4C_6H_4(CN)_2 + FeCl_3 \longrightarrow C_{32}Cl_8F_8N_8FeCl + FeF_3$$

case, when the amount of iron(III) chloride present is increased, and equimolar proportions of the reactants give chloroiron(III) hexadecachlorophthalocyanine (VII) [64% yield based on nitrile consumed (85%)], which yields tetrachlorophthalimide (42%) on vigorous oxidation.

Aluminium chloride also behaves as a chlorinating agent in this type of system, since its reaction with an equimolar proportion of tetrafluorophthalonitrile at 250° produces a green mixture of chloroaluminium polychloropolyfluorophthalocyanines with the approximate composition, $C_{32}Cl_{13}F_3N_8AlCl$. Oxidative degradation of this material gives mainly tetrachlorophthalimide.

The reactions of iron(III) and aluminium chlorides with phthalonitrile itself are known to lead to chlorinated phthalocyanines *via* electrophilic chlorination, but, as in the case of zinc chloride, the halogen exchange observed with the fluorine compounds must proceed by a different mechanism. Hexafluorobenzene itself reacts with aluminium chloride at 250° to give good yields of hexachlorobenzene,[13] and it seems likely that reactions of this type are facilitated by the Lewis acid character of the metal halide in the manner shown.
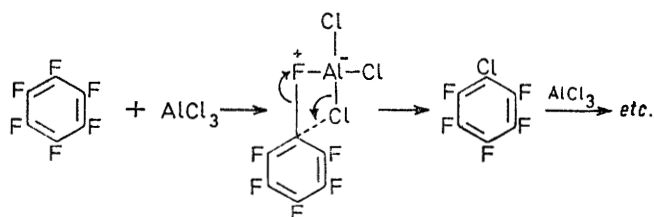
EXPERIMENTAL

All metal halides were rigorously dried before use; in addition iron(III) and aluminium chlorides were sublimed *in vacuo* at *ca.* 300°. All reactions leading to phthalocyanine formation were carried out under an atmosphere of dry nitrogen. Absorption spectra in the region 400—1000 nm. were measured on freshly prepared solutions in concentrated (18M) sulphuric acid with a Unicam SP 700 instrument; the absorption changed slowly if the solutions were kept. I.r. spectra (mulls in Nujol and hexachlorobutadiene) were recorded on a Perkin-Elmer No. 21 instrument.

Zinc Hexadecafluorophthalocyanine.—(a) *From zinc iodide.* An intimate mixture of zinc iodide (1·98 g., 6·2 mmoles) and tetrafluorophthalonitrile (5·01 g., 25 mmoles)[14] was heated under reflux at 250° (bath) for 90 min. Iodine (0·74 g., 90% based on $C_{32}F_{16}N_8Zn$ formed), estimated by titration against aqueous sodium thiosulphate, was evolved.

[12] Compare C. E. Dent and R. P. Linstead, *J. Chem. Soc.*, 1934, 1027.

[13] J. M. Birchall, W. M. Daniewski, and R. N. Haszeldine, unpublished observations.

[14] B.P. 1,026,290/1966 (*Chem. Abs.*, 1966, **64**, 19,507f).

The purple reaction mass was cooled, finely powdered, and extracted with light petroleum (b.p. 80—100°; 100 ml.) for 48 hr., water (100 ml.) for 168 hr., and ethanol (100 ml.) for 48 hr. Light petroleum extracted tetrafluorophthalonitrile (1·63 g., 33% recovery), m.p. 85° (lit.,[14] m.p. 83°), identified by i.r. spectroscopy, and the aqueous extract *contained only* zinc iodide (0·71 g.); fluoride ion was not detected. The green ethanolic extract was evaporated down to 20 ml. and added to light petroleum (b.p. 100—120°; 200 ml.) and the resulting precipitate (0·025 g.) was dried at 150° *in vacuo* but remained unidentified (Found: C, 48·8; H, 1·1; F, 25·1; N, 13·2%). The solid remaining after the extractions was dried at 250° *in vacuo* for 24 hr. and yielded purple crystals of *zinc hexadecafluorophthalocyanine* [2·81 g., 77% based on $C_6F_4(CN)_2$ consumed] (Found: C, 44·6; F, 34·8; N, 12·9; Zn, 7·6. $C_{32}F_{16}N_8Zn$ requires C, 44·4; F, 35·1; N, 13·0; Zn, 7·6%) [λ_{max} (log$_{10}$ ε) 458 (3·92), 700 (3·92), 780 (4·48), and 820 nm. (4·44); λ_{infl} 561 (3·30) and 736 nm. (4·03)]. Its i.r. spectrum shows bands at 3·88w, 6·13w, 6·56s, 6·73s, 6·90s, 7·43m, 7·64s, 7·93m, 8·70s, 9·29w, 10·39s, 10·66m, 11·99m, 13·05w, 13·42m, and 15·33m μm.

(b) *From zinc bromide.* Zinc bromide (1·41 g., 6·3 mmoles) and tetrafluorophthalonitrile (5·02 g., 25 mmoles) were heated at 250° for 90 min. Bromine (0·61 g., 80% based on $C_{32}F_{16}N_8Zn$ formed) was evolved, and extraction as before yielded tetrafluorophthalonitrile (0·50 g., 10%), zinc bromide (0·21 g.), and an unidentified product (0·25 g.) (Found: C, 42·6; H, 0·6; Br, 11·1; F, 26·1; N, 12·0%). The residue was dried at 250° *in vacuo* and then extracted with pentan-2-one (50 ml.) for 48 hr. The resulting solution was added to light petroleum (b.p. 100—120°; 500 ml.) and the purple crystalline precipitate was again dried at 250° *in vacuo* to yield zinc hexadecafluorophthalocyanine (4·14 g., 85%) (Found: C, 43·7; F, 33·6; N, 13·2; Zn, 7·3%). Sublimation of the product at 600° *in vacuo* gave a purer specimen as a blue amorphous powder (Found: C, 44·2; N, 13·1; Zn, 7·5%).

(c) *From zinc metal.* Zinc dust (3·27 g., 0·050 g.-atom), tetrafluorophthalonitrile (5·01 g., 25 mmoles), and α-chloronaphthalene (30 ml.) were stirred and heated under reflux for 48 hr. The cold mixture was diluted with light petroleum (b.p. 100—120°; 1 l.) and filtered, and the residue was stirred with aqueous 2M-hydrochloric acid (500 ml.) to dissolve unchanged zinc. The residual purple solid was washed with boiling water, dried, finely powdered, and extracted with pentan-2-one (100 ml.) for 48 hr. The extract was added to light petroleum (b.p. 100—120°; 1 l.), and the resulting purple precipitate was dried and identified as zinc hexadecafluorophthalocyanine (4·75 g., 87%) by i.r. spectroscopy.

Oxidation of Zinc Hexadecafluorophthalocyanine.—(a) *With concentrated nitric acid.* The finely powdered phthalocyanine (2·01 g.) was boiled in concentrated nitric acid (15 ml.) for 5 min., and the resulting clear yellow solution was diluted with water (30 ml.) and left for 3 hr. The precipitate was recrystallised from aqueous ethanol to give tetrafluorophthalimide (0·83 g., 45%) (Found: C, 43·6; H, 0·6; N, 6·4. Calc. for $C_8HF_4NO_2$: C, 43·9; H, 0·5; N, 6·4%), m.p. 218° (lit.,[15] m.p. 210—211°), identified by i.r. spectroscopy.

(b) *With chromic acid.* The phthalocyanine (1·02 g.) was added in portions to hot aqueous chromic acid (10 ml.; prepared by the addition of concentrated sulphuric acid to saturated aqueous potassium dichromate until a precipitate

began to appear). A vigorous reaction occurred, and the colour of the phthalocyanine was destroyed in 5 min. The solution was diluted with water (10 ml.) and kept for 12 hr., and the precipitate was recrystallised to yield tetrafluorophthalimide (0·76 g., 75%).

(c) *With cerium(IV) sulphate.* The phthalocyanine (1·04 g.), in concentrated sulphuric acid (30 ml.), was added to cold water (120 ml.). Aqueous 1M cerium sulphate was added dropwise, but no decolourisation occurred even on boiling the solution for 30 min. The phthalocyanine (0·91 g., 88%) was recovered.

Reaction of Tetrafluorophthalonitrile with Zinc Chloride.—(a) *At 250°.* (i) The nitrile (5·03 g., 25 mmoles) and zinc chloride (0·85 g., 6·2 mmoles) were heated at 250° for 7 hr. Chlorine (0·03 g.) was evolved. The cold reaction mixture was finely powdered and extracted with light petroleum (b.p. 80—100°; 100 ml.) for 48 hr., water (100 ml.) for 168 hr., and ethanol (100 ml.) for 48 hr. The light petroleum extract yielded tetrafluorophthalonitrile (3·10 g., 62%), m.p. 84°, identified by i.r. spectroscopy, and analysis of the aqueous extract showed it to contain zinc chloride (0·13 g.) and zinc fluoride (0·34 g.). The green ethanolic extract was evaporated down to 30 ml. and added to light petroleum (b.p. 100—120°; 300 ml.); the resulting precipitate was dissolved in acetone and chromatographed on alumina with benzene as the eluant. Evaporation of the main green band yielded an unidentified black solid (0·19 g.) (Found: C, 42·9; H, 0·6; Cl, 14·4; F, 21·1; N, 13·5%). The blue amorphous solid, remaining after the extractions, was dried at 250° *in vacuo* for 48 hr., to yield a mixture of zinc polychloropolyfluorophthalocyanines (1·42 g., *ca.* 64% yield) (Found: C, 41·5; Cl, 17·2; F, 23·5; N, 12·2; Zn, 6·9. $C_{32}Cl_4F_{12}N_8Zn$ requires C, 41·2; Cl, 15·4; F, 24·4; N, 12·0; Zn, 7·0%). The product (0·82 g.) was oxidised with hot chromic acid (10 ml.) to give a white crystalline solid (0·59 g.), m.p. 244—247°, identified as a mixture of tetrafluorophthalimide (trace), 4-chlorotetrafluorophthalimide (*ca.* 40% yield), and 4,5-dichlorodifluorophthalimide (*ca.* 15%) by i.r., [19]F n.m.r., and mass spectrometry; the yields are based on [19]F n.m.r. integral ratios.

(ii) In a second experiment, the nitrile (5·01 g., 25 mmoles) and zinc chloride (3·40 g., 25 mmoles) were heated as before and gave unchanged nitrile (2·50 g., 50%), zinc fluoride, and an unidentified black solid (0·25 g.). The blue-green residue from the extractions was dissolved in concentrated sulphuric acid and reprecipitated with water, to yield a mixture of halogenophthalocyanines (1·91 g., *ca.* 62% yield) (Found: C, 38·5; Cl, 25·6; F, 18·1; N, 11·4; Zn, 6·5. $C_{32}Cl_7F_9N_8Zn$ requires C, 39·1; Cl, 25·3; F, 17·4; N, 11·4; Zn, 6·7%).

(b) *At 160°.* Experiment (a) (ii) was repeated at 160°. Light petroleum extracted tetrafluorophthalonitrile (3·40 g., 68%), and fluoride ion was not detected in the aqueous extract. The residue from the extractions was zinc hexadecafluorophthalocyanine (1·31 g., 75%) (Found: C, 44·4; Zn, 7·3. Calc. for $C_{32}F_{16}N_8Zn$: C, 44·4; Zn, 7·6%), identified by i.r. spectroscopy. Oxidation of the product (0·51 g.) with hot concentrated nitric acid (10 ml.) gave tetrafluorophthalimide (0·35 g., 70%).

Reaction of Phthalonitrile with Zinc Bromide.—Phthalonitrile (5·01 g., 39 mmoles) and zinc bromide (2·25 g., 10 mmoles) were stirred and heated at 280° (bath) for 1 hr. Bromine (0·048 g.) was evolved, and extraction of the cold,

[15] B. Gething, C. R. Patrick, and J. C. Tatlow, *J. Chem. Soc.*, 1961, 1574.

finely powdered, reaction mass with water (100 ml.) for 24 hr. gave zinc bromide (0·93 g., 41% recovery). Extraction with acetone (100 ml.) for 24 hr. then gave phthalonitrile (2·51 g., 50%), and the residue was dissolved in concentrated sulphuric acid and reprecipitated with water to give a blue-green solid. This was dried at 250° *in vacuo* for 24 hr. and identified as a mixture of zinc phthalocyanine and zinc bromophthalocyanine (2·45 g., *ca.* 78% yield) (Found: C, 58·7; H, 2·5; Br, 10·8; N, 17·0; Zn, 9·9. $C_{32}H_{15\cdot1}Br_{0\cdot9}N_8Zn$ requires C, 59·2; H, 2·3; Br, 11·1; N, 17·3; Zn, 10·1%).

Zinc Phthalocyanine.—Phthalonitrile (5·01 g., 39 mmoles) and zinc iodide (3·19 g., 10 mmoles) were heated and stirred at 280° (bath) for 30 min. Iodine (1·48 g., 86% based on $C_{32}H_{16}N_8Zn$ formed) was evolved, and extraction of the reaction mass with water and then acetone yielded zinc iodide (0·61 g., 19%) and phthalonitrile (1·02 g., 20%), respectively. The residue was dissolved in concentrated sulphuric acid and reprecipitated with water to give a blue solid, identified by i.r. and u.v. spectroscopy as zinc phthalocyanine (3·91 g., 87%) (Found: C, 66·5; H, 2·9; Zn, 11·2. Calc. for $C_{32}H_{16}N_8Zn$: C, 66·5; H, 2·8; N, 19·4; Zn, 11·3%). Oxidation of the product (1·04 g.) with hot concentrated nitric acid (20 ml.) gave phthalimide (0·69 g., 69%), m.p. 236° (lit.,[16] m.p. 235°), identified by i.r. spectroscopy.

Zinc Hexadecachlorophthalocyanine.—(a) *From zinc iodide.* Tetrachlorophthalonitrile (5·02 g., 18·8 mmoles) and zinc iodide (1·50 g., 4·7 mmoles) were heated at 280° for 30 min. Iodine (0·69 g., 85% based on $C_{32}Cl_{16}N_8Zn$ formed) was evolved, and extraction with water yielded zinc iodide (0·43 g., 29%); chloride ion was not detected. Extraction with acetone gave a solid, which was sublimed at 250° *in vacuo* to yield tetrachlorophthalonitrile (1·11 g., 22%). The green amorphous residue from the extractions was dried at 250° and afforded *zinc hexadecachlorophthalocyanine* (3·60 g., 86%) (Found: C, 33·7; Cl, 50·1; N, 9·9; Zn, 5·7. $C_{32}Cl_{16}N_8Zn$ requires C, 34·0; Cl, 50·2; N, 9·9; Zn, 5·8%) [λ_{max} ($\log_{10}\varepsilon$) 513 (4·23), 771 (4·42), 804 (4·53), and 864 nm. (5·15)]; its i.r. spectrum shows bands at 6·78w, 7·20s, 7·30w, 7·56m, 7·67s, 7·87m, 8·26s, 8·64s, 8·75s, 9·15s, 10·62s, 12·85s, 12·98s, 13·45s, and 13·96w μm., and is closely comparable with that of copper(II) hexadecachlorophthalocyanine.[17] The product (1·03 g.) was oxidised with boiling nitric acid (20 ml.) to give tetrachlorophthalimide (0·78 g., 78%), m.p. 356° (lit.,[18] m.p. 345—347°), identified by i.r. spectroscopy.

(b) *From zinc chloride.* Tetrachlorophthalonitrile (5·03 g., 19 mmoles) and zinc chloride (1·35 g., 10 mmoles), heated at 290—300° for 90 min., similarly gave chlorine (0·03 g.), zinc chloride (1·04 g.), tetrachlorophthalonitrile (2·10 g., 42%), and zinc hexadecachlorophthalocyanine (2·66 g., 87% yield), identified by i.r. spectroscopy.

Copper Hexadecafluorophthalocyanine.—(a) *From copper metal.* Tetrafluorophthalonitrile (5·01 g., 25 mmoles) and fine copper turnings (12·7 g., 200 mg.-atom) were heated in refluxing α-chloronaphthalene (50 ml.) for 48 hr. with agitation. The cold mixture was added to light petroleum (b.p. 100—120°; 400 ml.) and the insoluble product was subjected to flotation in light petroleum to remove the excess of copper. The crude material was dried and dissolved in concentrated sulphuric acid (100 ml.) at 80°, and the solution was filtered through a glass sinter (porosity

3), diluted with cold water (1 l.), and kept for 24 hr. The resulting purple crystals were identified as copper(II) hexadecafluorophthalocyanine (4·20 g., 78%) (Found: C, 44·6; Cu, 7·3; N, 13·0. Calc. for $C_{32}CuF_{16}N_8$: C, 44·5; Cu, 7·4; N, 13·0%) [λ_{max} ($\log_{10}\varepsilon$) 446 (4·26), 779 (4·77), and 821 nm. (4·74); $\lambda_{infl.}$ 714 (4·39) and 761 nm. (4·65)]; the i.r. spectrum shows bands at 3·85w, 6·25w, 6·62s, 6·71s, 6·90s, 7·51s, 7·87m, 8·70s, 9·29w, 10·40s, 10·61m, 11·90m, 13·02w, 13·40s, and 15·19m μm. The product (1·01 g.) was oxidised with hot concentrated nitric acid (15 ml.) and gave tetrafluorophthalimide (0·61 g., 61%).

(b) *From copper(I) chloride.* An intimate mixture of tetrafluorophthalonitrile and copper(I) chloride (1·50 g., 15 mmoles) was stirred and heated at 220° for 2 hr. Extraction with light petroleum (b.p. 80—100°) and with water gave recovered nitrile (1·01 g., 17%) and copper(II) chloride (0·84 g.), respectively, but no fluoride ion. The residue was dissolved in concentrated sulphuric acid and reprecipitated with water to give the phthalocyanine (4·81 g., 87%) (Found: C, 44·4; Cu, 7·4; N, 13·1%), identified by i.r. spectroscopy and oxidative degradation.

(c) *From copper(II) chloride.* Tetrafluorophthalonitrile (5·00 g., 25 mmoles) and copper(II) chloride (3·36 g., 25 mmoles), heated at 250° for 7 hr., similarly gave chlorine (0·01 g.), unchanged nitrile (4·11 g., 82%), copper(II) chloride (2·80 g.), and the phthalocyanine (0·60 g., 62%) (Found: Cu, 7·3; F, 35·6. Calc. for $C_{32}CuF_{16}N_8$: Cu, 7·4; F, 35·1%).

Dichlorotin(IV) Hexadecafluorophthalocyanine.—Tetrafluorophthalonitrile (5·01 g., 25 mmoles) and tin(II) chloride (1·20 g., 6·3 mmoles) were stirred and heated at 250° for 90 min. Tin(IV) chloride (0·03 g.), identified by mass spectrometry, was evolved, and extraction of the cold reaction mass with light petroleum (b.p. 80—100°; 100 ml.) for 48 hr. gave unchanged nitrile (0·56 g., 11%). Extraction with hydrochloric acid azeotrope (100 ml.) for 28 days then gave tin(II) chloride (0·21 g.) (fluoride ion was not detected), and the purple residue was washed with boiling water until free from acid and dried at 250° to give *dichlorotin(IV) hexadecafluorophthalocyanine* (4·35 g., 79%) (Found: C, 38·8; Cl, 7·0; F, 29·8; N, 11·3. $C_{32}Cl_2F_{16}N_8Sn$ requires C, 38·8; Cl, 7·1; F, 30·7; N, 11·1%) [λ_{max} ($\log_{10}\varepsilon$) 407 (4·30), 710 (4·28), 756 (4·77), and 792 nm. (4·95); $\lambda_{infl.}$ 688 nm. (4·27)]. The i.r. spectrum of this compound shows bands at 6·13w, 6·56m, 6·68s, 6·84m, 7·42m, 7·75s, 7·93m, 8·75m, 10·24s, 11·97m, 13·12w, 13·47m, and 13·64w μm.

Reaction of Tetrafluorophthalonitrile with Iron(III) Chloride.—(a) *Mole ratio, 4 : 1.* The nitrile (5·01 g., 25 mmoles) and iron(III) chloride (1·00 g., 6·3 mmoles) were heated at 250° for 3 hr. Extraction with light petroleum (b.p. 80—100°; 100 ml.) for 48 hr. yielded unchanged nitrile (2·80 g., 56%) and extraction with hydrochloric acid azeotrope (100 ml.) for 14 days gave iron(III) chloride (0·29 g.) and iron(III) fluoride (0·44 g.). Extraction with ethanol (100 ml.) for 48 hr. gave an unidentified green solid (0·22 g.), and the residue from the extractions was washed with acetone and dried at 250° to give a mixture of chloroiron(III) polychloropolyfluorophthalocyanines (2·01 g.) (Found: C, 37·7; Cl, 33·0; F, 12·7; Fe, 5·4; N, 10·9. $C_{32}Cl_9F_8FeN_8$ requires C, 37·6; Cl, 31·2; F, 14·9; Fe, 5·6; N, 11·0%).

[17] H. F. Shurvell and L. Pinzuti, *Canad. J. Chem.*, 1966, **44**, 125.

[18] W. E. Rosen, V. P. Toohey, and A. C. Shabica, *J. Amer. Chem. Soc.*, 1957, **79**, 3167.

[16] F. Wild, 'Characterisation of Organic Compounds,' Cambridge University Press, 1947, p. 208.

(b) *Mole ratio*, 1 : 1. Tetrafluorophthalonitrile (5·01 g., 25 mmoles) and iron(III) chloride (4·05 g., 25 mmoles) similarly gave unchanged nitrile (0·75 g., 15%), iron(III) chloride and fluoride, the green unidentified solid (0·31 g.) and *chloroiron*(III) *hexadecachlorophthalocyanine* (3·45 g., (64%) (Found: C, 33·6; Cl, 52·3; Fe, 4·6; N, 9·8. $C_{32}Cl_{17}$-FeN_8 requires C, 33·3; Cl, 52·2; Fe, 4·8; N, 9·7%) [$\lambda_{max.}$ ($\log_{10} \varepsilon$) 500 (4·26) and 806 nm. (4·51); $\lambda_{infl.}$ 552 (4·22), 667 (4·11), 825 (4·50), and 965 nm. (3·73)]. Treatment of the phthalocyanine (1·04 g.) with boiling nitric acid (20 ml.) for 30 min. gave tetrachlorophthalimide (0·43 g., 42%).

Aluminium Halogenophthalocyanines.—Tetrafluorophthalonitrile (5·03 g., 25 mmoles) and aluminium chloride (3·31 g., 25 mmoles) were heated at 250° for 3 hr. Extraction with light petroleum, water, and butan-2-one yielded unchanged nitrile (2·51 g., 50%), aluminium chloride and fluoride, and an unidentified solid (0·25 g.), respectively. The green amorphous residue was washed with acetone and dried at 250° to yield a mixture of chloroaluminium polychloropolyfluorophthalocyanines (2·41 g.) for which satisfactory analyses could not be obtained (Found: C, 33·9; Cl, 40·6; F, 4·9; N, 9·8. $C_{32}AlCl_{14}F_3N_8$ requires C, 35·7; Cl, 46·1; F, 5·3; N, 10·4%). The product, which was identified by its absorption spectrum in sulphuric acid, reacted with boiling nitric acid to give an impure solid, shown by mass spectrometry to be mainly tetrachlorophthalimide.