

371. *Phthalocyanines and Related Compounds.† Part XV. Tetrabenztriazaporphin : its Preparation from Phthalonitrile and a Proof of its Structure.*

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With a Note on a Preliminary X-Ray Investigation.

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Tetrabenztriazaporphin, $C_{33}H_{19}N_7$, is an intensely coloured substance, closely resembling phthalocyanine in physical and chemical properties and identical with it in structure except that it contains one methin group in place of an atom of nitrogen in the great ring (see formula I). Its preparation from phthalonitrile by the action of methylmagnesium iodide and of methyl-lithium has been investigated. The homogeneity and structure of the products have been established, mainly by spectral analysis and quantitative oxidations. A number of metallic derivatives are described. The copper derivative has been compared with the copper compounds prepared by Helberger and von Rebay (*Annalen*, 1937, **531**, 279) and by Dent (J., 1938, 1).

The mechanism of the formation of the triazaporphin ring is discussed. Under controlled conditions phthalonitrile reacts with two equivalents of either methylmagnesium iodide or methyl-lithium to yield 3-amino-1 : 1-dimethylisoindole.

The close similarity in structure of tetrabenztriazaporphin and phthalocyanine has been confirmed by a preliminary X-ray investigation by Dr. J. M. Robertson. This indicates that a centre of symmetry is present, which is probably due to the fact that the molecules display a statistical centre of symmetry in the crystal.

In January, 1934, Dr. A. R. Lowe, in collaboration with one of us (R. P. L.), examined the reaction of Grignard compounds on phthalonitrile, in order to determine whether phthalocyanine derivatives, particularly *N*-alkylphthalocyanines, could be prepared in this way. The action of phenyl- and benzyl-magnesium halides on phthalonitrile had already been examined by Weiss and his collaborators (*Monatsh.*, 1924, **45**, 105 ; 1927, **48**, 449), who had isolated, with some difficulty, certain isoindole derivatives containing only one phthalonitrile unit. In our early experiments methylmagnesium iodide gave, among other products, a very poor yield of a beautifully crystalline solid with a purple reflex. The colour was greener than that of phthalocyanine, and the analytical figures agreed neither with phthalocyanine nor with the hypothetical dimethylphthalocyanine [Found : C, 76.4, 77.1 ;* H, 3.7, 3.6 ;* N, 19.1, 19.6, 19.5,* 19.3 ;* total of mean values, 99.7. Calc. for phthalocyanine ($C_{32}H_{18}N_8$) : C, 74.7 ; H, 3.5 ; N, 21.8%. Calc. for dimethylphthalocyanine ($C_{34}H_{22}N_8$) : C, 75.3 ; H, 4.1 ; N, 20.7%].

A parallel experiment carried out with benzylmagnesium chloride gave phthalocyanine. It appeared, therefore, that alkylphthalocyanines could not be obtained by this method, and in view of the poor yield, the product obtained by the use of methylmagnesium iodide was not further investigated at the time.

In 1936, Fischer and his collaborators (*Annalen*, **521**, 122 ; **523**, 154) announced the preparation of the first macrocyclic pigments containing four pyrrole rings united by some methin links and some nitrogen atoms, and, shortly afterwards, Helberger (*Annalen*, 1937, **529**, 205) described the copper derivatives of similar compounds containing benzene nuclei fused to the pyrrole rings. In view of these developments we re-examined the reaction between phthalonitrile and methylmagnesium iodide.†

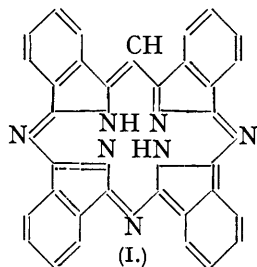
The production of a macrocyclic pigment from these reagents is complex, and we refer

† The general title has been modified because of the second meaning attaching to the word "Associated."

* Recent values on the original sample.

† Since this work was done, the I. G. Farbenindustrie A.-G. have also described the preparation of colouring matters of the phthalocyanine type by heating phthalonitrile with a Grignard reagent (B.P. 480,249).

to the mechanism later in this paper. In practice, two main stages are easily recognised : (i) A preliminary condensation which occurs in cold ethereal solution. If the product is decomposed, *e.g.*, with acid, at this stage, hardly any pigment is isolated. (ii) If the solvent is removed, and the residue heated with a little water, or with certain high-boiling liquids such as quinoline, *cyclohexanol* or α -naphthyl methyl ether, *magnesium tetrabenztriazaporphin* is formed. After removal of the metal by means of acid, *tetrabenztriazaporphin* (I), $C_{33}H_{19}N_7$, can be isolated in a beautifully crystalline form. The yield, of about 40%, is much superior to those reported for other metal-free substances of the tetrabenzporphin type, apart from phthalocyanine.



(This substance is presumed to be a resonance hybrid. The structure shown is chosen arbitrarily from a number of possible states.)

The analytical figures for different preparations are concordant and agree with formula (I). The results are not affected by crystallisation or by sublimation of the compound. Two crystalline forms can be isolated (needles and prisms), but these are identical in analysis and in spectra and can be converted one into the other. The substance, therefore, has the properties of an individual compound, but these facts are inconclusive, for an unusual difficulty arises in connection with it and similar compounds, in which some of the links between the *isoindole* nuclei are methin groups and some are nitrogen atoms.

It is shown later in this paper that the new compound is strictly isomorphous with phthalocyanine, and it may be that similar compounds containing more than one methin group in the great ring will also be isomorphous. These macrocyclic pigments may therefore be expected to form mixed crystals and be separable with difficulty. The analytical results given by the substance now under discussion might equally well be given by an equimolecular mixture of tetrabenzdiazaporphin ($C_{34}H_{20}N_6$) and phthalocyanine ($C_{32}H_{18}N_8$) or by some equivalent mixture of phthalocyanine with a less nitrogenous analogue.

In the present case the homogeneity has been established as follows. The new compound has an absorption spectrum resembling that of phthalocyanine and exhibiting two intense bands in the red region. It is compared below with phthalocyanine, the spectrum of which has been re-measured with the result shown (*cf.* Anderson, Bradbrook, Cook, and Linstead, *J.*, 1938, 1151) :

Tetrabenztriazaporphin :							
$\lambda_{\max.}$ A	6940	6520	6380	6220	5920	5700 (both diffuse)	4620
$\log \epsilon_{\max.}$	5.19	5.03	4.75	4.66	4.43	4.03	4.03
Phthalocyanine :							
$\lambda_{\max.}$ A	7030	6680	6360	6040	5760	5560	
$\log \epsilon_{\max.}$	5.23	5.22	4.75	4.52	4.02	3.88	

The introduction of the methin group brings about a general shift of the band heads towards shorter wave-lengths. The most easily detected differences are the shift in the maxima of the first two bands. The examination of known mixtures has shown that 5% of phthalocyanine can be detected spectroscopically in the tetrabenztriazaporphin, and we believe that the product of the Grignard reaction is substantially free from phthalocyanine. Hence, from the analytical figures, it must also be free from tetrabenzdiazaporphin or a less nitrogenous pigment.

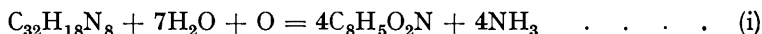
This is supported by a spectroscopic examination of the metallic derivatives. Tetrabenztriazaporphin reacts with metallic copper, zinc, and magnesium, and with ferrous chloride in boiling quinoline, to give the corresponding *copper*, *zinc*, *magnesium* and *ferrous* derivatives. These are of the same type as the metallic phthalocyanines, and have the general formula $C_{33}H_{17}N_7$ Metal^{II}. They differ from the corresponding metallic phthalocyanines in absorption spectra in the manner described in detail in the experimental section. The differences are clearly marked in the zinc derivatives. Zinc phthalocyanine has a very intense band in the red region at 6810 A ($\log \epsilon_{\max.}$ 5.35) and a feeble band at

6490 Å ($\log \epsilon_{\max.}$ 4.48). Zinc tetrabenztriazaporphin has two bands in this region, closer together and much more equal in intensity (6780 Å, $\log \epsilon_{\max.}$ 5.23 and 6540 Å, $\log \epsilon_{\max.}$ 5.00). Moreover, copper phthalocyanine has a sharp maximum at 6120 Å ($\log \epsilon_{\max.}$ 4.77), whereas the absorption curve of copper tetrabenztriazaporphin shows only a series of ill-defined inflexions in this region.

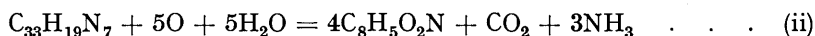
When tetrabenztriazaporphin is heated with cupric chloride, a monochlorinated *copper* derivative is formed. This resembles the corresponding derivative of phthalocyanine (Dent and Linstead, J., 1934, 1027). The *lithium* derivative of tetrabenztriazaporphin also resembles the corresponding metallic phthalocyanine in being soluble in cold alcohol, acetone and similar solvents (cf. Barrett, Frye, and Linstead, J., 1938, 1157). The new method therefore provides a simple and rapid method of preparing a considerable range of metallic compounds of this series.

The resemblance to phthalocyanine in spectrum and general properties, including the power of combining with metals, suggests the analogy in structure which is represented in (I). This general resemblance has also led Helberger and Dent (*loc. cit.*) to propose similar formulæ for the metallic compounds made by their methods. In no case, however, has the benzazaporphin structure been rigorously proved. This has now been done by two different methods.

It was shown by Dent, Linstead, and Lowe (J., 1934, 1036) that phthalocyanine and its metallic derivatives were quantitatively oxidised by acid ceric sulphate to phthalimide :



It would not be expected that tetrabenztriazaporphin would be oxidised to phthalimide so easily because of the presence of the methin bridge; and before complete fission could occur, this group would have to be oxidised to carbon dioxide and water. The oxidative fission of tetrabenztriazaporphin would then involve the process :



In practice we have been able to realise this reaction quantitatively, or semi-quantitatively, in all respects. Tetrabenztriazaporphin is more resistant towards oxidising agents than is phthalocyanine, but can be completely oxidised by both acid permanganate and acid ceric sulphate. Permanganate oxidation yields phthalimide in 84% yield (on the basis of the above equation), and at the same time 3 mols. of ammonia are liberated. Under similar conditions phthalocyanine yields 4 mols. of ammonia. For measuring the oxygen uptake quantitatively, rather more drastic conditions than those for the oxidation of phthalocyanine are necessary, the pigment being heated to 100° with a considerable excess of ceric sulphate. An amount of oxygen corresponding to nearly 5 atoms per molecule is then taken up. Under the same conditions, phthalocyanine takes up only 1.1 atoms of oxygen per molecule, and the method is therefore suitable for the estimation of mixtures of the macrocyclic pigments. Copper tetrabenztriazaporphin also is oxidised by acid ceric sulphate, but in this case the oxidation is slower, and the quantitative results not quite so accurate, about 4.7 atoms of oxygen per molecule being taken up. By a modification of the experimental technique we have also estimated the carbon dioxide liberated during the ceric sulphate oxidation. Phthalocyanine gave hardly any carbon dioxide; tetrabenztriazaporphin gave 1 mol. Equations (i) and (ii) are thus confirmed completely. These results exclude the possibility of the new pigment being a methylated phthalocyanine.

In experiments on the oxidation with ceric sulphate the initial blue-green pigment became purple. The purple compound reverted to the original pigment so readily as to prevent its isolation. Reducing agents such as stannous chloride brought about this reversal instantaneously. The purple compound was fairly stable to dilute sulphuric acid, but was very rapidly dissolved by the addition of more ceric sulphate.

Dr. J. M. Robertson kindly carried out a preliminary X-ray investigation of tetrabenztriazaporphin and its copper derivative, using monoclinic needles prepared by sublimation. The samples were analytically pure and showed no phthalocyanine bands in the spectra. Dr. Robertson reports as follows : " The crystals were similar in habit to the corresponding

phthalocyanines (see J., 1935, 615). They were examined photographically with Cu $K\alpha$ radiation. Rotation photographs about the needle axis (the b crystallographic axis) of the two compounds appeared to be identical with those of the corresponding phthalocyanines. Direct measurements of the periodicity gave the following results :

Tetrabenztriazaporphin : $b = 4.72, 4.71, 4.74, 4.72, 4.71$;

mean 4.725 Å (for metal-free phthalocyanine, $b = 4.72$ Å).

Copper tetrabenztriazaporphin : $b = 4.76, 4.80, 4.77, 4.78, 4.78$;

mean 4.78 Å (for copper phthalocyanine, $b = 4.79$ Å).

“The intensities of the reflections were examined, and compared with those of the corresponding phthalocyanines by moving-film photographs of ($h0l$) zones, taken on the two-crystal spectrometer (*Phil. Mag.*, 1934, **18**, 729). No additional reflections were observed and the intensities appeared to be practically identical with those of the corresponding phthalocyanines, although some very small and rather doubtful changes in the higher orders were noted in the case of the metal-free compounds.

“These results show that the structure, dimensions, and arrangement of the tetrabenztriazaporphin molecules in the crystal must be almost, or completely, identical with those in the corresponding phthalocyanine molecule. In particular, the molecule of tetrabenztriazaporphin appears to display a centre of symmetry in the crystal. This at first sight contradicts the chemical evidence leading to the structure (I). There are two possible explanations :

“(1) The deviation from centre-symmetry required by the chemical evidence is small, involving a substitution ($-\text{CH}^-$ for $-\text{N}^-$) which would have little effect on the dimensions or on the scattering power for X -rays. It is possible that much longer exposures and more careful examination might reveal additional intermediate reflections, due to a superlattice, which would change the space group and hence the conclusion drawn about the molecular symmetry. In view of the experimental conditions and the precautions taken, this seems unlikely.

“(2) It appears much more probable that the molecules display a *statistical* centre of symmetry in the crystal, due to a random distribution of the molecules with respect to the unique $-\text{CH}^-$ group. The differences in the potential energy for the molecule in different positions with respect to the $-\text{CH}^-$ group of its neighbours would obviously be very small, so that a random arrangement seems likely, and perhaps inevitable. Comparison should be made with the work of Hendricks (*Z. Krist.*, 1932, **84**, 85) on the statistical centre of symmetry reported in *p*-chlorobromobenzene, and with that of Pauling (*J. Amer. Chem. Soc.*, 1924, **46**, 2738) on ammonium oxyfluoromolybdate.”

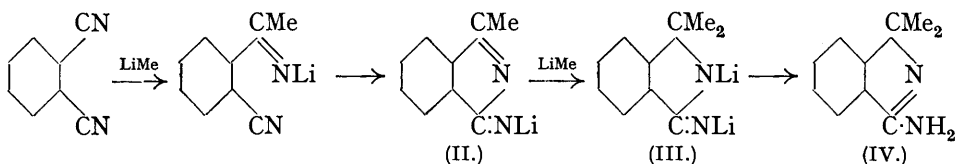
In view of Gilman and Kirby's demonstration (*J. Amer. Chem. Soc.*, 1933, **55**, 1265) that certain aromatic nitriles are more readily attacked by methyl-lithium than by methylmagnesium iodide, the reaction between phthalonitrile and methyl-lithium was next examined. As with the Grignard reaction, appreciable quantities of macrocyclic pigment were only obtained when the initial reaction was followed by a period of heating at a relatively high temperature. Thus, when phthalonitrile reacted with an equimolecular amount of methyl-lithium at 0° and the product was heated to about 200° with *cyclohexanol*, it gave some 15% of a pigment approximating in composition to tetrabenztriazaporphin. There are, however, indications that this material contains some tetrabenzdiazaporphin or a similar less nitrogenous pigment.

Under these conditions only a small proportion of the methyl groups supplied in the reagent appear as methin groups in the final product. Hence we examined the action of a deficiency of methyl-lithium on phthalonitrile, but although this gave a better yield of total pigment (35%), the product contained a large proportion of phthalocyanine.

When *n*-butyl-lithium (Ziegler and Colonius, *Annalen*, 1930, **476**, 135) was used in place of methyl-lithium, a mixture of a triaza-compound and phthalocyanine was obtained. This fact, taken together with earlier results with benzylmagnesium chloride, indicates that the tendency for organo-metallic compounds to yield macrocyclic pigments containing carbon links is greatest with methyl derivatives. Organo-metallic compounds containing

larger groups tend to give more phthalocyanine, and even with methyl reagents some phthalocyanine can be formed under suitable conditions.

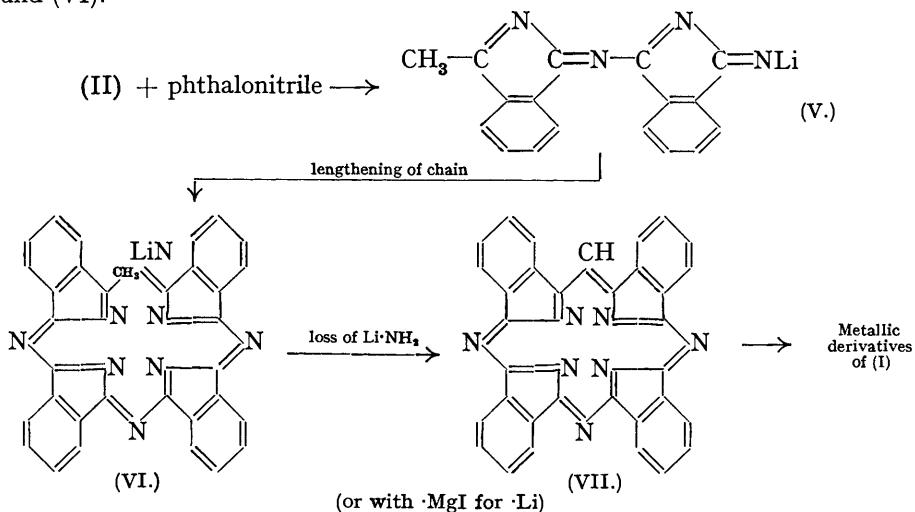
An insight into the mechanism of the reaction was provided by a study of the effect of an excess (2 mols.) of methyl-lithium on phthalonitrile. The product was "baked" at 200° with *cyclohexanol*. From the residue a basic product was isolated as the *picrate*, m. p. 255°. This yielded the free base, C₁₀H₁₂N₂, m. p. 144°, which is regarded as 3-*amino-1:1-dimethylisoindole* (IV), analogous to the amino-dibenzylisoindole of Weiss and Freund (*Monatsh.*, 1924, **45**, 105). The formation of the base is attributed to the following series of reactions :



Examples of the addition of alkyl-lithiums both to cyano-groups and to the $-C\equiv N$ bonds of heterocyclic nuclei have been observed by Ziegler (summary in *Angew. Chem.*, 1936, **49**, 455).

Since phthalonitrile can react with 2 mols. of methyl-lithium, it became of interest to examine the reaction with an excess of the Grignard reagent. A series of experiments were therefore performed in which the nitrile was treated in the cold with 1, 1.5, and 2 mols. of methylmagnesium iodide. No pigment was formed in any experiment, and a considerable amount of nitrile escaped reaction in the first two experiments, but not in the third. This showed that the first product (similar to II) reacted more readily with the Grignard reagent than did the free nitrile. The amino-dimethylisoindole (IV) formed in this reaction eluded isolation until it was found that it was so strong a base that it displaced ammonia from the ammonium chloride used in the working up of the organo-metallic compound. It was readily isolated from the aqueous layer and identified with the base made by the use of methyl-lithium.

The important fact emerges that in the preparation of tetrabenztriazaporphin from equimolecular quantities of phthalonitrile and methylmagnesium iodide, an excess of the nitrile remains at the end of the first condensation. This nitrile is clearly the intermediate responsible for the nitrogen links in the triaza-compound. The unique methin link might reasonably be provided by an intermediate of type (II) or of type (III). If (II) were concerned, it would react with a further molecule of phthalonitrile to give (V) and eventually, by a suitable lengthening of the chain and closing of the *isoindole* rings, the tetra-*isoindole* compound (VI).



So far the reaction scheme is reminiscent of that of Ziegler (*loc. cit.*) for diene polymerisation. The ring closure of (VI), involving an elimination of lithiumamide, would occur during the second stage of the reaction. The potential lithiumamide would attack the alcoholic reagent with the liberation of ammonia, or the methoxyl group of naphthyl methyl ether with the elimination of methylamine (both α -naphthol and methylamine have, in fact, been identified in the product in the latter case). Lithiumamide is known to undergo reactions of both these types. The unstable dehydro-compound (VII), obtained in this way, would finally acquire the metallic atom or atoms to form the derivatives of tetrabenztriazaporphin.

Alternatively, a similar chain of reactions might be started by the metallic derivative of aminodimethylisoindole (such as III). The final ring closure, corresponding to the change (VI) \longrightarrow (VII), would then involve the elimination of methylamine.

The mode of formation of the triazaporphin ring in these particular reactions is part of the broad problem of the mechanism of formation of methin and nitrogen links in macrocyclic pigments in general. As this is still being investigated in connection with a study of less nitrogenous analogues, further discussion may be postponed. It may be said, however, that of the alternatives mentioned above, the first appears more probable, because the interaction of free aminodimethylisoindole, phthalonitrile and magnesium acetate leads to a mixture of macrocyclic pigments containing magnesium tetrabenzmonoazaporphin and quite different from the almost homogeneous triaza-material produced by the Grignard reaction. The freedom of the latter product from less nitrogenous pigments is attributed to the ease of the combination of (II) with phthalonitrile.

The formation of phthalocyanine when a deficiency of methyl-lithium is used is attributed to a primary seizure of metal, without the introduction of a methyl group, to give a "cyanyl," $CN \cdot C_6H_4 - \dot{C} \cdot NLi$, analogous to the ketyls. This radical then undergoes a chain reaction with phthalonitrile, and the intermediate containing four units cyclises to phthalocyanine.

When pigment formation is carried out in the absence of free phthalonitrile, *i.e.*, from the product of its reaction with a large excess of Grignard reagent or methyl-lithium, more highly methinated compounds are formed. These will be described in a later paper.

Finally, the copper tetrabenztriazaporphin, prepared from the metal-free compound as described above, was compared with material obtained in poor yield by the method of Helberger and von Rebay (*Annalen*, 1937, **531**, 285) by the action of cuprous chloride on a mixture of phthalonitrile and *o*-cyanoacetophenone, and with that prepared by Dent's method (*loc. cit.*) from methylenephthalimidine. We find that both these products are substantially identical with our compound, and their structure is therefore confirmed. The product made by Helberger and von Rebay's method required a rather high amount of oxygen for complete oxidation (5.6 atoms) and therefore appears to contain a less nitrogenous pigment as impurity, probably the corresponding diaza-compound. This is not surprising, as Helberger and von Rebay obtained copper tetrabenzdiazaporphin by the same reaction, using a smaller proportion of phthalonitrile. The material made by Dent's method contained a small proportion of copper phthalocyanine, as it had a sharp absorption band at 6120 A.

EXPERIMENTAL.

Grignard Reaction on Phthalonitrile.—1 [With A. R. LOWE]. The Grignard compound prepared from 1 g. of magnesium and an excess of methyl iodide in 80 c.c. of dry ether was treated with 10 g. of phthalonitrile in the cold. The product was warmed for 15 hours on the steam-bath, the solvent removed, and the tarry residue decomposed with 300 c.c. of cold water, to which 15 c.c. of concentrated hydrochloric acid were subsequently added. The dark green residue was extracted successively with hot dilute hydrochloric acid and with hot alcohol. The final residue (0.5 g.) was dissolved in concentrated sulphuric acid and precipitated by water. It had the appearance of phthalocyanine, but was greener in shade. Crystallisation from quinoline gave long needles with a purple lustre. The analytical figures agreed with those required for tetrabenztriazaporphin, but the absorption spectrum showed that the product contained some phthalocyanine (see below).

A similar preparation, benzylmagnesium chloride being used, gave a small yield of free phthalocyanine, indistinguishable from authentic material in colour and spectrum and yielding correct analytical figures.

2. The best yield of pure tetrabenztriazaporphin was obtained as follows: A solution of methylmagnesium iodide was prepared from 2.4 g. of magnesium and 6.5 c.c. of methyl iodide in 100 c.c. of ether; this was decanted from the residual metal and added to a mixture of 12.8 g. of finely powdered phthalonitrile and 50 c.c. of ether. The liquid at once turned reddish-brown and the nitrile dissolved. After a minute or two, a dark brown tarry mass began to separate; the ether commenced to boil gently and the reaction was allowed to proceed without cooling. It was convenient not to use a reflux condenser, but to allow the ether to distil off during this operation. After a few hours the remainder of the ether was removed on the steam-bath. The tarry residue was rapidly heated to 200°. Several drops of water were then allowed to fall on the reaction mixture, whereupon a vigorous evolution of white fumes took place. After a few minutes, a little more water was added, until in all 3 c.c. had been used. Towards the end of the process, iodine vapour was liberated. Further addition of water then gave rise to no more white fumes. After a further $\frac{1}{2}$ hour at 200°, the powdery residue was cooled, crushed, and repeatedly extracted with a mixture of alcohol and 10% concentrated hydrochloric acid. When the extracts were no longer coloured brown, the residue was washed with absolute alcohol and dried in the steam-oven. The crude pigment thus obtained was freed from magnesium by dissolution in concentrated sulphuric acid, followed by filtration and precipitation with ice. The green precipitate was collected and washed repeatedly with hot water containing a little ammonia. It was dried at 100°, and crystallised from chloronaphthalene in the usual apparatus (Barrett, Dent, and Linstead, *loc. cit.*). Yield, 4.7 g.

Tetrabenztriazaporphin (I) formed needles with a strong purple reflex. It was sparingly soluble in pyridine, more soluble in quinoline and chloronaphthalene (green solution). The solution in concentrated sulphuric acid was tawny brown, and addition of a drop of nitric acid gave an intense crimson colour fading after a few minutes (*cf. Dent, loc. cit.*). When the substance crystallised from boiling chloronaphthalene, the needles were contaminated by plates with a similar reflex. No separation could be effected by chromatographic adsorption on alumina from chloronaphthalene solution, but the two kinds of crystals could be separated by fractional sedimentation in alcohol. The more compact plates sank first, and the needles could be poured off with the supernatant liquid. Recrystallisation of the plates from much chloronaphthalene gave only needles; recrystallisation of the needles from a concentrated solution gave both forms. The spectra of the solutions of the two forms were identical (see below). When heated in a current of carbon dioxide under reduced pressure, the compound tended to melt, and then sublimed, giving lustrous needles. Analyses of the various products are tabulated below:

	C.	H.	N.	Total, %.
Found (plates)	77.2	3.6	19.1, 19.1	99.9
(needles)	77.2	3.6	19.2, 19.2	100.0
(sublimed)	77.3	3.5	19.3	100.1
(another prepn.)	77.6	3.9	—	—
(original sample)	76.4, 77.1	3.7, 3.6	19.1, 19.6, 19.5, 19.3	99.8
Mean of above values	77.1	3.65	19.3	100.1
C ₃₃ H ₁₉ N ₇ , requires	77.2	3.7	19.1	—

The absorption spectra of all the compounds described in this paper were determined in chloronaphthalene solution by means of a Hilger constant-deviation spectrometer. The intensities of the main bands are of the same order as those of the corresponding bands of phthalocyanine. The main band of tetrabenztriazaporphin can easily be detected in a layer 1 mm. thick of a solution containing 1.56 mg. per litre.

The quantitative measurements of intensities were carried out by means of a Hilger-Nutting spectrophotometer with a solution of about 1 mg. of pigment in 100 c.c. of chloronaphthalene. In general, this solution gave convenient intensities when a 2 cm. column was used; for the strongest bands, dilution to one-fourth of this concentration was necessary. No change was observed after the solutions had stood for 5 days, providing they were reheated to dissolve any pigment which might have separated.

The spectra of the plates, needles and sublimed pigment, prepared as above, were identical, with maxima at:

I 6940, II 6635 (inflexion), III 6520, IV 6380, V 6220, VI 5920, VII 5700, VIII 4620 A.

Intensities: I > III > II > IV > V > VI > VIII > VII.

A quantitative examination of the spectrum of the needles gave the following results:

λ (A)	6940	6520	6380	6220	5920 (diffuse)	5700	4620
log ϵ	5.19	5.03	4.75	4.66	4.43	4.03	4.03

The original 1934 sample showed maxima at :

I 6920, II 6640, III 6500, IV 6350, V 6170, VI 5910 A.

Order of intensities : I > II > III > V > VI > IV.

There is a general resemblance to the triaza-compound, but the increased strength of the 6640 band indicates the presence of an appreciable proportion of phthalocyanine.

Oxidation of Tetrabenztriazaporphin.—After many comparative experiments, the following conditions were found to be satisfactory.

(i) *Measurement of oxygen taken up.* A known weight of the pigment (*ca.* 80 mg.) was dissolved in 5 c.c. of concentrated sulphuric acid and precipitated in a finely divided condition by the addition of about 50 g. of pure ice. *N*/10-Ceric sulphate (50 c.c.) was added, and the mixture kept at the b. p. for 20 minutes. The solution was then rapidly cooled and treated with a measured excess of *N*/10-ferrous ammonium sulphate (30—35 c.c.). After the addition of a few drops of disulphine-blue, the solution was titrated with ceric sulphate. Under these conditions, tetrabenztriazaporphin, prepared as above, took up 4.80, 4.76, 4.90 atoms of oxygen per mol.

These conditions are slightly more drastic than those originally used for the oxidation of phthalocyanine (Dent, Linstead, and Lowe, *loc. cit.*). When phthalocyanine was oxidised under the new conditions, the oxygen uptake was 1.11, 1.13, 1.08 atoms per molecule; this is sufficiently near to the theoretical value of 1.00 to make the method practicable for the estimation of mixtures.

(ii) *Measurement of carbon dioxide evolved.* During the oxidation by ceric sulphate, carbon dioxide was freely evolved, and was estimated as follows : About 150 mg. of the pure pigment were dissolved in sulphuric acid and precipitated with ice, and 50 c.c. of *N*/10-ceric sulphate were added, together with 100 c.c. of boiled-out distilled water. The mixture was then heated to boiling while air free from carbon dioxide was slowly aspirated through the solution by means of a filter pump. On its way to the pump, the vapour emerging from the reaction mixture passed through a splash-head, and then through a vertical condenser leading into an absorption flask containing 8 c.c. of *N*/5-baryta. Any carbon dioxide which escaped absorption was trapped in a Peligot tube containing a further 2 c.c. of the baryta solution. After 1 hour, during which some 80 c.c. of water had distilled over, heating was discontinued, and the current of air maintained for a further 2 hours. The baryta solution was then filtered through a sintered glass funnel, the pores of which had been blocked with barium carbonate, and the excess of baryta in the filtrate and washings was titrated with standard acid. The residual ceric sulphate in the oxidation vessel was estimated as already described.

	Mols. CO ₂ /mol. pigment.	Atoms O used.
Tetrabenztriazaporphin	0.93, 0.91 (calc., 1.0)	4.85, 4.76 (calc., 5.0)
Phthalocyanine	0.12 (calc., nil)	1.02 (calc., 1.0)

(iii) *Estimation of phthalimide and ammonia.* Phthalimide could not be isolated from the solution obtained when tetrabenztriazaporphin was oxidised with ceric sulphate, since the long period of heating led to hydrolysis to phthalic acid. 100—150 Mg. of the pigment were dispersed with the aid of sulphuric acid, and heated at 70° for 10 minutes with an excess of potassium permanganate solution. The product was cooled quickly, and decolorised with sodium bisulphite. The imide was then thoroughly extracted with ether, the extract dried, and the solvent removed in a weighed flask; a residue of phthalimide was left. The ammonia produced by hydrolysis of the aza-links was estimated in the aqueous solution after removal of the imide, by Kjeldahl's method. The results below are expressed as mols. of product per mol. of pigment.

	Yield of imide.	Yield of ammonia.
Tetrabenztriazaporphin	3.36, 3.04 (calc., 4.0)	3.03, 3.04 (calc., 3.0)
Phthalocyanine	3.80 (calc., 4.0)	3.97 (calc., 4.0)

The rather low yield of phthalimide from the triaza-compound may be due to mechanical loss (*e.g.*, absorption by the drying agent); the almost correct ammonia figure shows that little remains in the aqueous layer. The imide was in all cases identified by m. p. and mixed m. p. 229°.

A mixture of the triaza-compound and phthalocyanine was produced by the following modification of the preparative method; The reagent prepared from 4.8 g. of magnesium and 14 c.c. of methyl iodide in 100 c.c. of anisole was added to a solution of 25.6 g. of phthalonitrile

in 100 c.c. of anisole, at the b. p. The mixture became orange and then green and a little pigment crystallised. The heat of reaction kept the mixture at the b. p. for a few minutes; the product was then heated for a further 5 minutes and allowed to cool overnight. The product was decomposed with 250 c.c. of 20% ammonium chloride solution; the tar which separated was collected and extracted with alcohol until all the anisole was removed. The residue of crude pigment was purified by solution in concentrated sulphuric acid, filtration and precipitation with ice. The precipitate was washed, dried, and crystallised from chloronaphthalene. Yield, 4.5 g. of lustrous crystals. The substance showed three strong bands at 6950, 6640, 6480 Å and weaker bands at 6330, 6200 and 5950 Å (the last appeared to consist of two weak bands). The pigment contained phthalocyanine, as shown by the strong 6640 band and by analysis of a sublimed sample (Found: C, 76.2; H, 3.7; N, 20.2, 20.5. Calc. for $C_{32}H_{16}N_8$: C, 74.7; H, 3.5; N, 21.8%. Calc. for $C_{33}H_{18}N_7$: C, 77.2; H, 3.7; N, 19.1%).

Reactions with Methyl-lithium.—For the preparation and use of methyl-lithium, the technique described by Gilman, Zoellner, and Selby (*J. Amer. Chem. Soc.*, 1932, 54, 1957; 1933, 55, 1252) was followed, a yield of about 60% being obtained.

1. The methyl-lithium from 12.5 c.c. of methyl iodide and 3 g. of lithium in 120 c.c. of ether was blown through a gauze filter into an ice-cold solution of 12.8 g. of phthalonitrile in 120 c.c. of dry ether. The white precipitate which separated rapidly turned brown. The ether was then removed, 25 c.c. of cyclohexanol added, and the mixture heated at 200° for 2 hours, some ammonia being evolved. The green residue of lithium pigment was dissolved in hot alcohol, and the solution acidified with a slight excess of concentrated hydrochloric acid. This precipitated the pigment but not the tar. The pigment was washed, dried, and crystallised from chloronaphthalene. Yield, 1.0 g. of lustrous needles (Found: C, 77.6; H, 3.9; after sublimation: C, 78.1, 78.1; H, 3.85, 3.9; N, 18.3%). Spectrum: I 6950, II (6670), III 6520, IV 6390, V 6230, VI 5930 Å. Order of intensities: I > III > II, IV, V > VI. Although the spectrum closely resembles that of tetrabenztriazaporphin, the high carbon and low nitrogen figures indicate the presence of some less nitrogenous impurity (Calc. for tetrabenztriazaporphin, $C_{34}H_{20}N_8$: C, 79.7; H, 3.9; N, 16.4%).

2. A similar experiment was performed in more dilute solution (500 c.c. of ether), and the product decomposed by addition of water without the removal of solvent. A dark tar, containing no pigment, was thus obtained. It was washed with a little water, dried on filter-paper, and heated at 200° for 30 minutes with 25 c.c. of α -naphthyl methyl ether. Extraction of the product with alcohol left a pigment, which was purified as before. Yield, 1.2 g. (Found: C, 78.5, 78.7; H, 3.6, 3.6; N, 17.6%). The compound showed strong bands at 6960, 6520, and 6370 Å, and weaker bands at 6220 and 5930 Å. Here again, there is a definite indication of the presence of a less nitrogenous pigment.

During the heating at 200° a current of air was passed through the reaction vessel, and then through tubes containing broken glass moistened with hydrochloric acid. At the end of the heating the liquid in the absorption tubes was extracted with ether (A), and the acid layer evaporated to dryness. The residue was extracted thoroughly with alcohol, which left solid ammonium chloride. The alcoholic extract was evaporated to dryness, and the process repeated. The residue from the final extract was identified as methylamine hydrochloride by conversion into the base and by the colour reaction with tetrachloroquinone. The ethereal extract (A) was extracted with alkali. The neutral product was identified as α -naphthyl methyl ether (trinitrobenzene derivative, m. p. 137°) and the phenolic product as α -naphthol (ferric chloride reaction; picrate, m. p. 188°).

3. Experiment 1 was repeated, 1 mol. of methyl-lithium to 3 mols. of nitrile being used. From 12 g. of nitrile, there were obtained 3.5 g. of crystalline pigment (Found: C, 75.8; H, 3.8%). The spectrum showed strong bands at 6950, 6650 and 6510 Å and weaker bands at 6200 and 5950 Å. The prominent band at 6650 Å showed the presence of phthalocyanine; this was confirmed by analysis, and by ceric sulphate oxidation, which gave values of 2.8, 2.8 atoms of oxygen per mol. This product therefore contained approximately equal parts of phthalocyanine and tetrabenztriazaporphin.

4. The reaction between 1 mol. of methyl-lithium and 4 mols. of nitrile (12 g.) yielded 4.3 g. of a pigment identical in its spectrum with the above (Found: C, 75.7; H, 3.7%; oxidation values, 2.7, 2.7 atoms O).

During the course of these experiments, it was observed that if the heating with cyclohexanol was carried out at 250°, the pigment was insoluble in alcohol. Presumably this is due to removal of the lithium by the cyclohexanol.

5. Reaction of excess of methyl-lithium on phthalonitrile. An ethereal solution of methyl-

lithium prepared as above from 3 g. of lithium and 12.5 c.c. of methyl iodide was added to an ice-cooled suspension of 6.4 g. of phthalonitrile in ether (*ca.* 2 mols. of methyl-lithium to 1 mol. of nitrile). After 15 minutes' stirring, during which time the original buff precipitate became brown, the mixture gave a positive Gilman test (*J. Amer. Chem. Soc.*, 1925, **47**, 2002). The ether was then distilled off, and the pasty residue heated at 200° for $\frac{1}{2}$ hour in a wax-bath; 20 c.c. of cyclohexanol were added to destroy any residual methyl-lithium. The residue was cooled and extracted with boiling alcohol, and the extract filtered and treated with 50 c.c. of concentrated hydrochloric acid. It was then diluted with water to four times its original volume and boiled with activated charcoal. The solution was filtered, made alkaline with excess of caustic soda, and thoroughly extracted with ether. The reddish ethereal solution was dried over sodium sulphate and concentrated to 20 c.c. An ethereal solution of picric acid was then added so long as a precipitate was produced. The solid was repeatedly crystallised from absolute alcohol, 3-amino-1 : 1-dimethylisoindole picrate being obtained as a mass of canary-yellow needles (0.45 g.), m. p. 255° (Found : C, 50.15, 50.0; H, 4.3, 4.2; N, 17.7. $C_{10}H_{12}N_2 \cdot C_6H_3O_7N_3$ requires C, 49.4; H, 3.9; N, 18.0%).

The picrate was decomposed with caustic soda solution, and the base extracted with benzene. The benzene extracts were washed with a little water and dried over sodium sulphate, and the solvent removed. Careful recrystallisation of the residue from benzene-petrol gave free 3-amino-1 : 1-dimethylisoindole (IV), m. p. 144°. It formed needles, soluble in most organic solvents with the exception of petrol. It was somewhat soluble in water, the solution being strongly alkaline (Found : C, 74.7; H, 7.35; N, 17.3. $C_{10}H_{12}N_2$ requires C, 75.0; H, 7.5; N, 17.5%). A better method for the preparation of this base is given on p. 1820.

Reactions with Butyl-lithium.—*n*-Butyl-lithium was prepared, following Ziegler and Colonius (*loc. cit.*), from 3 g. of lithium and 18.9 c.c. of *n*-butyl chloride in 120 c.c. of ether. When the reagent was added to phthalonitrile (17 g.) in ether (100 c.c.), a purple colour appeared, changing to greenish-black. The mixture was decomposed with water and acidified with dilute hydrochloric acid. During these operations, the mixture became warm and the ether boiled; a black tar separated. This was filtered off from the water and ether and extracted with alcohol, whereupon a small quantity of pigment remained. This was apparently phthalocyanine (Found : C, 74.9; H, 3.7. Calc. for $C_{32}H_{18}N_8$: C, 74.7; H, 3.5%). Spectrum : I, 7000; II, 6650; III, 6500; IV, 6360; V, 6050; VI, 5790 Å. I, II > III, IV, V > VI.

In another experiment, the *n*-butyl-lithium from 2 g. of metal and 12.6 c.c. of *n*-butyl chloride was added to 12 g. of nitrile (equimolecular proportions assuming a 70% yield of butyl-lithium, as obtained by Gilman, Zoellner, and Selby, *loc. cit.*). The product was heated with cyclohexanol, as for methyl-lithium. The analysis and spectrum of the resulting pigment showed that it contained phthalocyanine and either tetrabenztriazaporphin or its *n*-propyl derivative (Found : C, 76.1; H, 4.0%). Spectrum : I, 6950; II, 6640; III, 6510; IV, 6330; V, 6210; VI, 5950 Å. Order of intensities : I, II, III > IV > V, VI.

Metallic Derivatives of Tetrabenztriazaporphin.—*Copper derivative.* Analytically pure tetrabenztriazaporphin, made by the Grignard reaction, was heated for 12 hours in boiling quinoline with an excess of copper bronze. On cooling, the copper derivative crystallised in needles with a purple lustre (Found : C, 68.6; H, 2.9; Cu, 11.6. $C_{33}H_{17}N_7Cu$ requires C, 68.9; H, 2.95; N, 17.1; Cu, 11.1%). When heated under reduced pressure, it tended to melt, and then sublimed in needles (Found : C, 68.8, 68.8; H, 3.1, 3.1; N, 17.1, 17.3; Cu, 10.8, 11.0%). Spectrum : I, 6840; II, 6550; III, 6270; IV, 6140; V, 6000 Å. Order of intensities : I > II > III, IV, V.

A simpler method of preparing this substance consisted in treating phthalonitrile with 1 mol. of methylmagnesium iodide as described on p. 1815. As soon as the nitrile (12.8 g.) had dissolved, and before tar commenced to separate, 5 g. of powdered cuprous chloride were added. The mixture was repeatedly stirred to distribute the cuprous chloride throughout the tar as it separated. The remainder of the experiment was carried out as described on p. 1815. Yield of copper derivative, 5.4 g. (Found : C, 69.4; H, 3.0; Cu, 10.6%). Oxygen uptake from ceric sulphate, 4.7, 5.0 atoms/mol. Spectrum : I, 6810; II, 6550; III, 6200; IV, 5950 Å. Order of intensities : I > II > III, IV.

A quantitative examination of the spectrum of sublimed copper pigment made by the first method yielded the following results :

λ (Å)	6840	6550	6270	6140	6000	4460
$\log \epsilon$	5.21	5.01	4.58	4.57	4.49	4.15

A diffuse band at 6440 Å, which appears only in unsublimed material, is presumably due to a trace of metal-free pigment, or perhaps, copper phthalocyanine.

In crystalline form the copper derivative was indistinguishable from free tetrabenztriporphin. It dissolved to a brownish-green solution in concentrated sulphuric acid; on dilution, it separated as a bluish-green precipitate, much greener than copper phthalocyanine. Dent (*loc. cit.*) observed that the addition of a few drops of nitric acid to the sulphuric acid solution of the copper tetrabenztriporphin made by his method yielded a brilliant red colour, which became brown on standing. The copper compound made by either of the methods described above gave a deep greenish-blue colour by the same treatment, provided that only one drop of nitric acid was used. More acid produced a red colour, which soon became brown. We have repeated this effect with material made by Dent's method.

A sample of copper tetrabenztriporphin has been prepared * from *o*-cyanoacetophenone by the method of Helberger and von Rebay (*loc. cit.*). The product was indistinguishable in appearance and properties from that described above (Found: C, 69.3, 69.1; H, 2.9, 3.1; N, 17.0; Cu, 10.0, 10.2%). Spectrum: I, 6800; II, 6550; III, 6450; IV, 6250; V, 5970 Å. Order of intensities: I > II > III > IV, V. Oxygen uptake, 5.6 atoms/mol.

A sample of copper tetrabenztriporphin prepared by Dent's method from methylenephthalimidine was kindly supplied by the Research Department of Imperial Chemical Industries, Ltd. (Dyestuffs Group). After crystallisation from chloronaphthalene, this appeared identical with the samples described above, and gave similar figures on analysis (Found: C, 68.8; H, 2.9; Cu, 9.8%). It was similar spectroscopically; the 6120 Å band of copper phthalocyanine was, however, also visible; I, 6800; II, 6560; III, 6460; IV, 6240; V, 6120; VI, 5950 Å. Order of intensities: I > II > III > V > IV > VI.

Tetrabenztriporphin, when boiled with cupric chloride in chloronaphthalene for 8 hours, gives *copper monochlorotetrabenztriporphin*, which is deposited as a microcrystalline greenish-blue solid. It cannot be sublimed (Found: C, 65.4; H, 2.6; Cl, 5.0; Cu, 9.6. $C_{33}H_{16}N_7ClCu$ requires C, 65.0; H, 2.6; Cl, 5.8; Cu, 10.4%). Spectrum: I, 6830; II, 6560; III, 6450; IV, 6000. Order of intensities: I > II > IV > III.

Zinc and magnesium derivatives. These were both prepared from the parent compound and the respective metals, as described for the copper derivative. Owing to the solubility of the magnesium compound, it was necessary to limit the quantity of quinoline used, in order that the product should crystallise. Sublimed samples were used for analysis and spectrum measurements. *Zinc* derivative (Found: C, 68.8, 69.1; H, 3.0, 3.1; Zn, 10.9, 11.2. $C_{33}H_{17}N_7Zn$ requires C, 68.8; H, 2.95; Zn, 11.4%). Spectrum:

λ (Å)	6780	6540	6260	6130	5980	4440	4265
log ε	5.23	5.00	4.43	4.42	4.38	4.20	4.51

Magnesium derivative (Found: C, 72.6; H, 3.2; Mg, 4.6. $C_{33}H_{17}N_7Mg$ requires C, 74.0; H, 3.2; Mg, 4.3%). Spectrum:

λ (Å)	7220	6810	6580	6300	6150	6000	4480
log ε	4.36	4.96	4.82	4.30	4.38	4.18	4.18

On standing in air, the crystals appeared to hydrate in the same manner as do those of magnesium phthalocyanine (Barrett, Dent, and Linstead, J., 1936, 1719). No definite compound was, however, isolated.

A simple method for the preparation of magnesium tetrabenztriporphin consisted in the reaction of equimolecular amounts of methylmagnesium iodide and phthalonitrile (12.8 g.) as previously described. After the heating period, the product was removed from the reaction vessel and freed from impurities by thorough extraction with alcohol. The residue was then directly extracted with chloronaphthalene. This gave 7.1 g. of crude pigment; recrystallisation from chloronaphthalene yielded 5.1 g. of magnesium tetrabenztriporphin in bronze needles.

Ferrous tetrabenztriporphin was prepared by boiling 5 g. of the metal-free pigment with 2.5 g. of anhydrous ferrous chloride in 100 c.c. of quinoline. The pigment soon dissolved, giving a greenish-blue solution. After about ½ hour, the solution was cooled and diluted with benzene (3 vols.). After filtration from a little tar, the solution was shaken with dilute hydrochloric acid to remove the quinoline. The ferrous pigment was precipitated; after filtration, washing with alcohol, and drying, it crystallised from chloronaphthalene in bronze needles. A sample was sublimed for analysis and spectrum measurements (Found: C, 70.0, 69.9; H, 3.1, 3.3; Fe, 10.3, 9.9. $C_{33}H_{17}N_7Fe$ requires C, 69.9; H, 3.0; Fe, 9.9%). Spectrum (in chloronaphthalene):

λ (Å)	6570	6350 (diffuse to 6260)	5820
log ε	4.74	4.67	4.23

* We are indebted to Mr. F. G. Rundall for this material.

Like ferrous phthalocyanine, this compound was soluble in aniline, and gave large crystals of a solvated pigment; it was also very soluble in pyridine. Absorption spectrum in pyridine :

λ (A)	6460	6250 (diffuse to 6110)	5920	5710
$\log \epsilon$	4.98	4.83	4.46	4.36

Preparation of 3-Amino-1 : 1-dimethylisoindole (III).—A mixture of 25 g. of finely powdered phthalonitrile and 100 c.c. of sodium-dried benzene was cooled in a freezing mixture and, when the benzene began to crystallise, a Grignard reagent prepared from 12 g. of magnesium and 32 c.c. of methyl iodide in 200 c.c. of ether was added. The liquid became reddish-brown and the nitrile dissolved. After 7—8 minutes, the addition product was poured on ice (1 kg.), with vigorous stirring to prevent local overheating. A brownish-yellow solid separated. The mixture was then warmed with 70 g. of ammonium chloride. The greater part of the benzene soon separated on the surface; this was decanted as far as possible, and any base was extracted from it with a concentrated solution of ammonium chloride. The benzene, which contained a little unchanged nitrile, was discarded. The combined aqueous extracts were boiled to drive off the residual benzene, and filtered from the tar which remained undissolved. The tar was extracted with a boiling solution of 25 g. of ammonium chloride in 150 c.c. of water. The combined aqueous solutions, containing the organic base and magnesium chloride, were treated with aqueous ammonia and a slight excess of sodium phosphate (200 g.). After a short heating on the steam-bath, the precipitate of magnesium ammonium phosphate was filtered off and washed with a little hot water. The cooled filtrate was made strongly alkaline with 150 g. of caustic soda, and continuously extracted with ether for 2 days. Evaporation of the ether then left aminodimethylisoindole as a reddish gum in variable yield (4—8 g.). This sometimes solidified on standing; usually, however, it was necessary to boil its solution in toluene with dry animal charcoal and allow it to crystallise after filtration. By repeating this process, the base could be obtained in colourless needles, m. p. 146°, mixed m. p. with the base from methyl-lithium, 145° (Found : N, 17.65. Calc. : N, 17.5%). It gave a picrate, m. p. and mixed m. p. 255°.

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