Conjugated Macrocycles. Part XXVI. Octamethyltetrazaporphin.*

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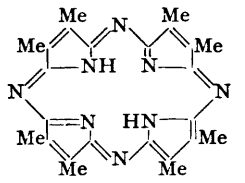
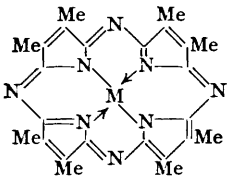
The reaction of dimethylmalei- and dimethylfumaro-nitriles with various organomagnesium compounds gave magnesium octamethyltetrazaporphin (II; M = Mg). Removal of magnesium from this compound yielded the metal-free pigment (I) which was converted into the copper, nickel, cobalt, and zinc pigments (II; M = Cu, Ni, Co, or Zn). Their structures have been established by analogy with other tetrazaporphins and by degradation.

The synthetical methods described for the preparation of tetrazaporphin from maleinitrile (Linstead and Whalley, *J.*, 1952, 4839) are now applied to the preparation of octaalkyltetrazaporphins (France, Jones, and Imperial Chemical Industries Limited, B.P. 689,387, 689,388, 689,389; France and Imperial Chemical Industries Limited, B.P. 721,763; Linstead, Whalley, and Ficken, B.P. 713,208). Of these the simplest is octamethyltetrazaporphin (I) in which there are no complications of positional isomerism.

Octamethyltetrazaporphins were readily prepared from dimethylmalei- and dimethylfumaro-nitrile (Piggott and Beech, *J.*, 1955, 423) by the use of solutions obtained by decomposing methylmagnesium iodide with alcohols (Ficken and Linstead, *J.*, 1952, 4846). Of the large number of alcohols examined, *n*-butanol and *n*-pentanol were the most satisfactory. The action of dimethylfumaronitrile on a decomposed Grignard reagent in butanol or *iso*pentanol gave magnesium octamethyltetrazaporphin (II; M =

(I) 

 (II)

Mg) in *ca.* 50% yield. *n*-Butanol was used for preference as slightly higher and more consistent yields were obtained. Dimethylfumaronitrile is to be preferred to the *cis*-isomeride for preparative purposes on account of its greater availability.

Magnesium octamethyltetrazaporphin, like the magnesium derivatives of other macrocycles, forms various solvates. Of these only the monopentanolate was obtained analytically pure. The alcohol was removed from this by heating it at 10^{-5} mm., to give the unsolvated

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magnesium octamethyltetrazaporphin. Treatment with absolute ethanol then gave a crystalline product which contained between one and two mols. of ethanol.

The metal was easily removed from magnesium octamethyltetrazaporphin with boiling glacial acetic acid, to yield crystalline octamethyltetrazaporphin (I). Demetallation with mineral acids caused partial or complete breakdown of the macrocycle (cf. Linstead and Whalley, *loc. cit.*; Ficken and Linstead, *loc. cit.*).

Octamethyltetrazaporphin forms a series of metal derivatives. These show two characteristics noted before for metallic phthalocyanines and other similar macrocyclic pigments : first, there is a tendency for the metal derivatives to form mixed crystals with the parent compound; secondly, several of the derivatives form solvates, and the tendency to do this depends upon the metal.

Copper octamethyltetrazaporphin (II; M = Cu) was obtained by reaction of the metal-free pigment with copper bronze in boiling *o*-dichlorobenzene. In chlorobenzene the reaction did not proceed to completion and mixed crystals of metal-free and copper pigments were obtained. Nickel and zinc octamethyltetrazaporphins (II; M = Ni and M = Zn) were obtained by extracting the metal-free pigment into boiling *o*-dichlorobenzene containing a large excess of anhydrous nickel chloride or zinc acetate. Direct refluxing of metal-free pigment with the metallic salt invariably gave a mixture. The zinc compound (the only known zinc tetrazaporphin other than zinc phthalocyanine) was obtained in an unsolvated form by crystallisation from chlorobenzene but from pyridine gave a solvate containing about 1 mol. of pyridine. The pigment thus shows some resemblance to zinc phthalocyanine which has now been found to give a monopyridine solvate, which is stable at 120°/10 mm.

The physical properties of the octamethyltetrazaporphins are closely similar to those of the tetra*cyclo*hexenotetrazaporphins (Ficken and Linstead, *loc. cit.*). They are more stable to heat and to mineral acids than the unsubstituted tetrazaporphins but are not sufficiently stable to heat to permit the use of sublimation for purification or for the growth of large crystals.

The solubilities in organic solvents are low. The metal-free compound is very sparingly soluble in chlorobenzene, to give a violet-blue non-fluorescent solution (cf. tetrazaporphin). The zinc and magnesium pigments are slightly soluble in hot chlorobenzene (non-fluorescent solutions) but completely insoluble in the cold. The magnesium pigment is fairly soluble in the higher primary alcohols : both the magnesium and the zinc pigment dissolve in cold pyridine, giving blue solutions with a strong fluorescence, crimson in daylight and brilliant vermilion (indistinguishable from that of magnesium tetra*cyclo*hexenotetrazaporphin) in ultraviolet light. Magnesium octamethyltetrazaporphin, like other magnesium macrocycles (including chlorophyll), gives a bright red chemiluminescence when added to hot hydrocarbon solvents, such as tetralin, containing peroxide.

The light absorptions of all the pigments have been measured over the range 3000—10,000 Å and correspond closely to those of the tetra*cyclo*hexenotetrazaporphins, a hypsochromic shift of about 20 Å being observed for the main peaks in the visible region for the magnesium and metal-free pigments. A small bathochromic shift was noted in the case of the nickel, cobalt, and copper pigments. The spectrum of the zinc pigment resembles that of the magnesium pigment, both having a very intense band in the ultraviolet spectrum. Nickel octamethyltetrazaporphin, like nickel tetrazaporphin and nickel and palladium tetra*cyclo*hexenotetrazaporphin, shows an unusual double band in the ultraviolet spectrum.

Solutions of magnesium octamethyltetrazaporphin and magnesium tetra*cyclo*hexeno-tetrazaporphin (unlike those of magnesium tetrazaporphin) decomposed quite rapidly in daylight. A solution of each was left out of doors from June to September and the almost decolorised solutions were examined. The magnesium octamethyltetrazaporphin solution gave an almost 50% yield of dimethylmaleimide and a small amount of unidentified oil. Magnesium tetra*cyclo*hexenotetrazaporphin under similar conditions gave 3 : 4 : 5 : 6-tetrahydrophthalimide.

The close similarity at every point between octamethyl- and tetra*cyclo*hexeno-tetrazaporphins leaves little doubt as to the structures of the former compounds, and this was

conclusively confirmed as follows: Oxidation of metal-free octamethyltetrazaporphin with chromium trioxide in sulphuric acid (cf. Fischer and Walach, *Annalen*, 1926, **450**, 180; Muir and Neuburger, *Biochem. J.*, 1949, **45**, 163; Ficken and Linstead, *loc. cit.*) gave an 80% yield of dimethylmaleimide, thus showing that formation of the pigment had not created new C–C bonds. The nitrogen content of the aqueous layer after extraction of the imide, corresponded to four aza-links. Oxidation with ceric sulphate by the method used for the phthalocyanines (Dent, Linstead, and Lowe, *J.*, 1934, 1036) gave results higher than the 1 atom of oxygen required for the degradation of one molecule of pigment. This was probably due to subsequent oxidation of the double bond of the imide.

Alternative methods for the preparation of tetrazaporphins from dimethyl-malei- and -fumaro-nitrile were tried. Nickel, cobalt, and traces of copper octamethyltetrazaporphin were obtained by the urea-melt method (cf. Linstead and Whalley, *loc. cit.*). Because of the very high volatility of dimethylfumaronitrile, urea-melt reactions with this nitrile were carried out in sealed tubes. Sodium and lithium alkoxides, successful for the preparation of phthalocyanines and tetra*cyclo*hexenotetrazaporphins, gave very low yields of octamethyltetrazaporphins because of decomposition of the nitrile in alkaline solution. Magnesium alkoxides (cf. magnesium tetrazaporphin) reacted very slowly with dimethylfumaronitrile to give lower yields of magnesium octamethyltetrazaporphin than those obtained by the Grignard-reagent method.

Dimethylmalei- and dimethylfumaro-nitrile both give tetrazaporphin pigments much more readily, and in better yield than the unsubstituted maleinitrile (Linstead and Whalley, *loc. cit.*). However, they showed less tendency to pigment formation than phthalonitrile and, as was to be expected, reacted in much the same way as 3 : 4 : 5 : 6-tetrahydrophthalonitrile (Ficken and Linstead, *loc. cit.*).

The ease of formation of pigments from dimethylfumaronitrile is somewhat surprising as intermediates with a *cis*-configuration must be involved in forming the pyrrole-like corners of the azaporphin ring. Fumaronitrile itself shows no detectable tendency to pigment formation. Clearly an inversion of configuration occurs in the dimethyl series at some stage in there action sequence. Dimethylmaleinitrile is completely isomerised by ammonium toluene-*p*-sulphonate at 200°.

Experimental

Continuous extractions of macrocyclic pigments were carried out with an all-glass modification of the " hot extraction " apparatus described by Barrett, Dent, and Linstead (*J.*, 1936, 1726).

Magnesium Octamethyltetrazaporphin.—Dry *n*-butanol (75 c.c.) was slowly added to cooled, ethereal methylmagnesium iodide (prepared from 3 g. of magnesium), and the ether was allowed to evaporate. Dimethylfumaronitrile (12 g.) was then added and the mixture refluxed for 6 hr. The *n*-butanol was evaporated under reduced pressure and the residue triturated with water and washed with aqueous ethanol (1 : 1) until the washings were colourless. Extraction of the residue with dry *n*-pentyl alcohol gave dark blue needles, with a bronze reflex, of *magnesium octamethyltetrazaporphin monopentanolate* (8·4 g., 55%) (Found: C, 64·7; H, 7·2; N, 20·4. $C_{29}H_{36}N_8OMg$ requires C, 64·9; H, 6·7; N, 20·9%). Heating the solvate at 185°/10^{-5} mm. gave *magnesium octamethyltetrazaporphin* (Found: C, 64·6; H, 5·7; N, 24·5; Mg, 5·6. $C_{24}H_{24}N_8Mg$ requires C, 64·3; H, 5·4; N, 25·0; Mg, 5·4%). Treatment of the unsolvated material with absolute ethanol gave an *ethanolate* (Found: C, 62·8; H, 6·4; N, 22·7. $C_{24}H_{24}N_8Mg,2C_2H_5{\cdot}OH$ requires C, 63·2; H, 6·1; N, 22·7%).

Metal-free Octamethyltetrazaporphin.—Magnesium octamethyltetrazaporphin monopentanolate (8·4 g.) was boiled with glacial acetic acid (50 c.c.) for 15 min. Water (200 c.c.) was added and the solid filtered off and washed with water and ethanol. The residue was extracted with chlorobenzene, *octamethyltetrazaporphin* crystallising as purple prisms (4·5 g., 65%) from the extract (Found: C, 67·4; H, 6·3; N, 26·0. $C_{24}H_{26}N_8$ requires C, 67·6; H, 6·1; N, 26·3%).

Other Metal Derivatives.—The metal-free pigment (1·0 g.) was extracted into boiling *o*-dichlorobenzene (60 c.c.) containing anhydrous nickel chloride (10 g.). When extraction was complete, the mixture was boiled for 1 hr. and allowed to cool. The solid was filtered off and washed with light petroleum. The excess of nickel chloride was washed out with water and the dried residue extracted with chlorobenzene. *Nickel octamethyltetrazaporphin* (0·89 g., 78%) crystallised

as purple prisms with a bronze reflex from the extract (Found: C, 59·7; H, 5·1; N, 23·0; Ni, 11·7. $C_{24}H_{24}N_8Ni$ requires C, 59·7; H, 5·0; N, 23·2; Ni, 12·2%).

The *zinc* pigment (0·91 g., 79%) was prepared similarly from the metal-free pigment (1·0 g.) and zinc acetate (10 g.) and crystallised from chlorobenzene (Found: C, 59·0; H, 5·1; N, 23·0; Zn, 13·7. $C_{24}H_{24}N_8Zn$ requires C, 58·9; H, 4·9; N, 22·9; Zn, 13·4%). Crystallisation from pyridine gave an indefinite *pyridine solvate* (Found: C, 60·6; H, 5·7; N, 20·9. $C_{29}H_{29}N_9Zn$ requires C, 61·2; H, 5·1; N, 22·2%).

The metal-free pigment (100 mg.) was refluxed with copper bronze (1 g.) in *o*-dichlorobenzene (50 c.c.) for 3 hr. The mixture was then cooled and filtered and the solid extracted with chlorobenzene, giving *copper octamethyltetrazaporphin* (49 mg., 42%) (Found: C, 59·3; H, 5·2; N, 23·5; Cu, 12·7. $C_{24}H_{24}N_8Cu$ requires C, 59·0; H, 4·9; N, 23·0; Cu, 13·0%).

Urea-melt Method.—(i) *Nickel octamethyltetrazaporphin.* A mixture of dimethylmaleinitrile (1·06 g.), urea (5·0 g.), anhydrous nickel chloride (0·5 g.), ammonium molybdate (0·1 g.), and nitrobenzene (6 c.c.) was stirred at 155—160° for 4 hr. The mixture was treated with 0·5N-hydrochloric acid (100 c.c.), and the nitrobenzene removed by steam-distillation. The filtered residue was stirred with 0·5N-sodium hydroxide at 60° for 15 min. The solid was filtered off, dried, and extracted with *o*-dichlorobenzene, to give nickel octamethyltetrazaporphin (0·13 g., 12%). (ii) The *cobalt* pigment (0·10 g., 9%) was prepared similarly, anhydrous cobaltous chloride (0·5 g.) being used (Found: C, 60·0; H, 5·7; N, 24·0; Co, 12·6. $C_{24}H_{24}N_8Co$ requires C, 59·6; H, 5·0; N, 23·2; Co, 12·2%).

Zinc Phthalocyanine Solvate.—Zinc phthalocyanine was recrystallised from pyridine, giving purple prisms of *zinc phthalocyanine pyridine solvate* (Found: C, 67·7; H, 3·5; N, 19·3. $C_{37}H_{21}N_9Zn$ requires C, 67·6; H, 3·2; N, 19·2%) which was stable at 120°/10 mm. Spectrum in pyridine: max. at 3475 (log ε 4·81), 6070 (4·59), 6460 (4·56), 6720 (5·45).

Oxidation of Octamethyltetrazaporphin.—A solution of the metal-free pigment (82 mg.) in concentrated sulphuric acid (2 c.c.) was cooled in ice-salt and poured on ice (3 g.). Chromium trioxide (85 mg.), dissolved in the minimum amount of water, was added and the mixture allowed to warm to room temperature until the pigment was completely oxidised. Excess of chromium trioxide was removed by treating the solution with ferrous sulphate (3 g.) in water (25 c.c.). The solution was extracted with ether overnight, and the ether-extracts were evaporated. Sublimation of the residue yielded dimethylmaleimide (75 mg., 80%), m. p. and mixed m. p. 119—120°.

The ammonium salts contained in the residual aqueous layer were determined by the Kjeldahl method (Found: N, 12·7. Calc. for 4 aza-links: N, 13·1%).

Photochemical Decomposition of Pigments.—(a) *Magnesium octamethyltetrazaporphin.* The pigment (200 mg.) was dissolved in pyridine (100 c.c.), and the solution exposed to daylight during June—August. Most of the fluorescence had then disappeared. The solution was filtered to remove precipitated magnesium salts, and the pyridine evaporated under reduced pressure. The residue was extracted with methanol, traces of pigment were removed by stirring the solution with charcoal, and the solvent was evaporated. Sublimation of the residue gave dimethylmaleimide (87 mg., 47%), m. p. and mixed m. p. 116—119°.

(b) *Magnesium tetracyclohexenotetrazaporphin* (with G. E. Ficken). A solution of magnesium tetra*cyclo*hexenotetrazaporphin pyridine hydrate (560 mg.) in pyridine (50 c.c.) was completely decolorised after treatment in the manner described above. The solution was filtered and evaporated to dryness under reduced pressure. Extraction with light petroleum (b. p. 60—80°) gave a trace of 3 : 4 : 5 : 6-tetrahydrophthalimide, m. p. 162—165°, mixed m. p. 164—167°. Extraction of the residue with benzene gave impure 3 : 4 : 5 : 6-tetrahydrophthalimide (79 mg., 15%).

Spectra.—During preparative work, absorption spectra (see Table) in the visible region were measured on a Hilger–Nutting spectrometer. For the measurement of intensities, a Unicam Spectrophotometer SP 500 was used, a hydrogen lamp being employed for readings below 4000 Å and a tungsten lamp for higher wavelengths. Solutions were prepared by boiling an

Pigment	Solvent	Absorption maxima (Å)				log ε			
Metal-free ...	PhCl	3430	5560	5970	6270	4·89	4·66	3·94	4·86
Magnesium ...	C_5H_{11}·OH	3420	5465	5950		4·96	4·23	5·08	
	C_5H_5N	3460	5480	5970		4·94	4·21	5·06	
Nickel	$C_6H_4Cl_2$	3210	3410	5470	5920	4·57	4·52	4·26	4·82
Copper	$C_6H_4Cl_2$	3430	5420	5930		4·83	4·19	5·02	
Zinc	C_5H_5N	3465	5510	5950		4·93	4·17	5·02	
Cobalt	C_6H_5Cl	3455	5420	5890		4·66	4·27	4·86	

accurately weighed amount (0·5—0·7 mg.) of the pigment with the solvent, cooling, and dilution to 100 c.c.

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