372. *Phthalocyanines and Related Compounds. Part XVI. The Halogenation of Phthalocyanines.*

By P. A. Barrett, E. F. Bradbrook, C. E. Dent, and R. P. Linstead.

As the central ring system of the phthalocyanine molecule is of an aromatic type, it is to be expected that the four benzene rings fused to it will be comparatively easily substituted and not deactivated as in ordinary derivatives of phthalic acid. This has been verified experimentally by a study of the halogenation of phthalocyanine.

Under mild conditions phthalocyanine reacts with free halogens to yield additive compounds. At high temperatures and in the presence of catalysts the benzene rings are readily substituted. The action of other halogenating agents also has been studied. The orientation of the products has been determined by degradation and by measurements of absorption spectra. Substitution is uneven, and goes through the 4-chloro- and 4 : 5-dichloro- to the tetrachloro-stage. The most highly halogenated phthalocyanines obtained by us contain 12 to 13 atoms of halogen in the molecule and are bright green. The preparation of these substances by a variety of methods is described and their properties are recorded.

It was pointed out in 1935 that the presence of large rings of conjugated double and single bonds cause the phthalocyanine and porphyrin molecules to acquire an aromatic character (Linstead, *Ann. Reports*, **32**, 361). Measurements of molecular dimensions by the *X*-ray method (Robertson, J., 1936, 1203) have since provided precise evidence that the central 16-atom ring of phthalocyanine is a resonance hybrid of a similar type to the aromatic. The abnormal behaviour of the electrons of the great ring is also shown by measurements of magnetic anisotropy (Lonsdale, *Proc. Roy. Soc.*, 1937, *A*, **159**, 157).

Derivatives of phthalic acid such as the anhydride or dinitrile contain two deactivating groups and nuclear substitution is difficult. When, however, the two nitrile groups become merged into the central phthalocyanine ring, it is to be expected that this state of affairs will no longer hold. The corner benzene rings will be united to a pseudo-aromatic unit and the nuclear reactivity should tend to resemble that of diphenyl rather than that of phthalonitrile. It may be recalled that Robertson finds the length of the bonds connecting the benzene rings to the central ring to be 1·49 A, very similar to the bond connecting the two nuclei of diphenyl. In practice it is to be expected that the reactivity will be controlled to some extent by the low solubility of phthalocyanine.

The halogenation of phthalocyanine proceeds readily under conditions which do not effect halogenation of phthalonitrile or phthalic anhydride. As in the case of aromatic compounds, under mild conditions phthalocyanine forms additive compounds with halogens. The position of the halogen atoms in these compounds is unknown. They are easily converted, particularly by heat, into substitution products in which the halogen atoms enter the benzene nuclei. In both processes the phthalocyanine skeleton is preserved. These facts are therefore in satisfactory agreement with theoretical expectation.

Phthalocyanine reacts rapidly at room temperature with bromine in carbon tetrachloride solution without elimination of hydrogen bromide. The amount of halogen removed from the solution depends upon the concentration and reaches a maximum at 8 g.-atoms per g.-molecule of phthalocyanine. When the insoluble *octabromide* so obtained is warmed with alkali, all the halogen is removed and phthalocyanine is re-formed. Most of the halogen is also removed if the dry octabromide is heated. If the product is left in contact with bromine in carbon tetrachloride for several weeks, a slow irreversible fixation of halogen occurs and the final product contains a considerable amount (up to 40%) of bromine not removable by warm alkali. The same change can be effected more readily by heating the octabromide in high-boiling solvents. The two stages in the reaction correspond with addition, and with substitution in the benzene rings. The substituted bromophthalocyanines formed in this way will still add a further 8 g.-atoms of bromine from carbon tetrachloride solution.

When phthalocyanine is heated with bromine to 300° under pressure, both addition and substitution occur. Much hydrogen bromide is evolved and a brown solid is formed. After the additive bromine has been removed, a green *bromophthalocyanine* containing over 60% of stable bromine remains. The limit of substitution obtainable in this way appears to be reached when 13 of the 16 nuclear hydrogen atoms have been replaced. Lower temperatures give less highly brominated products.

The addition of chlorine resembles that of bromine but is less easily followed quantitatively. At room temperature chlorine gas converts free phthalocyanine and many of its metallic derivatives into brown *chlorides,* from which the halogen is completely liberated by warm alkali. When, however, phthalocyanine is heated at 250° with liquid chlorine under pressure, addition and substitution both occur and the brown product yields a green *dodecachlorophthalocyanine* on treatment with alkali. These high-temperature reactions provide another illustration of the great stability of the phthalocyanine ring.

Phthalocyanine can also be chlorinated by the action of boiling thionyl chloride, sulphuryl chloride, and similar reagents noted in the experimental section. No additive products appear under the conditions of reaction, and hydrogen chloride is at once evolved. The products are blue to blue-green and not very highly chlorinated. When heated with sulphuryl chloride under pressure at 230°, phthalocyanine gives a green chloro-derivative containing 13 atoms of chlorine per molecule. High chlorination can be achieved without the use of pressure by passing chlorine gas through a suspension (partial solution) of phthalocyanine in thionyl chloride at the boiling point. This reaction is assisted by the presence of catalysts, particularly sulphur monochloride, pyridine and iodine (see also B.P. 461,268). The products are green and contain from 10 to 13 atoms of chlorine per molecule.* If catalysts such as aluminium and ferric chloride are used, the metal becomes attached to the centre of the phthalocyanine ring and cannot be displaced. Chlorination and bromination can also be effected by the action of the free halogens in fuming sulphuric acid solution, but considerable fission occurs and the yields are small. Iodination has not been realised. Copper phthalocyanine, like the metal-free compound, is readily brominated by bromine under pressure. Typical chlorophthalocyanines easily yield their copper and lead derivatives on treatment with copper and litharge respectively in high-boiling solvents. This shows that the central acidic hydrogen atoms are not affected by the halogenation.

Properties of Halogenated Phthalocyanines.—On the introduction of the first four atoms of halogen the colour becomes slightly duller but is otherwise very little changed. Further substitution leads to progressively greener shades, a pure green being obtained when about 10 atoms of halogen have been introduced. Bromine has a greater influence than chlorine. Measurements of absorption spectra and their bearing on the problem of orientation are discussed later.

Chlorination of phthalocyanine leads to an increase of the solubility in chloronaphthalene until about 8 atoms of chlorine have been introduced. More highly chlorinated phthalocyanines are, however, very sparingly soluble. Bromination similarly produces an increase in solubility until about 4 atoms of bromine have entered, after which the solubility decreases. Another well-defined alteration in properties lies in the behaviour with sulphuric acid. Phthalocyanine itself dissolves fairly readily to give a yellow-brown solution. With the entry of halogen atoms the solubility in sulphuric acid decreases and the colour of the solution changes progressively to a brownish-red. These solutions have no clearly banded spectra.

The halogenated phthalocyanines described in this paper could not be obtained macrocrystalline. Sublimation led to decomposition, and crystallisation gave micro-crystals which may have been mixtures. No separation could be achieved by fractional extraction with boiling solvents, there being no perceptible change in the colour of successive extracts.

Orientation.—The structures of a number of chlorophthalocyanines prepared by different methods of chlorination have been determined by degradation to the corresponding chlorophthalic acids. This has been effected in the two stages : (i) oxidative fission to chlorophthalimides by ceric sulphate in sulphuric acid (Dent, Linstead, and Lowe, J., 1934, 1036) and (ii) hydrolysis by sulphuric acid at 170° to the corresponding chlorophthalic acids or anhydrides. These acids were then separated by taking advantage of the difference between the ease with which they yield anhydrides, or by means of partial esterification.

Typical results are summarised below :

Chlorine content (g.-atoms/mol.).	Chlorophthalic acids isolated.
5·5	4-monochloro- (53%)
8·2	4 : 5-dichloro- (22%) ; tetra- (3%)
10 (made with $SbCl_5$)	4 : 5-dichloro- (23%) ; tetra- (19%)
10 (made without $SbCl_5$)	4 : 5-dichloro- (33%) ; tetra- (26%)
13	4 : 5-dichloro- (5%) ; tetra- (50%)

The figures in parenthesis give the yields of fission products expressed in terms of the corresponding chloro*iso*indole corners of the phthalocyanine molecule. Thus, 25% dichloro- indicates that the yield of dichlorophthalic acid corresponded with the fact that one of the four corners was dichlorinated.

It will be seen that only three acids have been isolated. The total equivalent yields never exceed 60% and sometimes are much lower. The bulk of the loss occurs during the hydrolysis of the imides, and the separation of the acids, for a good yield of mixed imides is obtained in the oxidation. The loss may be shared among the various fission products, or it may occur at the expense of one or two. Comparative experiments under

---

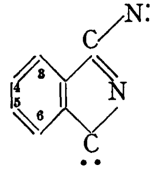
* A high degree of chlorination can be achieved in phthalic anhydride solution in the presence of antimony pentachloride (Dent, Silvester, and Imperial Chemical Industries, Ltd., B.P. 478,256). Many other methods of halogenating phthalocyanines have been described in recent patent literature by Imperial Chemical Industries, Ltd., and the I. G. Farbenindustrie A.-G. (B.P. 474,740, 499,415, 500,471).

the same conditions show that pure 3 : 4-, 3 : 6-, 4 : 5-dichloro- and tetrachloro-phthalimides are all hydrolysed to the corresponding acids or anhydrides in good yield, that of the 3 : 6-derivatives being the worst (70%). The absence of trichlorophthalic acids from the fission products might be thought to indicate a specific instability, but this point cannot be regarded as settled, because the imides obtained by the oxidation of the chlorophthalocyanines contain some coloured impurity which may catalyse their gross decomposition.

It appears that comparatively little tetrachlorophthalic anhydride is decomposed during fission, because the yields are fairly high in relation to the chlorine contents of the parent pigments. This is probably owing to the sparing solubility of the tetrachloro-anhydride in sulphuric acid.

Although obviously no exact analysis of structure is possible, a comparison between the product isolated and the total chlorine originally present leads to the following general conclusions : (1) Nuclear substitution occurs preferentially in the two β (4 and 5)-positions (phthalic acid numbering as in I). (2) Substitution is uneven. Thus a chlorophthalocyanine containing ten atoms of chlorine in the molecule gives a large amount of tetrachlorophthalic anhydride. This may mean that it is a mixture, for example, of octachloro- and hexadecachloro-phthalocyanine, but as no separation could be achieved, it is more likely that the actual molecules are unsymmetrically substituted, for example, as represented in (II).

(I.)



4Cl	2Cl
2Cl	2Cl

(II.)

To obtain independent evidence of orientation, the absorption spectra of chlorophthalocyanines, prepared by chlorination and containing from 1 to 13 atoms of chlorine, were compared with those of pure chlorophthalocyanines made from derivatives of chlorophthalic acids of known orientation (see Table V). The introduction of chlorine generally leads to a slight progressive shift of the absorption maxima towards the red and to a weakening or extinction of the weaker bands of the phthalocyanine spectrum. Owing to the lack of symmetry (or lack of homogeneity), the spectra of the chlorination products were not sharply defined, particularly after 8 chlorine atoms had been introduced. The octachlorophthalocyanine produced by direct chlorination, however, bore a general resemblance in spectrum to (4 : 5)-octachlorophthalocyanine.*

Solutions of the pigments in concentrated sulphuric acid generally showed only a broad area of transmission from green to red. This was shifted towards the red by chlorination, particularly by substitution in the 3 : 6-positions. In this respect the octachlorinated pigment resembled the 4 : 5- rather than the 3 : 6-derivative. The transmission in sulphuric acid did not approach that of the 3 : 6-compound until 12 or 13 chlorine atoms had entered the molecule, at which stage, of course, a considerable amount of 3 : 6-substitution must have occurred. The evidence from these sources, therefore, although not conclusive, supports the chemical evidence that substitution occurs primarily in the 4- and 5-positions.

A minor problem, left outstanding in previous work, has been solved by applying the same general methods. It was shown by Dent and Linstead (J., 1934, 1029) that cupric chloride reacted with phthalonitrile to yield a copper monochlorophthalocyanine containing one nuclear chlorine atom. This has now been shown to be in the 4-position by separation of the fission products into phthalic and 4-chlorophthalic acids. The substitution which accompanies phthalocyanine formation thus occurs in the same position as that of the isolated pigment.

---

* See footnote to Table V.

EXPERIMENTAL.

Halogen analyses were all carried out by the Liebig (lime) method.

A. *Reaction with Free Halogens at Room Temperature.*—(i) Chlorine was passed over thin layers of the phthalocyanines named below. When no further change could be seen, the products were analysed :

Substance.	Time of reaction, hrs.	% Cl in product.
Metal-free phthalocyanine	400	41·0 (*ca.* 9 g.-atoms)
Ferrous ,,	90	43·0
Copper ,,	500	29·5
Lead ,,	44	26·0

All the products were brown and viscous, and from them by treatment with caustic soda solution the original phthalocyanines were regenerated, practically free from chlorine.

(ii) Finely powdered phthalocyanine was shaken in a tall glass-stoppered cylinder with solutions of bromine in carbon tetrachloride of known strength. The solid was allowed to settle and, after a suitable interval, the bromine content of the supernatant solution was determined by titration of an aliquot part with standard thiosulphate solution. From the reduction in strength, the bromine absorbed by the phthalocyanine was calculated. Blank experiments showed the bromine solution to be stable under the reaction conditions. The results are in Table I.

TABLE I.

Expt.	Normality of Br.	Time of reaction, hrs.	Br absorbed, g.-atoms/mol.	" Stable " Br, g.-atoms/mol.
1	0·1	66·0	3·0	—
2	0·9	0·5	4·9	—
3	2·4	2·0	6·4	—
4	2·4	3·0	6·4	—
5	2·4	100	8·3	1·08
6	4·5	0·75	6·8	—
7	6·5	1·0	7·7	nil
8	6·5	13 days	11·9	—
9	6·5	6 weeks	16·7	4·5
10	Pure Br	3 weeks	—	4·9

Except when the N/10-bromine was used, the addition appeared to be complete in about 10 minutes. The product of experiment (7) was digested for 2 hours at 90° with N-sodium hydroxide in 50% alcohol to remove labile bromine. The residual pigment, crystallised from chloronaphthalene, was pure phthalocyanine (Found : C, 74·7; H, 3·4. Calc. : C, 74·7; H, 3·5%). The products of experiments (5) and (9) were similarly purified. Their bromine contents are indicated in the last column of Table I. Brominated phthalocyanine containing 3·1 atoms of nuclear bromine per molecule, when treated under the conditions of experiment (7), took up a further 7·7 atoms of bromine per molecule.

B. *Halogenation at High Temperatures without Pressure.*—In these experiments (Table II), phthalocyanine was heated with the named reagents and solvents under reflux in a ground-glass apparatus. In the experiments recorded in Table II*b*, a moderate stream of chlorine gas was passed continuously through the mixture. All the products, except those prepared in carbon tetrachloride solution, were poured into water, and the filtered and washed precipitate was finely ground and treated with cold 10% aqueous sodium hydroxide to remove labile chlorine and hydrochloric acid. When carbon tetrachloride was used, the pigment was filtered off directly and treated with sodium hydroxide.

C. *Halogenation under Pressure.*—(i) *Chlorination.* Phthalocyanine was heated in a Carius tube with an amount of halogenating agent 50% in excess of that required for complete chlorination. The products were poured into water and made alkaline with sodium hydroxide, and the chlorophthalocyanines filtered off and washed with alcohol. The pigment was then finely ground, again treated with aqueous alkali to ensure the removal of labile halogen, washed, and dried. The results are summarised in Table III.

(ii) *Bromination.* Phthalocyanine and the metal derivatives named in Table IV were heated in a Carius tube with bromine (50% in excess of that required for complete halogenation). Much hydrogen bromide was evolved when the tubes were opened. The excess of bromine was allowed to evaporate and the labile (additive) bromine was removed by heating the products under reduced pressure to 260°; green nuclear bromophthalocyanines were left. Experiments 44—53 below refer to reactions with liquid bromine. A few miscellaneous experiments are appended.

TABLE II.

Halogen without Pressure.

a. Chlorination by Reagents other than Chlorine, at the b. p.

					Product.		
Expt.	Phthalocyanine, g.	Reagent.	Quantity.	Time, hrs.	Yield, % wt.	Cl content, g.-atoms per mol.	Colour, etc.
11	2	Sulphuryl chloride	30 c.c.	1	85	5·5 *	Blue
12	2	Sulphuryl chloride	120 c.c.	12	102	—	Greenish-blue
13	2	Sulphuryl chloride Aluminium chloride	75 c.c. 1 g.	12	65	1·15 *	Blue, contained aluminium
14	1	Thionyl chloride	100 c.c.	16	100	—	Blue
15	15	Thionyl chloride Sulphuryl chloride	300 c.c. 73 c.c.	22	140	8·3 *	Blue-green
16	1	Thionyl chloride Sulphur monochloride	80 c.c. 3 c.c.	26	95	—	Blue
17	1	Phosphorus trichloride	30 c.c.	19·5	100	—	Dull blue
18	1	Phosphorus oxychloride	50 c.c.	20	102	—	Dull blue
19	1	Phosphorus oxychloride Phosphorus pentachloride	50 c.c. 5 g.	21	90	—	Blue

b. Chlorination by Chlorine Gas in the Presence of Solvents and Catalysts. Reaction at the b. p. of the solvent unless otherwise stated.

					Product.		
Expt.	Phthalocyanine, g.	Solvent or catalyst.	Quantity.	Time, hrs.	Yield, % wt.	Cl content, g.-atoms per mol.	Colour, etc.
20	2	Sulphuryl chloride	150 c.c.	6·5	100	—	Greenish-blue
21	15	Thionyl chloride	300 c.c.	10·5	115	6·8 *	Blue-green
22	1	Thionyl chloride Sulphur monochloride	100 c.c. 3 c.c.	5·5	105	10·2 †	Green
23	2	Thionyl chloride Iodine	150 c.c. 0·2 g.	13·5	120	—	Green
24	2	Thionyl chloride Pyridine	150 c.c. 4 c.c.	14·5	100	—	Green
25	2	Thionyl chloride Ferric chloride	150 c.c. 0·4 g.	14	150	—	Dull green, contained Fe
26	1	Carbon tetrachloride	100 c.c.	7	93	—	Blue
27	1	Carbon tetrachloride Sulphur monochloride	100 c.c. 3 c.c.	7	95	—	Blue
28	1	20% Oleum	100 c.c.	6 hrs. at 20°	40	—	Blue-green
29	1	Phosphorus oxychloride Phosphorus trichloride	100 c.c. 3 c.c.	7·5	97	—	Greenish-blue
30	15	Phthalic anhydride	150 g.	8 hrs. at 260°	120	5·9	Greenish-blue
31	10	Phthalic anhydride Antimony pentachloride	150 g. 2 c.c.	2½ hrs. at 260°	150	8·2	Blue-green
32	50	Phthalic anhydride Antimony pentachloride	300 g. 4 c.c.	7½ hrs. at 260°	160	10·0	Green
33	25	Phthalic anhydride Antimony pentachloride	150 g. 2 c.c.	6 hrs. at 270°	150	13·2	Yellowish-green

c. Bromination by Bromine in Solvents at the b. p.

			Product.		
Expt.	Solvent.	Time, hrs.	Yield, % wt.	Br content, g.-atoms per mol.	Colour.
34	Carbon tetrachloride	9	60	1·4	Blue
35	Nitrobenzene	8	110	3·4	Greenish-blue
36	Thionyl chloride	42	150	—	Greenish-blue
37	20% Oleum at 60°	2	80	4·0	Greenish-blue

* Product crystallised from chloronaphthalene before analysis.

† Product passed through sulphuric acid before analysis.

TABLE III.

Expt.	Reagent.	Temp.	Time, hrs.	Product. Yield, % wt.	Cl content, g.-atoms/mol.	Colour.
38	Liquid chlorine *	250°	6	160	12·2	Green †
39	Thionyl chloride	140	18	130	5·5	Greenish-blue ‡
40	Thionyl chloride	230	3·5	150	—	Greenish-blue †
41	Sulphuryl chloride	230	4·5	150	12·9	Green §
42	Sulphuryl chloride Aluminium chloride	210	0·5	15	—	Green †
43	Phosphorus pentachloride	210	2·5	130	4·8	Greenish-blue †

* Introduced in a thin-walled glass bulb, which was broken after the Carius tube had been sealed.
† Crystallised from chloronaphthalene.
‡ Washed with alcohol. § Passed through sulphuric acid.

TABLE IV.

Expt.	Phthalocyanine used.	Temp.	Time, hrs.	Product. Yield, % wt.	Br content, g.-atoms/mol.	Colour.
44	Metal-free	300°	2·5	110	8·8	Green
45	Metal-free	300	3	71	9·5	Green
46	Metal-free	140	18	120	10·4	Dull green *
47	Metal-free	300	2·5	115	11·7	Green †
48	Metal-free	290	5	105	(a) 12·2	Yellow-green †
					(b) 12·5	Duller than 48 (a) ‡
49	Metal-free	290	10·5	—	(a) 12·8	Green *
					(b) 13·0	Green †
50	Product of (35)	300	2·5	100	9·6	Green, blue tinge †
51	Copper phthalocyanine	210	2·5	120	5·3	Blue, little greener than copper phthalocyanine †
52	Product of (51)	290	5	145	12·6	Green *
53	Lead phthalocyanine	250	6	Charred		
54	Product of (7) without bromine	290	2·5	100	1·1	Blue
55	Metal-free + iodine	220	4	No hydrogen iodide evolved		
56	Metal-free + iodine	280	4	Charred		

* Washed with pyridine. † Crystallised from chloronaphthalene.
‡ Passed through sulphuric acid (recovery, 63%).

Metallic Derivatives.—2 G. of a chlorophthalocyanine (product 15), containing 8·3 atoms of chlorine per molecule, were heated under reflux with 0·5 g. of reduced copper in 100 c.c. of chloronaphthalene for 18 hours. The solution deposited the copper derivative as a blue amorphous solid on cooling. A copper derivative of a chlorophthalocyanine containing 10·0 atoms of chlorine per molecule was made similarly. It was very sparingly soluble and bluer than the parent metal-free compound. Product (15) when boiled with an equal weight of litharge in chloronaphthalene rapidly gave a green solution. After 18 hours' boiling the solution deposited the lead derivative as a yellow-green powder on cooling. The blue-green parent substance was regenerated on passing the lead compound through sulphuric acid.

Absorption Spectra.—(i) *In chloronaphthalene.* The absorption spectra of metal-free and copper compounds prepared from chlorinated intermediates of known orientation, and metal-free compounds prepared by direct chlorination, have been measured by means of a Hilger constant-deviation direct-reading spectrometer. The positions of the maxima are tabulated below; a value enclosed in brackets indicates that only the short-wave edge of the absorption band was clear cut. The relative intensities of the bands are indicated by Roman numerals, (I) being the most intense.

(ii) *In sulphuric acid.* The absorption spectra of every compound examined, except copper phthalocyanine, which gave a single band with a maximum at 6330 A, showed only end absorption in the red and green regions. For purposes of comparison, the absorption limit in the shorter-wave region (generally green) corresponding with an absorption limit of 6500 A in the red was determined from absorption curves, and the values so obtained are given in the last column of Table V.

Fissions.—(1) A solution of copper monochlorophthalocyanine (10 g.) (Dent and Linstead, *loc. cit.*) in 80 c.c. of concentrated sulphuric acid was filtered and poured on ice (200 g.). The

TABLE V.

Substance.	Absorption maxima (A) in chloronaphthalene.	Limit in green in sulphuric acid.
Metal-free phthalocyanine *	7030 (I), 6680 (II), 6360 (IV), 6040 (III)	5160
(3)-Tetrachlorophthalocyanine ‡	7070 (I), 6820 (II), 6420 (IV), 6110 (III)	5500
(4)-Tetrachlorophthalocyanine	7000 (I), 6680 (II), 6340 (IV), 6030 (III)	5830
(3 : 6)-Octachlorophthalocyanine	[6950] (I), 6570 (II), 6230 (III)	6160
(4 : 5)-Octachlorophthalocyanine	[6940] (I), 6610 (II)	5670
Copper phthalocyanine	6800 (I), 6440 (III), 6070 (II)	5270
Copper (4)-monochlorophthalocyanine	6740 (I), 6460 (III), 6090 (II)	—
Copper (3)-tetrachlorophthalocyanine	6900 (I), 6540 (III), 6200 (II)	5390
Copper (4)-tetrachlorophthalocyanine	6790 (I), 6470 (III), 6100 (II)	5560
Copper (3 : 4)-octachlorophthalocyanine	6860 (I), 6210 (II)	5450
Copper (3 : 6)-octachlorophthalocyanine	[7050] (I), 6610 (III), 6320 (II)	5870
Copper (4 : 5)-octachlorophthalocyanine	End absorption only	5640
Product 13† (1·15 Cl)	6980 (I), 6660 (II), 6310 (IV), 6020 (III)	5360
,, 43 (4·8 Cl)	7010 (I), 6720 (II), 6360 (III), 6020 (IV)	5550
,, 11 (5·5 Cl)	7060 (I), 6730 (II), 6420 (III), 6100 (IV)	—
,, 31 (8·2 Cl)	[6950] (I), [6650] (II)	5640
,, 32 (10·0 Cl)	[*ca.* 7100]	5900
,, 38 (12·2 Cl)	[*ca.* 6900] (I), [6350] (II)	6000
,, 33 (13·1 Cl)	[*ca.* 6790] (I), 6140 (II)	6040

* Main bands only are given. See also Parts XIII and XV.

† These products are all chlorinated metal-free phthalocyanines containing the number of chlorine atoms per molecule indicated in parenthesis.

‡ The numbers given as prefixes in parentheses refer to the orientation of the chlorine atoms in the parent chlorophthalic acids. For example, (3)-tetrachlorophthalocyanine implies the symmetrical compound containing four 3-chlorophthalic acid corners in the molecule, and copper (4)-monochlorophthalocyanine denotes a compound containing one 4-chlorophthalic and three unsubstituted phthalic residues.

mixture was warmed to 60°, and an excess of ceric sulphate solution added. After 15 minutes the colour was almost completely discharged, and after 10 hours the precipitated imides were collected and washed with water, more material being recovered from the filtrate and washings by extraction with ether. The combined imides (9·5 g.) were heated at 170° for 3 hours with 30 c.c. of sulphuric acid and 5 c.c. of water. The product was cooled and poured on ice, and the organic acids isolated by means of ether (yield, 9·2 g.) and purified through alkali (yield, 9·0 g.). The dry acids were then stirred for 90 minutes at room temperature with 10 c.c. of butyl acetate (following a method due to Dr. E. G. Beckett). The liquid was filtered through sintered glass, and the residue of phthalic acid washed thrice with chloroform (2 c.c.). Evaporation of the filtrate yielded a solid residue (2·1 g.), which was freed from a little tar by washing with benzene. After crystallisation from benzene it melted at 147°, and was identified as 4-chlorophthalic acid (m. p. 150°) by mixed m. p. and conversion into the anhydride.

(2) 15 G. of the product of experiment 32 (10·0 Cl) were suspended in concentrated sulphuric acid (80 c.c.) and a cold solution of ceric sulphate in sulphuric acid was added in drops with mechanical stirring until the green colour was discharged. The product was then stirred at room temperature for several hours and poured on ice. The imides (13 g.) were recovered by ether extraction and dissolved in concentrated sulphuric acid (100 c.c.). The solution after dilution with 20 c.c. of water was heated at 170° for 2 hours, cooled, and poured on ice. The acids (10 g.) were isolated by means of ether, dissolved in 100 c.c. of 98·5% sulphuric acid, and heated at 100° for 2 hours. The product was cooled to 0°, poured on ice, and rapidly extracted twice with a mixture of toluene and ether (100 c.c. of each). The extract was dried over calcium chloride, the solvent removed under reduced pressure, and the solid residue warmed for 5 minutes with 50 c.c. of toluene at 80°. The supernatant liquid (A) was poured off through a filter, and the extraction repeated. The residual solid (3·5 g., m. p. 191—194°) was fairly pure 4 : 5-dichlorophthalic acid (m. p., pure, 200°), with which it was identified by conversion into the ethyl ester, m. p. 60° (crystallised from petroleum), 61° in admixture with an authentic specimen (m. p. 61°) (Found : Cl, 24·9. Calc. : Cl, 24·4%).

The combined toluene extracts (A) contained the anhydrides of the chlorophthalic acids which lose water more readily. The anhydrides were isolated by evaporation, dissolved in 65% sulphuric acid, and separated into acid and anhydride by means of toluene exactly as before. The acid fraction contained only a little 4 : 5-dichlorophthalic acid (0·39 g., m. p. 190°); the anhydride fraction was freed from tarry material by extraction with a very little cold toluene, which left 3·2 g. of crystalline solid, m. p. 235—240°. Crystallisation from toluene, followed by precipitation from toluene solution with petroleum, yielded almost pure tetrachlorophthalic anhydride, m. p. and mixed m. p. 250° (Found : Cl, 49·2. Calc. : Cl, 49·7%).

Typical results of the fissions of other chlorophthalocyanines in an identical manner are summarised below :

(3) Product 11 (5·5 Cl). 10 G. yielded 6·0 g. of 4-chlorophthalic acid, m. p. 150° (identified as the anhydride, m. p. 97°), and no other pure product.

(4) Product 31 (8·2 Cl). 10 G. yielded 2·6 g. of 4 : 5-dichlorophthalic acid and 0·45 g. of tetrachlorophthalic anhydride.

(5) Product 33 (13·2 Cl). 10 G. yielded 0·5 g. of 4 : 5-dichlorophthalic acid and 6·0 g. of tetrachlorophthalic anhydride. In another experiment, the acids (11 g.) obtained from the fission of 15 g. of the same material (product 33) were esterified in boiling ethyl alcohol by the Fischer–Speier method, and the product separated as usual into neutral and acid fractions. The acid fraction (9·2 g.) melted at 75—85°, and at 92° after crystallisation from benzene. A mixed m. p. determination showed it to be the acid ethyl ester of tetrachlorophthalic acid. The neutral fraction (2·0 g.) was an oil which after 2 weeks deposited about 0·5 g. of ethyl 4 : 5-dichlorophthalate, identified by m. p. and mixed m. p. (61°).

In an endeavour to improve the yield obtained in the hydrolysis, an imide obtained by the oxidation of 20 g. of a dodecachlorophthalocyanine was divided into two equal portions. Half was hydrolysed by sulphuric acid direct, the other half was purified by dissolution in aqueous sodium hydroxide and reprecipitation and was then hydrolysed. The yields of chlorophthalic acids obtained in the two experiments were, however, very similar (6·7, 6·4 g.).

Control Experiments on Authentic Imides.—The chlorophthalimides named below were treated under the conditions used for the fission of phthalocyanines, *viz.*, treatment with ceric sulphate in concentrated sulphuric acid, followed by hydrolysis with 95% sulphuric acid at 170—180° for 1 hour. The yields of the corresponding chlorophthalic acids or anhydrides are given below :

Chlorophthalimide	3 : 4-dichloro-	3 : 6-dichloro-	4 : 5-dichloro-	tetrachloro-
% Yield of acid or anhydride	80	70	85	90

We are indebted to Imperial Chemical Industries, Ltd., for grants and gifts of chemicals and to Drs. R. Fraser Thomson and E. G. Beckett for their kind assistance.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W. 7.
THE UNIVERSITY OF SHEFFIELD.

[*Received, July 24th*, 1939.]