

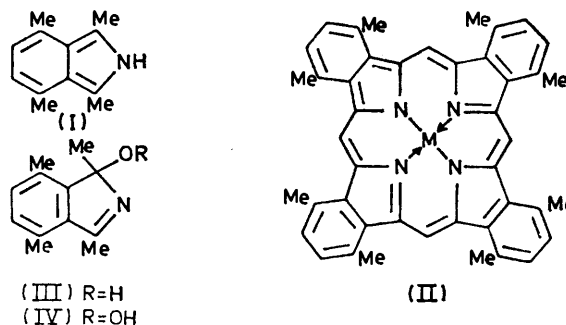
The Formation of Metal Octamethyltetrabenzporphyrins from Isoindole Precursors

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The preparation and properties of several metal complexes (Mg, Mn, Co, Ni, Cu, and Zn) of octamethyltetrabenzporphyrin are described. Experiments concerning the mode of formation of these compounds from 1,3,4,7-tetramethylisoindole are discussed.

IN 1893 Gabriel¹ reported the preparation of 1-methylisoindole by the metal-acid reduction of 1-chloro-4-methylphthalazine. Much later Linstead, considering the possibility of employing isoindoles as tetrabenzporphyrin precursors, attempted to repeat Gabriel's preparation, the solitary, but apparently authentic, record of an isoindole at that time, but without success.² The product was recognised as the corresponding isoindoline, and thus it emerged that at that time the isoindoles were not known.³ Examination of other possible precursors revealed that certain phthalimidines gave tetrabenzporphyrins on heating with metal powders or salts,^{4,5} and later work⁶ showed that the self-condensation of 1,3-di-iminoisoindoline was an excellent route to the related phthalocyanine system. Hence, when 1,3,4,7-tetramethylisoindole (I) † became available,⁷ one of the first experiments, which might in other circum-

stances seem curious, was pyrolysis with copper powder in a hard glass tube. A brilliant blue pigment was formed, and further experiments, with magnesium,⁸ led to the isolation of magnesium octamethyltetrabenzporphyrin as the dipyrindine complex (II; M = Mgpy₂).



Demetallation gave the free ligand base (II; M = H₂).

⁴ J. H. Helberger and D. B. Hevér, *Annalen*, 1938, **536**, 173.

⁵ P. A. Barrett, R. P. Linstead, F. G. Rundall, and G. A. P. Tvey, *J. Chem. Soc.*, 1940, 1079.

⁶ J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.*, 1955, 3536.

⁷ C. O. Bender and R. Bonnett, *Chem. Comm.*, 1966, 198.

⁸ C. O. Bender, R. Bonnett, and R. G. Smith, *J. Chem. Soc. (C)*, 1970, 1251.

† Use of the name isoindole (which usually implies the 2*H*-form) in this paper does not imply the absence of the tautomeric 1*H*-form.

¹ S. Gabriel and A. Neumann, *Ber.*, 1893, **26**, 705.

² R. P. Linstead and E. G. Noble, *J. Chem. Soc.*, 1937, 933.

³ Cf. also H. Lund and E. J. Jensen, *Acta Chem. Scand.*, 1970, **24**, 1867.

In this paper we report further examples of this reaction, and comment on the mode of formation and properties of the products.

Two preparative methods have been used. In the first, already described for the magnesium complex,⁸ the metal powder is heated with the isoindole (I) in a sealed tube (400°; 3 h). This has been used for the iron and zinc complexes. The second method, which, where applicable, is more convenient experimentally, involves refluxing the metal acetate with 1,3,4,7-tetramethylisoindole in 1,2,4-trichlorobenzene: the metalloporphyrin is gradually precipitated, and may be obtained reasonably pure by washing with water and organic solvents. This method has been used for the

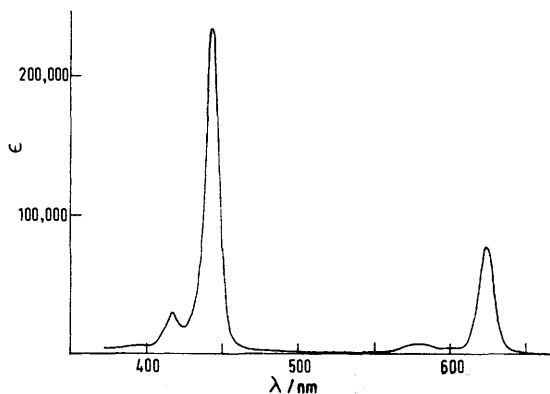


FIGURE 1 Electronic spectrum of nickel octamethyltetrabenzporphyrin in pyridine

preparation of the magnesium, manganese, cobalt, nickel, and copper complexes. In the preparation of the nickel complex, the hydroxy- (III) or hydroperoxy- (IV) derivatives may be employed in place of the isoindole (I), with essentially the same result.

Properties of the Metal Complexes of Octamethyltetrabenzporphyrin.—The complexes (II) were dark blue crystalline solids which did not melt below 300°. They were generally sparingly soluble in organic solvents, but when they did dissolve (e.g. in pyridine or 1-chloronaphthalene) gave green solutions which showed two very strong absorptions, at ca. 450 and 640 nm (see Figure 1 and Experimental section). Solutions of the magnesium and zinc complexes emitted a dull scarlet fluorescence when irradiated with u.v. light (360 nm).

Analytical figures for the copper and nickel complexes accorded with the structures (II; M = Cu or Ni). The cobalt(II) complex was oxidised to the cobalt(III) state and was isolated as the pyridine bromide (II; M = pyCoBr). The magnesium and zinc complexes were more soluble in pyridine, and were isolated from this solvent as the dipyridine complexes (II; M = Mgpy₂ or Znpy₂), which were analysed: figures for the manganese compound corresponded to an aquopyridine complex.

Mass spectra were determined for the copper and nickel complexes, an accurate molecular ion determin-

ation being made on the latter. The spectra were dominated by the molecular ion region, but doubly charged molecular ions were important, and even triply charged ions could be detected. Little fragmentation occurred (Figure 2). Such behaviour accords with the marked aromatic stabilisation of the system (II), and resembles the behaviour of other metalloporphyrins. Copper phthalocyanine has been reported⁹ to undergo depolymerisation (to phthalonitrile) in the mass spectrometer, both thermal and electron-impact processes being implicated: an analogous reaction (to give *o*-cyanophenylacetylene derivatives) has not been detected for the two metal tetrabenzporphyrins studied here. In both complexes a peak of low abundance was observed at $M + 14$, the possible significance of which is discussed later.

Curiously, the free base, and the magnesium, zinc, and nickel complexes, which were expected to be diamagnetic systems, capable of furnishing normal n.m.r. spectra, gave broad e.s.r. signals, g ca. 2.002. A sample of magnesium tetrabenzporphyrin prepared by Linstead's method⁵ showed similar absorption. Observations of this kind have also been reported in the phthalocyanine series and were originally attributed¹⁰ to the availability of a thermally attainable triplet state, but more recent work has implicated a paramagnetic impurity.¹¹ We consider that the latter explanation is the correct one here, since repeated recrystallisation of nickel octamethyltetrabenzporphyrin significantly reduced the intensity of the e.s.r. signal. Organic radical impurities, possibly of a polymeric nature, could well be produced during the preparation, which is a high-temperature process, and subsequently be extremely difficult to remove from the sparingly soluble tetrabenzporphyrins. It is considered that, additionally, one-electron oxidation processes may generate radical cations which are subsequently stabilised, for example in a molecular aggregate. Experiments in which the radical cation of magnesium tetrabenzporphyrin has been generated by anodic oxidation in tetrahydrofuran (to give a broad signal with hyperfine structure)¹² have demonstrated that this suggestion is reasonable.

Formation of Octamethyltetrabenzporphyrins.—In order to generate the tetrabenzporphyrin system (II) each monomer unit (I) must dispose of a carbon-bound methyl group. Such a requirement is not without precedent in this series: thus Helberger and Hevér found that 3-ethylphthalimidine served as a tetrabenzporphyrin precursor.⁴ The fate of this γ -carbon fragment has been examined by determining the composition of the gases formed in the preparation of magnesium octamethyltetrabenzporphyrin by the sealed tube reaction. Analysis by g.l.c. and by mass spectrometry showed that the main gaseous products were methane and ethane.

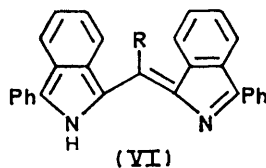
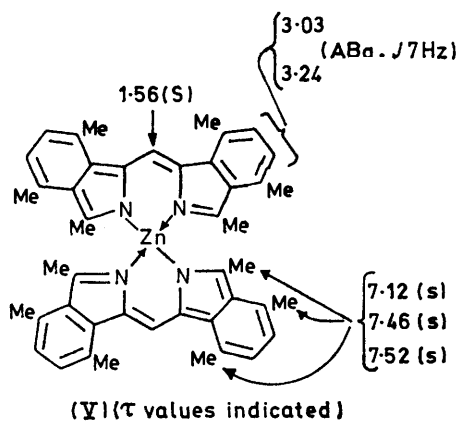
¹⁰ F. H. Winslow, W. O. Baker, and W. A. Yager, *J. Amer. Chem. Soc.*, 1955, **77**, 4751.

¹¹ A. B. P. Lever, *J. Chem. Soc.*, 1965, 1821; H. A. O. Hill and M. M. Norgett, *J. Chem. Soc. (A)*, 1966, 1476.

¹² R. Bonnett, K. D. Sales, and R. G. Smith, unpublished work.

⁸ H. C. Hill and R. I. Reed, *Tetrahedron*, 1964, **20**, 1359.

When the progress of nickel complex formation in 1,2,4-trichlorobenzene was followed spectroscopically it was observed that a broad maximum appeared initially at *ca.* 550 nm, and that it gradually disappeared as the strong bands (*ca.* 440 and 630 nm) characteristic of the metal tetrabenzporphyrin system emerged. Attempts to prepare the zinc (and cadmium) tetrabenzporphyrin complexes by this method were unsuccessful, the reactions stopping at an intermediate stage (λ_{\max} 570 nm). These intermediates proved difficult to isolate, but the zinc intermediate was obtained crystalline in low yield, and was formulated as the zinc bis(dipyrromethene) complex (V). Although the percentage of carbon was low, other analytical data, including an accurate molecular ion measurement, accorded with this structure, as did the n.m.r. spectrum. The zinc complex (V) was



soluble in common organic solvents, including hexane, to give reddish purple solutions which emitted an orange fluorescence in u.v. light. The complex underwent photoreactions readily, and solutions were rapidly decolourised in normal laboratory light. The dibenzdipyrromethene system appears to have been encountered only recently, and those examples of it known up to the present have been stabilised by phenyl substituents. In 1968 Ivanov and his colleagues¹³ reported the triphenyl derivative (VI; R = Ph), which was obtained either by treating 2,3-diphenylindene with ammonia, or, rationally, from 1-phenylisindole and benzaldehyde. The crystals were noted¹⁴ to have a marked metallic lustre [also evident with compound (V)] and to possess¹⁵ λ_{\max} 612 nm. Australian workers (also in 1968)¹⁶ re-

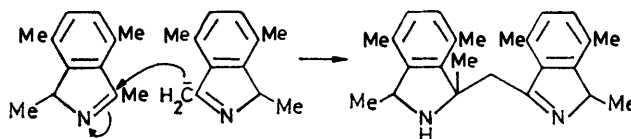
¹³ T. P. Ivanov and A. Draganov, *Monatsh.*, 1968, **99**, 1990; *Ann. Inst. Chim. Tech. Sofia*, 1955, **2**, 151, and later papers in this journal.

¹⁴ I. K. Svirenski, *Compt. rend. Acad. bulg. Sci.*, 1968, **21**, 793.
¹⁵ I. K. Svirenski and C. P. Ivanov, *Compt. rend. Acad. bulg. Sci.*, 1970, **23**, 1505.

ported that the reaction of phenylmagnesium bromide with *o*-cyano- β -bromostyrene gave the diphenyl derivative (VI; R = H): this substance gave blue solutions (λ_{\max} 590 nm) which were sensitive to photo-oxidation.

That the self-condensation reaction with zinc (and, presumably, cadmium) salts stopped at the dibenzdipyrromethene stage [*e.g.* (V)] is thought to reflect the considerable tendency for these ions to adopt tetrahedral, in preference to square planar (or octahedral), configurations in their complexes.¹⁷ Even in refluxing 1-chloronaphthalene (b.p. 263°) the reaction with zinc acetate stopped at this stage. However, when the zinc complex (V) was pyrolysed (360°; 3 h), zinc octamethyltetrabenzporphyrin was formed (40%). This evidence, and the spectroscopic detection of analogous stages elsewhere (*e.g.* with nickel; see before) strongly suggest that complexes of type (V) are intermediates in tetrabenzporphyrin formation.

The initial self-condensation of (I) might be regarded as an aldol condensation involving azomethine functions in the tautomeric 1*H*-isindole system as illustrated.



Attempts to observe base catalysis (specifically with $\text{KO}^t\text{Bu}-\text{Me}_2\text{SO}$ in the formation of the nickel complex) were abortive, no macrocyclic product being formed: addition of acid to the reaction mixture in 1,2,4-trichlorobenzene only slightly depressed the yield of the nickel complex, however, and an acid-catalysed aldol condensation must still be considered as a possibility for the first step. Overall, and in spite of the meagre effect of a radical trap (hydroquinone) and a radical source (di-*t*-butyl peroxide) on the formation of the nickel complex (II; M = Ni) in 1,2,4-trichlorobenzene (see Experimental section) we tend to regard the sequence of reactions as being predominantly radical in character because (i) the formation of methane and ethane suggests that methyl radicals are involved; (ii) the reaction requires a high temperature. This is illustrated by the efficiency of formation of the nickel complex (II; M = Ni) in various closely related aromatic solvents at their b.p.s (Table 1); and (iii) the dehydro-dimer (VII),

TABLE 1

Solvent	B.p. (°C)	Yield (%)
1-Chloronaphthalene	263	68
1,2,4-Trichlorobenzene	213	75
1,2-Dichlorobenzene	182	11
Chlorobenzene	131	0

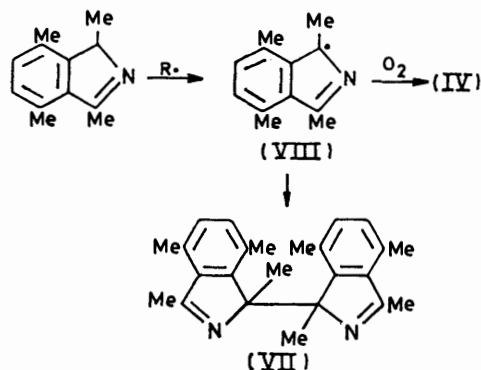
which would be expected to give isindolyl radicals readily on thermolysis, is an excellent precursor: when heated with nickel acetate in 1,2,4-trichlorobenzene it

¹⁶ G. M. Brown, R. G. Curtis, W. Davies, T. A. A. Dopheide, D. G. Hawthorne, J. R. Hlubucek, B. M. Holmes, J. F. Kefford, J. L. Osborne, A. V. Robertson, and E. C. Slater, *Austral. J. Chem.*, 1968, **21**, 483.

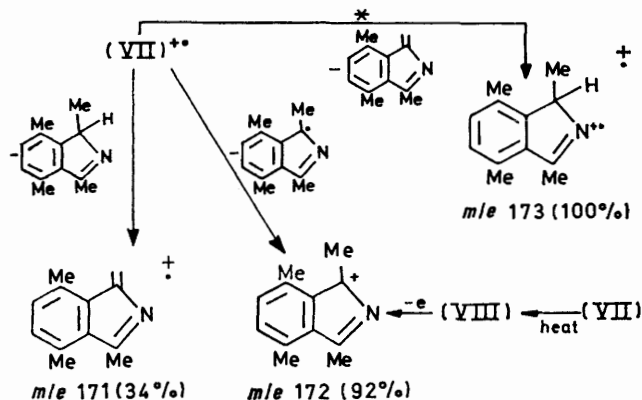
¹⁷ A. B. Blake and F. A. Cotton, *Inorg. Chem.*, 1964, **3**, 5.

gave the nickel complex (II; $M = Ni$) in virtually quantitative yield.

The dehydro-dimer (VII), a bi(1*H*-isoindol-1-yl) derivative, was formed in low yield when 1,3,4,7-tetramethylisoindole was kept in solution for a protracted period, and its discovery resulted from the detection in the n.m.r. spectra of certain samples of 1,3,4,7-tetramethylisoindole of an unusual peak, a weak singlet at about τ 9.1. Presumably this dimer arises following an initial hydrogen abstraction which generates the tertiary, benzylic, aza-allylic radical (VIII): in the presence of oxygen this radical would give, initially at least, the hydroperoxide (IV),⁸ but in an inert medium it could dimerise to give (VII). Although structure (VII) is



unusual and highly hindered, extensive evidence supports it. The substance gave satisfactorily analytical figures, and the mass spectrum showed the expected molecular ion (accurate mass measurement) in low abundance, together with fragments (the formation of which is rationalised in Scheme 1) arising from cleavage at the direct linkage. Structure (VII) received further support from the i.r. spectrum (no NH absorption) and the electronic spectrum (1*H*-isoindole chromophore, λ_{max} 248, 295, and 305 nm). The n.m.r. spectrum

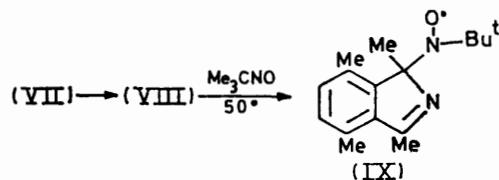


SCHEME 1 Fragmentation of the dehydro-dimer (VII) in the mass spectrometer

accorded with the proposed structure, the angular methyl groups being slightly shielded (τ 9.04) by the

† Structure (VII) corresponds to two isomers [*meso*- and (\pm)-]; however, the sharp n.m.r. signals suggest that we have a single substance.

benzenoid rings.† That the bi-isoindol-1-yl (VII) readily underwent cleavage at the direct linkage was indicated in the mass spectrum, and was further supported by trapping experiments with 2-methyl-2-nitrosopropane in the dark at 50°, when a triplet e.s.r. signal, with a_N 15.3, attributed to a nitroxide radical adjacent to a fully substituted centre [as in (IX)] was observed.



A similar signal, with additional structure which has not been interpreted, was observed when the isoindole (I) was subjected to the same trapping experiment.

These observations support our contention that radical processes are important in the remarkable self-condensation sequence reported here. Scheme 2 sets out one rationalisation of the sequence in terms of radical intermediates. As an alternative to an initial aldol-type condensation (see before) the products of disproportionation of the radical (VIII) are envisaged as undergoing Diels-Alder addition (a process for which there is ample analogy in this series⁸). Cleavage of the direct linkage (dotted) of the adduct is then followed by metallation and the sequential loss of methyl fragments: the $M + 14$ peaks in the mass spectra of (II; $M = Ni$) (Figure 2)

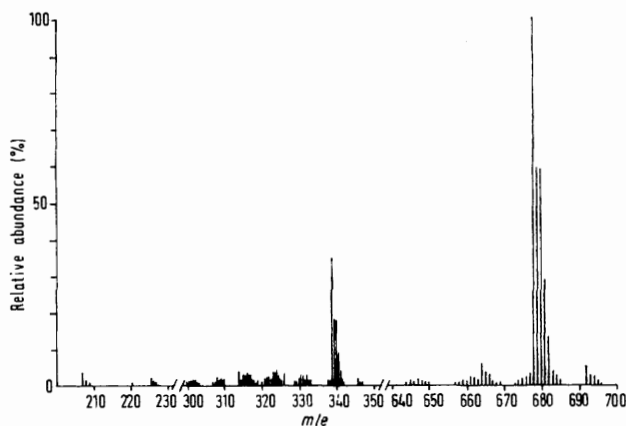
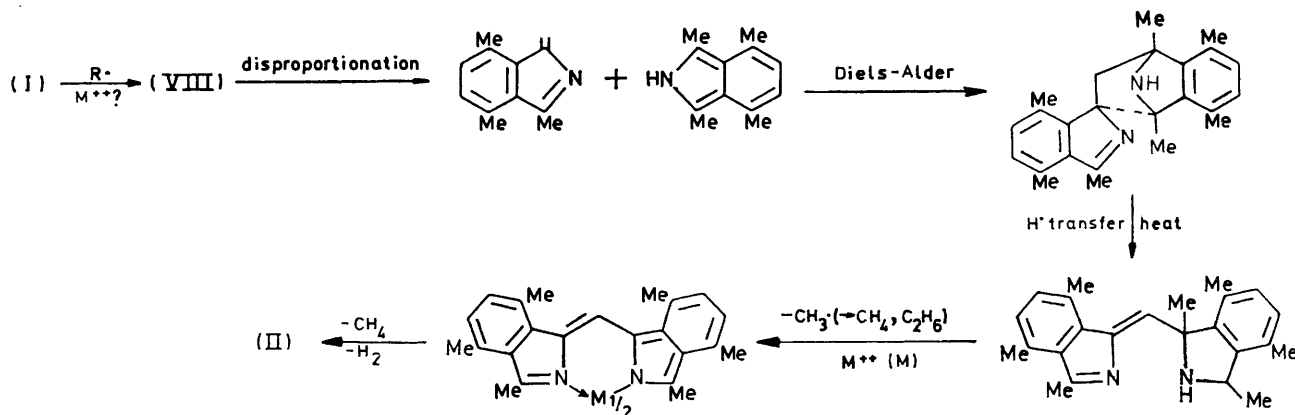


FIGURE 2 Mass spectrum of nickel octamethyltetrabenzporphyrin (direct insertion at 340°)

and (V) (see Experimental section) may represent impurities in which this unaccustomed elimination is incomplete, or in which methyl radicals have attacked the system elsewhere (*cf.* the behaviour of nickel 1,19-dialkyl-tetradehydrocorrins salts on pyrolysis¹⁸). The formation of (V) and (II) represents increasing degrees of aromatic stabilisation, the latter system being particularly favoured in this sense. In essence the metal ion acts as a template for the formation of the tetrabenzporphyrin system (yields are minute in the absence of a suitable

¹⁸ R. Grigg, A. W. Johnson, K. Richardson, and K. W. Shelton, *J. Chem. Soc. (C)*, 1969, 655.



SCHEME 2 Rationalisation of the formation of metal complexes of octamethyltetrabenzporphyrin

metal salt); but whether or not the highly aromatic system (II) can be generated under moderate conditions appears to be largely determined by the stereochemical preferences of the co-ordinated metal ion.

EXPERIMENTAL

Spectroscopic measurements were made as previously indicated.⁸ E.s.r. spectra were measured with a Decca X3 spectrometer incorporating a Newport M4X magnet system. Values of ν (cm^{-1}) and λ (nm; ϵ in parentheses) refer to maxima unless otherwise stated. Mass spectra are quoted as m/e (% relative abundance). Light petroleum refers to the fraction of b.p. 60–80°.

Nickel Octamethyltetrabenzporphyrin.— 1,3,4,7-Tetramethylisoidole (0.100 g), nickel acetate tetrahydrate (0.50 g), and 1,2,4-trichlorobenzene (5 ml) were refluxed under nitrogen (4 h). The progress of the reaction was followed spectroscopically: a broad absorption at 550 nm appeared and was replaced by a typical metalloporphyrin spectrum (λ ca. 430 and 630 nm). Next day the crystalline precipitate was filtered off and washed in turn with hot water, benzene, and ether to give nickel octamethyltetrabenzporphyrin (0.070 g, 71%), dark needles possessing a coppery reflex (spectroscopic yield, including mother liquors, 75%). A sample recrystallised from pyridine–light petroleum (Found: C, 77.55; H, 5.3; N, 8.5%; M^+ , 678.230. $\text{C}_{44}\text{H}_{36}\text{N}_4\text{Ni}$ requires C, 77.75; H, 5.35; N, 8.25%; M 678.229 for ^{58}Ni) showed ν (KBr) 3036, 3020, 2968, 2870, 1840w, 1595w, 1570, 1562, 1468, 1446, 1375, 1320, 1272, 1244, 1194, 1052, 1034, 1017, 929, 828, 820, and 804; λ (pyridine) 395 (5000), 417 (28,000), 444 (240,000), 528infr (1200), 531 (1400), 584 (8700), 602 (5200), and 629 (75,000), λ (chloronaphthalene) 407infr (24,000), 431 (84,000), 588 (7300), 613infr (9200), and 638 (62,000); e.s.r. spectrum (solid; room temp.), broad singlet, g 2.0025; m/e 692 (5), 682 (13), 681 (24), 680 (54), 679 (54), 678 (100), 340 (18), 339.5 (18), 339 (39), 226.6 (0.5), 226.3 (0.5), and 226 (1.5).

The nickel complex was also formed in the yields stated when the following precursors were employed under the foregoing conditions: 1-hydroxy-1,3,4,7-tetramethyl-1*H*-isoidole (58%); 1-hydroperoxy-1,3,4,7-tetramethyl-1*H*-isoidole (83%) (with Dr. M. A. R. KHAYAT, University of Baghdad).

In the absence of nickel acetate, and under the general conditions just described, octamethyltetrabenzporphyrin was formed in 5% yield (estimated spectroscopically) from the isoidole.

Effect of Conditions on the Formation of Nickel Octamethyltetrabenzporphyrin.— 1,3,4,7-Tetramethylisoidole (100 mg) and nickel acetate tetrahydrate (50 mg) were refluxed in solvent (5 ml) under the stated conditions (Table 2) for 4 h under nitrogen. The total yield of nickel complex (*i.e.* isolated solid plus amount indicated by spectroscopic estimation of mother liquors) was determined.

Solvent	Additive (mg)	Yield (%)
1,2,4- $\text{C}_6\text{H}_3\text{Cl}_3$	Hydroquinone (100)	75
	$(\text{Bu}^t\text{O})_2$ (118)	61*
	H_2SO_4 (29)	74
	Air	59
	Air	70
1- $\text{C}_{10}\text{H}_7\text{Cl}$		68
Quinoline		20
PhNO_2		Trace
Me_2SO		9
Me_2SO	KOBu ^t (150)	0
1,2- $\text{C}_6\text{H}_4\text{Cl}_2$	+	11
PhCl		0
PhCl	$(\text{Bu}^t\text{O})_2$ (10)	0

* Isolated yield only.

Copper Octamethyltetrabenzporphyrin.—A similar reaction with copper(II) acetate monohydrate, gave blue needles (20%) of copper(II) octamethyltetrabenzporphyrin. This was sparingly soluble in pyridine. It was washed with aqueous ammonium chloride before drying for analysis (Found: C, 77.2; H, 5.05; N, 7.8%; M^+ , 683. $\text{C}_{44}\text{H}_{36}\text{CuN}_4$ requires C, 77.2; H, 5.3; N, 8.2%; M , 683 for ^{63}Cu); ν (KBr) 1595, 1568, 1468, 1446, 1382, 1318, 1270, 1242, 1195, 1048, 1020, 917, 827, and 806; λ (chloronaphthalene; absorbance ratios in parentheses) 406 (0.22), 431 (1.00), 585 (0.07), 607 (0.07), 635 (0.67); m/e 697 (3), 685 (60), 684 (50), 683 (100), 342.5 (18), 342 (16), 341.5 (30), 341 (10), 228.3 (1), 228 (1), 227.6 (1.5), 62 (25), and 40 (29).

Dipyridinemagnesium Octamethyltetrabenzporphyrin.— 1,3,4,7-Tetramethylisoidole (0.25 g), magnesium acetate tetrahydrate (0.20 g), and 1,2,4-trichlorobenzene (10 ml) were refluxed under nitrogen for 65 h, after which the band at 550 nm, clearly apparent after 17 h, had virtually disappeared. The precipitate was filtered off, and was washed with hot water, ethanol, light petroleum, and benzene before being extracted with pyridine. Addition of light petroleum gave dark blue crystals (0.072 g, 25%) of dipyridinemagnesium octamethyltetrabenzporphyrin.⁸

Manganese Octamethyltetrabenzporphyrin.—A similar experiment in which manganous acetate tetrahydrate replaced

the magnesium compound (44.5 h reflux) gave 48% of *manganese complex*, which was obtained as blue micro-crystals from pyridine–light petroleum (Found: C, 76.9, 76.0; H, 5.15, 5.65; N, 8.85, 8.75. $C_{44}H_{38}N_4MnOH$, C_5H_5N requires C, 76.25; H, 5.5; N, 9.1%), λ (pyridine; absorbance ratios in parentheses) 428 (0.22), 455 (1.00), 596 (0.05), and 640 (0.19).

Bromo(pyridine)cobalt(III) Octamethyltetrabenzporphyrin.—1,3,4,7-Tetramethylisoindeole (0.50 g), cobalt(II) acetate tetrahydrate (0.30 g), and 1,2,4-trichlorobenzene (20 ml) were refluxed under nitrogen (20 h). The solid was filtered off and washed with water, ethanol, light petroleum, and benzene, and finally the cobalt octamethyltetrabenzporphyrin (0.26 g, 53%) was extracted with pyridine.

Pyridine (8 ml) containing cobalt octamethyltetrabenzporphyrin (0.05 g) and 48% hydrogen bromide (2 ml) was aerated on a steam-bath (45 min) and then poured into water (50 ml). The solution was exhaustively extracted with chloroform, and the extract was washed, dried, and taken to dryness. Crystallisation of the residue from chloroform–light petroleum gave *bromo(pyridine)cobalt(III) octamethyltetrabenzporphyrin* as a blue micro-crystalline solid (0.052 g, 84%) (Found: C, 70.25; H, 4.65; N, 8.2. $C_{46}H_{41}BrCoN_8$ requires C, 70.2; H, 4.9; N, 8.35%; ν (KBr) 1600, 1595, 1570, 1462, 1446, 1374, 1316, 1270, 1240, 1192, 1050, 1015, 925, 824, and 810; λ (pyridine) 396infr (13,000), 422 (38,000), 453 (190,000), 544infr (3600), 594 (13,000), and 645 (82,000), λ (chloronaphthalene) 434infr (36,000), 463 (126,000), 542infr (4200), 592 (13,000), and 638 (77,000).

Dipyridinezinc Octamethyltetrabenzporphyrin.—An intimate mixture of 1,3,4,7-tetramethylisoindeole (1.03 g) and zinc powder (11.75 g) was heated in a sealed tube (400°; 3 h). The resulting solid was extracted (Soxhlet) with light petroleum (4 h), benzene (3 h), and pyridine (7 h). The pyridine extract was filtered hot and diluted with light petroleum to give purple prisms (0.35 g, 28%) of *dipyridinezinc octamethyltetrabenzporphyrin*, m.p. $\leq 360^\circ$ (Found: C, 76.8; H, 5.25; N, 10.0. $C_{54}H_{46}N_6Zn$ requires C, 76.8; H, 5.5; N, 9.95%; λ (pyridine) 414 (59,000), 440 (457,000), 587 (16,000), 610 (9900), and 636 (158,000); e.s.r. spectrum (solid; room temp.), single line, g 2.0016.

Bis-[3,4,7-trimethyl-1-(3,4,7-trimethyl-1H-isoindeol-1-ylidene)methyl]isoindeole]zinc.—1,3,4,7-Tetramethylisoindeole (0.50 g), zinc acetate dihydrate (0.25 g), and 1,2,4-trichlorobenzene (25 ml) were refluxed under nitrogen (6 h). The cold solution was filtered, and the filtrate was taken to dryness. Preparative t.l.c. of the residue on alumina irrigated with 20% light petroleum in benzene was attended by decomposition, but the reddish purple band (R_F ca. 0.8) was excised and extracted with benzene, and the solvent was removed by lyophilisation. The reddish solid (0.015 g, 3%) was crystallised from benzene–hexane to give *bis-[3,4,7-trimethyl-1-(3,4,7-trimethyl-1H-isoindeol-1-ylidene)methyl]isoindeole]zinc* as tiny needles with a golden sheen (a satisfactory carbon analysis was not obtained) (Found: C, 74.8; H, 6.65; N, 7.7%; M^+ , 718.297. $C_{46}H_{46}N_4Zn$ requires C, 76.7; H, 6.45; N, 7.8%; M , 718.301 for ^{64}Zn); ν (CCl_4) 3030, 2960, 2930, 2860, 1590, 1565, 1460, 1280, 1240, 1170, 1050, 1015, and 880; τ ($CDCl_3$) 1.56 (2H, s, *meso*-H), 3.03 and 3.24 (each 4H, d, J 7 Hz, benzenoid H), and 7.12, 7.46, and 7.52 (36H, all s, MeC=C). The mass spectrum showed some ions of greater m/e than the molecular ion (718; 100%) including 746 (23%), attributed to the ion $C_{48}H_{50}N_4Zn$ (Found: 746.334; requires 746.333 for ^{64}Zn), possibly arising by

transmethylation reactions on the probe: m/e 746 (23), 736 (29), 735 (25), 734 (41), 733 (31), 732 (58), 723 (23), 722 (49), 721 (42), 720 (68), 719 (55), 718 (100), 359 (27), 328 (32), 326 (50), 324 (31), 256 (22), 254 (21), 196 (24), 182 (35), 180 (35), 124 (23), 82 (25), 55 (26), and 57 (25); λ (hexane–benzene, 9:1) 373 (11,500), 402 (8700), 468 (5200), 502 (17,000), 518 (29,000), 538 (100,000), 556infr (113,000), and 576 (400,000).

When the zinc complex (0.2 mg) was heated in a sealed evacuated capillary (360°; 4 h) and the product was dissolved in pyridine, zinc tetramethyltetrabenzporphyrin was formed (40%; estimated spectroscopically as the dipyridine complex).

Gaseous By-products in the Formation of Magnesium Octamethyltetrabenzporphyrin by the Sealed Tube Method.—1,3,4,7-Tetramethylisoindeole (0.60 g) and magnesium powder (1.0 g) were intimately mixed and heated under argon in a sealed tube (slow heating to 400°; then 3 h at this temperature). The tube was opened in a vacuum system, and the contents were examined by g.l.c. and mass spectrometry. This showed that the main products were methane and ethane, together with smaller amounts of propane and, possibly, ethylene. G.l.c. indicated methane (50% relative abundance, possibly augmented by traces of air), ethane and ethylene (35%), and propane (15%). The electronic spectrum of the solid product in pyridine confirmed the formation of magnesium octamethyltetrabenzporphyrin.

Radical Trapping.—The substrate (1 mg) was dissolved in 1,2,4-trichlorobenzene (0.5 ml) and, in the dark, 2-methyl-2-nitrosopropane (ca. 1 μ g in the same solvent) was added. The e.s.r. spectrum was recorded in the dark at 50°, a blank determination being carried out with the radical trap under the same conditions. Both 1,3,4,7-tetramethylisoindeole and 1,1',3,3',4,4',7,7'-octamethylbi-(1H-isoindeol-1-yl) gave triplets with a_N 15.3: the spectrum from the isoindeole contained additional structure.

1,1',3,3',4,4',7,7'-Octamethylbi-(1H-isoindeol-1-yl).—1,3,4,7-Tetramethylisoindeole (0.10 g) was dissolved in dry benzene (20 ml), purged with nitrogen, and kept in the dark for 20 h. The red solution was evaporated to ca. 1 ml, and ether was added to precipitate the *product* (10 mg), which crystallised from ether as pale pink plates, m.p. 194–196° (*in vacuo*; decomp.) (Found: C, 83.75; H, 8.25; N, 8.35%; M^+ , 344.225. $C_{24}H_{28}N_2$ requires C, 83.7; H, 8.2; N, 8.15%; M 344.225); ν (Nujol) 1615, 1582, 1490, 1364, 1328, 1286, 1026, 916, and 825; λ (EtOH) 248infr (10,400), 295 (4300), and 305 (4200); τ ($CDCl_3$) 2.93 (4H, s, benzenoid H), 7.33, 7.37, and 7.39 (18H, all s, MeC=C), and 9.05 (6H, s, MeC=C); m/e (128°) 344 (5), 173 (100), 172 (92), 171 (34), 170 (10), and 115 (9).

When this compound (9 mg) was refluxed (4 h) in 1,2,4-trichlorobenzene (1 ml) with nickel acetate (5 mg), spectroscopic estimation showed that nickel octamethyltetrabenzporphyrin was formed in virtually quantitative yield.

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