Conjugated Macrocycles. Part XXVII. The Formation of Tetrazaporphins from Imidines. Tribenzotetrazaporphin.*

By J. A. Elvidge and R. P. Linstead.

[Reprint Order No. 6284.]

Condensations between imidines (with elimination of ammonia) are discussed. Self-condensation of 4 mols. of either a saturated or an unsaturated (or aromatic) imidine can yield only compounds containing the tetrazaporphin skeleton at unfavourable hydrogenation levels, and so can yield tetrazaporphins only through supplementary oxidation–reduction processes. The condensation between imidines at different hydrogenation levels, however, can yield directly tetrazaporphins or their di- or tetrahydro-derivatives. The preferred reaction will be between 3 mols. of unsaturated and 1 mol. of saturated imidine. There is distinct evidence, experimentally, that these guiding principles operate.

Metal-free phthalocyanine is formed by heating di-imino*iso*indoline, in appreciable yields only in the presence of hydrogen donors. Heating the imidine with metal salts or metals gives the metal phthalocyanines under mild conditions.

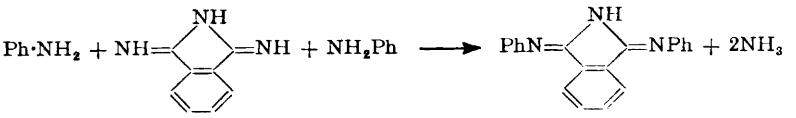
Magnesium tetrazaporphin is prepared in low yield by heating succinimidine with magnesium formate. The metal-free pigment could not be obtained directly from succinimidine.

The condensation of succinimidine with di-imino*iso*indoline (in the absence of metals) readily gives a mixture of tetrazaporphin pigments, containing mainly phthalocyanine and a new blue compound, tribenzotetrazaporphin, isolated by chromatography. Its structure follows from the elementary analysis, the light absorption spectrum, and oxidative degradation.

It has been shown that the newly discovered imidines (Elvidge and Linstead, *J.*, 1952, 5000; Clark, Elvidge, and Linstead, *J.*, 1953, 3593; Elvidge and Linstead, *J.*, 1954, 442;

* Part XXVI, *J.*, 1955, 3521.

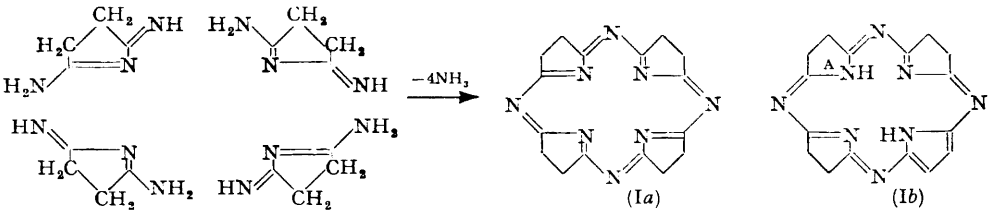
Ficken and Linstead, *J.*, 1955, 3525; Linstead and Whalley, *J.*, 1955, 3530) react readily with 2 mols. of a primary base with elimination of ammonia. This reaction involves both of the extranuclear imino-groups (real or potential) of the imidine and for our present purpose can be exemplified by the reaction between di-imino-*iso*indoline and aniline :



The process occurs alike with imidines derived from saturated, unsaturated, or aromatic 1 : 2-dinitriles.

Imidines can be represented as imino-amino-structures or as di-imines. In addition, imidines of the succinic series might exist or react as 2 : 5-diaminopyrroles. Imidines could thus conceivably provide *both* components in a process of the above kind. Elimination of ammonia between molecules of the same imidine or of dissimilar imidines could theoretically lead to products of two main types, either linear polycondensation products or macrocycles. The imidine from phthalic acid (1 : 3-di-imino*iso*indoline) reacts very easily with suitably oriented diamines to give cross-conjugated macrocycles containing four heterocyclic corner units (Elvidge and Linstead, *J.*, 1952, 5008; Clark, Elvidge, and Linstead, *J.*, 1954, 2490). This illustrates, experimentally, the readiness with which imidines yield *syn*-condensation products and suggests that they might self-condense to give tetrapyrrolic macrocycles of the tetrazaporphin type.

There are, however, complications arising from the hydrogenation level of the system. This can be exemplified by the hypothetical self-condensation of succinimidine, represented below as an interaction of four molecules in the imino-amine form; the first macrocyclic product would be the octahydride (I*a*) of a dehydrotetrazaporphin or its tautomer (I*b*), the hexahydride of tetrazaporphin. Compound (I*a*) contains an inner ring which, although conjugated, is of a type which appears to be unstable. Thus, phthalocyanines and tetrazaporphins show no tendency to lose their two central hydrogen atoms by

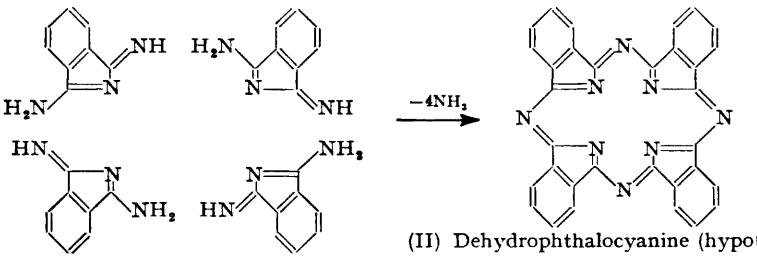


dehydrogenation (Linstead and Weiss, *J.*, 1950, 2981), and the same appears to be true of porphyrins. In compound (I*b*) the formal conjugation is broken at ring A. There are reasons, therefore, to expect that these substances would have a low degree of stability and would not be formed with the same facility as the tetrazaporphins themselves.

The self-condensation of unsaturated or aromatic imidines (which for the present purpose are formally equivalent) can be exemplified by 1 : 3-di-imino*iso*indoline. Four mols. of this, without oxidation–reduction, could only yield a macrocycle at the unfavourable dehydrotetrazaporphin hydrogenation level (II). This can be formulated as generalisation (i), that *self-condensation of imidines of* 1 : 2-*dicarboxylic acids can yield only compounds containing the tetrazaporphin skeleton at comparatively unfavourable hydrogenation levels, and can only yield tetrazaporphins themselves through supplementary oxidation–reduction processes.*

The equivalent generalisations would obviously hold for condensations between dissimilar imidines at the same hydrogenation level. If, however, we examine the condensation between imidines at different hydrogenation levels, the case is altered. Three mols. of an unsaturated or aromatic imidine can react with one mol. of a saturated imidine to

give a macrocycle at the fully " aromatic " tetrazaporphin level. Thus the reaction between di-imino*iso*indoline and succinimidine (written below as diaminopyrrole) could take the course illustrated, to give (III). This is not, however, the only possible mode of reaction between these substances. If the proportion of saturated to aromatic imidine were raised to 2 : 2, then the formation of a dibenzotetrazaporphin could be envisaged, which would be at the dihydro-level (corresponding, for example, to that of the chlorins of the chlorophyll series). If the proportion of saturated imidine were further raised to 3 : 1, the product could be a tetrahydromonobenzotetrazaporphin (corresponding in hydrogenation level to bacteriochlorophyll). Our knowledge of these types of structure, although



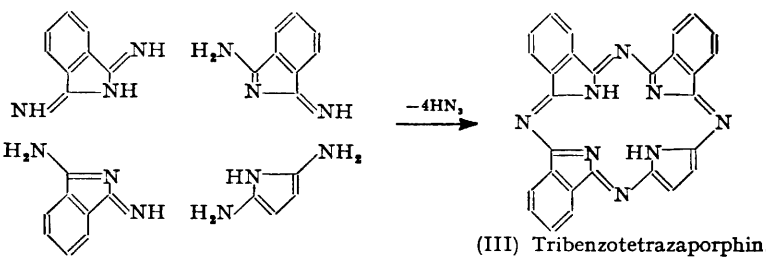
(II) Dehydrophthalocyanine (hypothetical)

very incomplete, suggests that, while neither of these systems would be as stable as the fully " aromatic " tetrazaporphin state, both would have a reasonable stability. These two modes of combination may therefore be possible, if less favourable than that leading to tribenzotetrazaporphin (III).

These considerations yield generalisation (ii), that *condensation between (dissimilar) imidines at different hydrogenation levels can yield, without oxidation–reduction processes, either tetrazaporphins themselves or their di- or tetra-hydro-derivatives.*

If postulates (i) and (ii) were correct and no other factors operated reasonable corollaries would be : (iii) dissimilar imidines at different hydrogenation levels will combine preferentially one with another, rather than by autocondensation ; and (iv) the preferred mode of condensation will be that involving three mols. of unsaturated (or aromatic) imidine and one mol. of saturated imidine.

Clearly, however, this approach is over-simplified. It would only be expected to determine the nature of the condensations if all the intermediate stages up to the final closure of the macrocycle were reversible. The actual primary reaction, which may well be an addition, must be affected by the reactivities of the imino- and amino-groups present in the system. Very little is as yet known on this subject, which is now under investigation. Moreover it is to be expected that in practice the primary reactions will be supplemented and to some extent obscured by oxidation–reduction processes. These considerations may affect the likelihood of a particular condensation, the proportions in which dissimilar



(III) Tribenzotetrazaporphin.

imidines will combine, the state of hydrogenation of the product, and even the occurrence or absence of self-condensation of a single imidine under a particular set of reaction conditions. The position is further complicated as each intermediate stage may become involved in oxidation–reduction processes. Reversible deaminations (imidine $\rightleftharpoons$ dinitrile + NH_3) are also possible complications.

We have now made a preliminary experimental exploration of this field. In summary, we find: first, that mixtures of imidines can condense to give tetrapyrrolic macrocycles without the intervention of metallic reagents; secondly, that there is distinct evidence of the operation of the principles formulated above, which are however to some extent obscured by oxidation–reduction.

The main substances examined were succinimidine and di-imino*iso*indoline.* Their self-condensations were first examined. When heated alone, di-imino*iso*indoline melted at about 196°, and then evolved ammonia. This was due mainly to a reversal of imidine formation, for phthalonitrile sublimed and only a trace of a green pigment was produced. In boiling ethanol, butanol, or 2-ethoxyethanol, the formation of phthalocyanine was negligible. The main products in the last case were ammonia and tricyanocyaphenine, the cyclic trimeride of phthalonitrile (Dent and Linstead, *J.*, 1938, 715; Linstead and Lowe, *J.*, 1934, 1022). The presence of hydrogen donors greatly improved the formation of phthalocyanine. Thus in boiling butanol containing succinonitrile, di-imino*iso*indoline gave a 34% yield of phthalocyanine, whilst a boiling solution of di-imino*iso*indoline in tetralin gave 45% of phthalocyanine quite rapidly. In contrast, in nitrobenzene (a dehydrogenating agent) at the same temperature virtually no phthalocyanine was formed.

These processes are noteworthy as providing mild methods for the preparation of phthalocyanine in the absence of metals. None of them is as efficient as the equivalent reaction between the same imidine and metal salts. For example, in hot formamide with nickel acetate, the imidine almost at once forms nickel phthalocyanine quantitatively. Less effective was copper powder in boiling butanol, which gave from the imidine a 24% yield of copper phthalocyanine in 5 min.

The conversion of succinimidine into tetrazaporphin proved as difficult as expected. None at all could be detected by the use of purely organic media, although unstable coloured products of other types were obtained. However, Mr. J. S. Fitt found that traces of magnesium tetrazaporphin were formed by heating succinimidine with magnesium acetate in nitrobenzene, and with magnesium formate in boiling 2-ethoxyethanol alone or mixed with nitrobenzene. The last combination of reagents was most reliable, and from 1-g. quantities of succinimidine the average yield of magnesium tetrazaporphin was 3%. The pigment was identified spectroscopically and by conversion into metal-free tetrazaporphin. This new preparation of tetrazaporphin is inferior in yield to that from maleinitrile (Linstead and Whalley, *J.*, 1952, 4839), although it is perhaps a little better in time and labour. It affords the magnesium pigment in 3 stages from acrylonitrile (acrylonitrile ⟶ succinonitrile ⟶ succinimidine ⟶ magnesium tetrazaporphin) instead of in 4 stages from maleic anhydride (maleic anhydride ⟶ maleic ester ⟶ maleamide ⟶ maleinitrile ⟶ magnesium tetrazaporphin). The new method provides a synthesis of an azaporphin pigment from the very simple primary reagents, acetylene, hydrogen cyanide, and ammonia.

Mixed Condensation: *The Formation of Tribenzotetrazaporphin.*—The elimination of ammonia proceeded more readily from a mixture of succinimidine and di-imino*iso*indoline than from either component alone. When equivalent quantities were heated together in boiling butanol the two imidines were converted almost completely into a dark insoluble product. This was made up mainly of a charcoal-like insoluble poly-condensation product together with about 20% of a chlorobenzene-soluble blue pigment. The pigment was largely composed of phthalocyanine (main bands at 698 and 665 mμ) and of a new blue compound (main bands at 675 and 594 mμ) subsequently shown to be tribenzotetrazaporphin. There were also traces of a third pigment (main bands at 640 and 590 mμ) which may be a related tetrazaporphin. The first extracts of the crude reaction product also yielded pigment with bands at 752 and 721 mμ but this was labile and did not survive the working up. There is little doubt that it was a hydro-derivative. When the molar proportion of succinimidine to aromatic imidine was raised to 3 : 1, the yield of dark insoluble product was again high but extraction yielded only about 2% of mixed macrocyclic pigments (bands at 720, 698, 675, 640, 590, 548 mμ).

* Preliminary examination of the formation of pigments from 3 : 4 : 5 : 6-tetrahydro- and hexahydrophthalimidine (Ficken and Linstead, *loc. cit.*) gives results in general agreement.

Reaction in boiling butanol of the two imidines in the molar proportion of 1 of succinimidine to 3 of di-imino*iso*indoline, however, gave a more satisfactory product, 32% of mixed pigment being obtained from the crude material. This process was made the basis of further work.

Purification of tribenzotetrazaporphin. This is time-consuming. Although the tribenzo-pigment is soluble in benzene and chlorobenzene in which its tetrabenzo-analogue (phthalocyanine) is ordinarily insoluble, traces of phthalocyanine are carried through and can be separated only by chromatographic procedures. These are arduous because the solutions are (necessarily) so very dilute. The essential steps are : (i) Reduction of the phthalocyanine content by repeated extraction with chlorobenzene (the phthalocyanine largely remains in the residues). (ii) Removal of phthalocyanine from the extracts by chromatography on tartaric acid or mucic acid, two novel adsorbents. (iii) Final purification of tribenzotetrazaporphin from traces of a related (? di- or mono-benzo) pigment by chromatography on kieselguhr.

The product of stage (i) already gave correct elementary analyses for tribenzotetrazaporphin, $C_{28}H_{16}N_8$. The light absorption curve of its chlorobenzene solution, however, showed the presence of traces of phthalocyanine and this was confirmed by chromatography on alumina or mucic acid. For stage (ii) the preferred procedure was, first, chromatography of a chlorobenzene solution on tartaric acid : phthalocyanine came through rapidly, followed by the new pigment. This was taken up in benzene and rechromatographed on tartaric acid, which eliminated the last traces of phthalocyanine. At stage (iii), elution from the kieselguhr with chlorobenzene removed the tribenzotetrazaporphin and left a persistent contaminant as a small mauve band.

Properties of tribenzotetrazaporphin. The new compound is intermediate in properties between phthalocyanine and tetrazaporphin (Linstead and Whalley, *J.*, 1952, 4839). It crystallises from its vividly royal-blue solutions in small needles with a purple reflex. It decomposes without melting at about 400°. Sublimation (at 350°/15 mm. in nitrogen) was not a useful method of purification but gave a most interesting result, some phthalonitrile and phthalocyanine being formed. Evidently the phthalocyanine was derived from thermal breakdown of the tribenzo-compound.

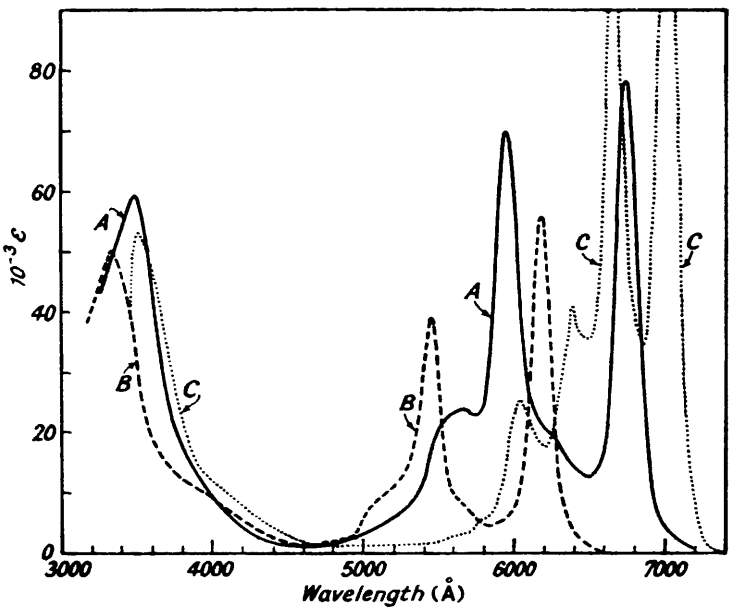
The solubility of tribenzotetrazaporphin, although low, is considerably greater than that of phthalocyanine. A wide range of solvents (for example, benzene, anisole, pyridine, morpholine) dissolve it to the extent of 1—10 mg. per l. The solutions so obtained dissolve phthalocyanine to an appreciable extent, although it is quite insoluble in the pure solvents. The solutions of the mixed pigments are considerably greener than those of the pure tribenzo-compound and show the characteristic absorption bands of both components. This mutual solubility effect may be due to association between the two kinds of molecules, this being facilitated by their similarities in shape and size. The two pigments also form mixed crystals. Solutions of tribenzotetrazaporphin have a dull red fluorescence in ultraviolet light, considerably weaker than the rose-red fluorescence of tetrazaporphin itself. Solutions of phthalocyanine in chloronaphthalene show no ultraviolet fluorescence.

The light absorption of tribenzotetrazaporphin in chlorobenzene over the range 320—1000 mμ is recorded in the Figure, together with the curves for tetrazaporphin and phthalocyanine. Comment is reserved until the collection of corresponding data on the metallic derivatives has been completed.

Structure of tribenzotetrazaporphin. The empirical formula is $C_7H_4N_2$. The compound forms metallic derivatives (Elvidge, Golden, and Linstead, work in progress) of the general composition $C_{28}H_{14}N_8M$ where M is a bivalent, tetraco-ordinate metal. Hence the parent compound can be presumed to be $C_{28}H_{14}N_8 \cdot H_2$. This corresponds to an aggregate of three phthalonitrile units ($C_8H_4N_2$) together with one maleinitrile unit ($C_4H_2N_2$) and the two replaceable atoms of hydrogen. The presence of the last-named is confirmed by quantitative oxidation with ceric sulphate, by which the pigment is destroyed with the consumption of 1 atom of oxygen (cf. Dent, Linstead, and Lowe, *J.*, 1934, 1036). The light absorption at the long-wave end of the visible region is of the general tetrazaporphin type, and the first ultraviolet band resembles closely in position and intensity the similar bands of known tetrazaporphins. This evidence leads to the tribenzotetrazaporphin

structure, one canonical form of which is shown as (III). The evidence has been completed by comparison of the oxidation of the new pigment with that of phthalocyanine. For this purpose we used hydrogen peroxide in sulphuric acid solution. With this reagent almost the theoretical amount of the phthalic residues (corresponding to four corners of the molecule) was isolated from phthalocyanine, 80% being in the form of phthalimide, the rest as phthalic acid. Tribenzotetrazaporphin, on the other hand, yields phthalic derivatives to an extent corresponding to only three corners of the molecule (82% as phthalimide, the rest as phthalic acid). No definite fragment was isolated corresponding to the simple pyrrole corner. This was not surprising as virtually no maleic derivative could be isolated from the oxidation of tetrazaporphin itself (Linstead and Whalley, *loc. cit.*). The phthalic acid from the oxidation of tribenzotetrazaporphin was accompanied by some gum, and this presumably corresponds with the degradation of the pyrrole fragment.

Absorption of (A) *tribenzotetrazaporphin* (*in chlorobenzene*), (B) *tetrazaporphin* (*in chlorobenzene*), *and* (C) *phthalocyanine* (*in chloronaphthalene*).



Experimental

Extractions and extractive crystallisations were performed with an all-glass apparatus similar to that described by Barrett, Dent, and Linstead (*J.*, 1936, 1726).

Self-condensation of 1 : 3-*Di-imino*isoindoline.—(a) *Exploratory work.* (i) Di-imino*iso*indoline (0·5 g.) was heated in a Monax test tube. The imidine melted, became green, bubbled, and evolved ammonia rapidly, and up the sides of the tube phthalonitrile (40 mg.) sublimed (m. p. and mixed m. p. 140°). The melt darkened and became a brownish-black, and, on stronger heating, phthalonitrile distilled up the tube (yield 0·1 g.; m. p. and mixed m. p. 135°). (ii) Di-imino*iso*indoline (0·5 g.) was heated in boiling butanol (25 c.c.) for 100 min., during which ammonia was slowly evolved. The filtrate from traces of blue pigment was evaporated to small bulk and treated with ether (a few drops). Di-imino*iso*indoline (0·1 g.) gradually crystallised having m. p. and mixed m. p. *ca.* 190°. (iii) [With P. F. Clark] Di-imino*iso*indoline (1 g.) was heated in boiling 2-ethoxyethanol (25 c.c.) for 20 hr., during which ammonia was slowly evolved and the solution became greenish and then a faint blue. The filtrate from traces of phthalocyanine was cooled, whereupon tricyanocyaphenine (0·19 g.) separated, having m. p. 300° undepressed by authentic material (Dent and Linstead, *loc. cit.*).

(b) *Formation of phthalocyanine.* (i) Di-imino*iso*indoline (1·8 g.), heated in boiling butanol

(20 c.c.) with succinonitrile (1 g.) for 3·5 hr., evolved ammonia and gave dark needles of phthalocyanine (0·47 g.), and a second crop (80 mg.; total yield, 0·55 g., 34%) after a further hour's boiling; $\lambda_{max.}$ in chloronaphthalene at 6990, 6650, 6400, 6000 Å. (ii) Di-imino*iso*indoline (1 g.), heated in boiling tetralin (25 c.c.) for 100 min., gave beautifully crystalline phthalocyanine (0·4 g., 45%), $\lambda_{max.}$ in chloronaphthalene at 6990, 6640, 6400, 6000 Å. (iii) Only 8 mg. of phthalocyanine ($\lambda_{max.}$ in chloronaphthalene at 6990, 6650, 6000 Å) were obtained by heating the imidine (1 g.) in boiling nitrobenzene (25 c.c.) for 100 min.

(c) *Metal phthalocyanines.* (i) [With MARGARET WHALLEY] Di-imino*iso*indoline (0·2 g.) and nickel chloride (0·2 g.) were dissolved separately in hot formamide (2·5, 12·5 c.c., respectively), and the hot solutions were mixed. Pigment separated almost at once. Next day, the nickel phthalocyanine was collected, washed with ethanol, and extractively crystallised from chloronaphthalene. The yield was 0·19 g., 96%; $\lambda_{max.}$ in chloronaphthalene at 6710, 6030 Å. (ii) The imidine (0·5 g.) and copper powder (0·5 g.) were heated together in boiling butanol (20 c.c.) for 5 min., and the mixture of metal and pigment was collected and washed with methanol. Extractive crystallisation from chloronaphthalene yielded copper phthalocyanine (0·12 g., 24%), $\lambda_{max.}$ in chloronaphthalene at 6780 Å.

Self-condensation of Succinimidine [with JOHN S. FITT].—(a) *Exploratory work.* (i) When succinimidine was heated in boiling ethanol or butanol, alone or with mild dehydrogenating agents ($PhNO_2$, quinones), ammonia was evolved and the solutions became a dark purple, but no tetrazaporphin was formed. (ii) No magnesium tetrazaporphin was obtained by heating succinimidine and magnesium formate or acetate in benzene, toluene, 2-ethoxyethanol, or di-butyl ether, in each case in the presence of quinones, or in 2-ethoxyethanol in the presence of benzoyl peroxide or magnesium oleate, or by heating succinimidine and magnesium acetate in 2-ethoxyethanol with selenium dioxide, hexamethylenetetramine, or nitrobenzene. Heating succinimidine in *cyclo*hexene or dihydronaphthalene with palladium was also ineffective. (iii) Variable small amounts of magnesium tetrazaporphin were formed by short heating of succinimidine with magnesium acetate in nitrobenzene, or with magnesium formate in 2-ethoxyethanol, best in the presence of nitrobenzene.

(b) *Preparation of magnesium tetrazaporphin.* A mixture of succinimidine (1 g.), magnesium formate (10 g.; dried at 75—80°), nitrobenzene (50 c.c.), and 2-ethoxyethanol (50 c.c.; dried over K_2CO_3) was boiled for 15 min., then allowed to cool, and the solid was collected and washed with methanol. The filtrate was evaporated at 100°/20 mm., and the residual nitrobenzene solution run on to a column (14 × 1·5 cm.) of alumina (Spence, type H). The nitrobenzene and a brown impurity were washed through with benzene, and the pigment was eluted with methanol–benzene (1 : 5). The strongly red-fluorescent solution was warmed on the steam-bath until the methanol had distilled out (disappearance of the fluorescence). From the residual benzene, magnesium tetrazaporphin crystallised (average yield, 44 mg., *ca.* 70% pure); $\lambda_{max.}$ in MeOH–C_6H_6 at 5850, 5370 Å. Treatment of the magnesium pigment (69 mg.) with acetic acid (Linstead and Whalley, *J.*, 1952, 4839) gave tetrazaporphin (8 mg.), $\lambda_{max.}$ in C_6H_6 at 6170, 5440 Å.

*Condensation of Succinimidine with Di-imino*isoindoline : *Tribenzotetrazaporphin.*—(a) *Exploratory work.* (i) One equiv. each of succinimidine (2·35 g.) and 1 : 3-di-imino*iso*indoline (3·5 g.) were heated together in boiling *n*-butanol (40 c.c.). Ammonia was evolved, the solution rapidly became dark, and after 2·5 hr. the dark solid (4·1 g.) was collected and washed with ethanol and ether. Continuous extraction of the solid with hot acetone overnight, and then benzene for 3 hr., removed dark brown material and some blue pigment ($\lambda_{max.}$ at 7520, 7210, 6900, 6740, 6530, 5920, 5400 Å). Extraction with hot chlorobenzene for 17 hr. then gave the very dark purplish crude pigment (788 mg.) and a blue supernatant solution, and a charcoal-like residue (2·63 g.) was left in the Soxhlet thimble, from which boiling chloronaphthalene extracted virtually no more pigment. Re-extraction of the crude pigment with hot chlorobenzene overnight gave pigment (662 mg.) which from its absorption spectrum in chlorobenzene appeared to be a mixture (*ca.* 3 : 5) of phthalocyanine and a new pigment with $\lambda_{max.}$ *ca.* 6730, 5920 Å. A substantial separation was achieved by repeated fractional extraction (5 times) with benzene and hot chlorobenzene : the benzene-soluble material and the residues in the Soxhlet thimbles were set aside, whilst the pigment extracted by chlorobenzene was passed to the next extractor (for extraction first with benzene, and then hot chlorobenzene). The crude tribenzotetrazaporphin (113 mg.) crystallised from the chlorobenzene as microscopic dark bluish-purple needles (Found : C, 72·3; H, 3·6; N, 23·9%). Light absorption in chlorobenzene : max. at 6720, 6300, 5920 Å (ε 36,300, 14,500, 37,100). The colour of the solution was peacock-blue. On chromatography of a portion in chlorobenzene on alumina (Spence, type H;

Brockmann grade, II), a green diffuse band washed down the column rapidly, followed slowly by one or two violet-blue bands. The number of blue bands apparently depended on the concentration of the initial solution (they were evidently the result of pigment crystallising out on the column): separate extracts revealed no significant differences. Evaporation of the first green eluate afforded a trace of phthalocyanine, identified spectroscopically ($\lambda_{max.}$ in chloronaphthalene at 7000, 6600, 6400, and 6000 Å). Phthalocyanine is ordinarily insoluble in chlorobenzene: the very dilute solution from the columns was not stable and eventually deposited the pigment. Extraction of the violet-blue bands with hot chlorobenzene gave (with considerable retention on the alumina) a royal-blue solution which fluoresced a weak dull-red in ultraviolet light. The pigment, recovered by evaporation of the solvent, contained 3·9% of ash (Found: C, 70·1; H, 3·5%), which was incompletely removed by aqueous hydrochloric acid (Found: ash, 0·12; C, 71·9; H, 3·7%). Light absorption in chlorobenzene: max. at 6750, 6250, 5920, 3470 Å (ε 61,800, 18,200, 57,600, 53,700). The foregoing benzene extracts were a more reddish-blue, showed a considerably stronger pinkish fluorescence in ultraviolet light, and slightly stronger intensity absorption at *ca.* 6400 Å, which suggested the presence of a further contaminant.

Chromatographic separation of the phthalocyanine from crude pigment mixture was also effected on mucic acid with chlorobenzene. A little phthalocyanine was washed through first, followed slowly by a broad bluish-purple band from which the required pigment was recovered, uncontaminated with ash; and a greenish-blue band, largely of phthalocyanine, formed at the top of the column. The best results were obtained on columns of tartaric acid powder, which neither retained nor destroyed any pigment, and ran rapidly (see below).

(ii) Boiling succinimidine (3 g., 3 equivs.) with 1 : 3-di-imino*iso*indoline (1·5 g., 1 equiv.) in butanol (50 c.c.) for 15 hr. yielded 4 g. of crude charcoal-like product. After exhaustive extraction with methanol and acetone to remove brown material, extraction with benzene and chlorobenzene afforded crude pigment (75 mg.) ($\lambda_{max.}$ in chlorobenzene: 7200, 6750, 6400, 5900, 5480 Å).

(iii) Succinimidine (1 g., 1 equiv.) and 1 : 3-di-imino*iso*indoline (4·3 g., 3 equivs.), heated together in boiling ethanol (40 c.c.) for 15 hr., afforded 1·7 g. of crude product, from which crude pigment (285 mg.) was eventually extracted with benzene and chlorobenzene ($\lambda_{max.}$ in chlorobenzene: 6920, 6740, 6390, 5910, 5460 Å).

(b) *Preparation of crude pigment.* Succinimidine (1 g., 1 equiv.) and 1 : 3-di-imino*iso*indoline (4·3 g., 3 equivs.) were heated together in boiling ethanol (40 c.c.) for 48 hr., and the solid product (4·2 g.) was extracted exhaustively with a hot mixture of methanol (50 c.c.), acetone (50 c.c.), and ethanol (30 c.c.). The crude pigment (3·0 g.) was extracted exhaustively with benzene (yield, 125 mg. of pigment) and then hot chlorobenzene (1·183 g. of pigment). Systematic extraction with these two solvents through 8 stages afforded crude tribenzotetrazaporphin (*a*, 156·5 mg. bulked from benzene extractions; *b*, 419 mg., from chlorobenzene). Both fraction *a* and *b* showed $\lambda_{max.}$ at 5910—5930, 6400—6420, 6740—6770 Å, but the intensity at 6400 Å was higher for *a* than *b*, and *b* showed an additional max. at *ca.* 6920 Å. Chromatography of small samples in chlorobenzene on alumina showed that *a* and *b* were both contaminated by phthalocyanine. Hence the fractions *a* and *b* were combined.

(c) *Chromatographic purification.* The crude tribenzotetrazaporphin (20 mg.) was chromatographed first in chlorobenzene (2 l.) on mucic acid or, better, on powdered tartaric acid hydrate (B.P.; Hopkin and Williams, Ltd.), and the column (6·4 × 30 cm.) was eluted with chlorobenzene. Phthalocyanine was washed through first, followed by the purplish-blue pigment which was recovered (*ca.* 13 mg.) by distillation of the solvent. The pigment (10 mg.) was then chromatographed in benzene (2 l.) on a tartaric acid column (6·4 × 30 cm.) to remove last traces of phthalocyanine, which was again washed through first. Evaporation of the second runnings afforded phthalocyanine-free tribenzotetrazaporphin (recovery, 90%) (Found: C, 71·9; H, 3·75; N, 23·8%). Light absorption in chlorobenzene: max. at 6750, 6400, 5940, 5670, 3480 Å (ε = 72,800, 23,100, 69,700, 24,600, 64,700).

The twice chromatographed pigment (50 mg.) was extracted (Soxhlet) with benzene overnight (yield, 34 mg.) and then chlorobenzene (yield, 16 mg.). The two fractions differed in the intensity of absorption at 6420 Å, the benzene fraction absorbing the more intensely.

The pigment (20 mg.) was finally chromatographed in chlorobenzene (2 l.) on kieselguhr (acid-washed; British Drug Houses, Ltd.) (column, 6·4 × 15 cm.) and eluted with chlorobenzene. A mauve band remained on the column. Evaporation of the eluate and extractive crystallisation of the residue from chlorobenzene gave *tribenzotetrazaporphin* as microscopic very dark bluish needles, decomp. *ca.* 400° (Found: C, 72·2; H, 3·65; N, 24·2. $C_{28}H_{16}N_8$

requires C, 72·4; H, 3·5; N, 24·1%). Light absorption in chlorobenzene: max. at 6750, 5940, 5660, 3490 Å (ε = 78,300, 69,000, 22,900, 59,600); min. at 6500 Å (ε = 12,500) (see Figure).

Oxidation of Tribenzotetrazaporphin with Ceric Sulphate.—Portions of the pigment (13·8, 10·5 mg.) were dusted into separate quantities (5 c.c.) of concentrated sulphuric acid which had been cooled in ice-salt. The solutions were swirled, and each was treated with crushed ice (20 g.) and then 0·00932N-ceric sulphate (10·00 c.c.). The pigment was destroyed almost at once. 0·00760N-Ferrous sulphate (10·00 c.c.) was added to each solution and the excess back-titrated with the ceric sulphate (4·47, 3·00 c.c.), *o*-phenanthroline being used as indicator. The uptake of oxygen was therefore 0·99, 1·00 atom-equiv. (1 mol. of a tetrazaporphin requires 1·0 atom-equiv. of O).

Oxidative Degradation of Tribenzotetrazaporphin.—The pigment (72·8 mg.) was dissolved in concentrated sulphuric acid (2 c.c.; chilled in ice-salt) by stirring. Hydrogen peroxide (*ca.* 1 c.c.; 30-vol.) was added in drops, and the solution removed from the cooling-bath. After 45 min. the solution was light brown. The solution was cooled in ice, and crushed ice (20 g.) was added, followed after 10 min. by powdered ferrous sulphate (1 g.). The solution was extracted with benzene for 22 hr., the extract evaporated, and the residue extracted with dry ether. Evaporation of the latter afforded phthalimide (56·8 mg., 82% of 3 mols.), m. p. and mixed m. p. 230—231°. (There was no loss in weight on treatment with aqueous sodium hydrogen carbonate.) The aqueous solution was then extracted with ether overnight. The extract was evaporated and the residue dried in a vacuum-desiccator ($CaCl_2$). By extraction of the dry residue with dry ether, and evaporation of the latter, a mixture of gum and needles was obtained. Rapid washing with ether removed the gum and left phthalic acid (14·5 mg.), m. p. 190—191° (decomp.).

Oxidative Degradation of Phthalocyanine.—The pigment (74·7 mg.) was oxidised similarly and the solution worked up as above to yield phthalimide (68·0 mg., 79·5% of 4 mols.), m. p. 229—230°, and phthalic acid (unaccompanied by any gum) (17·7 mg.), m. p. 193° (decomp.).

Action of Heat on Tribenzotetrazaporphin.—The pigment was heated in a stream of nitrogen in a " cold-finger " apparatus at 350°/15—20 mm. for 3 hr. A dark blue sticky sublimate was obtained and, higher up the condensing surface, some colourless prisms of phthalonitrile, m. p. and mixed m. p. 141°. Washing the coloured sublimate with cold chlorobenzene gave a green solution (phthalocyanine present) (max. at 5950, 6260, 6740, 6950 Å). The residue on the condensing surface was a hard purplish-blue solid (substantially tribenzotetrazaporphin) (max. in chloronaphthalene at 6750, *ca.* 6250, 5950 Å).

Absorption Spectra.—The instruments used for the light absorption determinations were as described by Linstead and Whalley (*J.*, 1952, 4839). Solutions containing about 0·5 mg. of pigment in 100 c.c. of solvent were used.

Analyses were carried out in the Microanalytical Laboratory (Mr. F. H. Oliver) of this Department.

Department of Chemistry, Imperial College of Science and Technology,
South Kensington, London, S.W.7. [*Received, March 30th,* 1955.]