789. *Conjugated Macrocycles. Part XXXI.* Catalytic Hydrogenation of Tetrazaporphins, with a Note on its Stereochemical Course.†*

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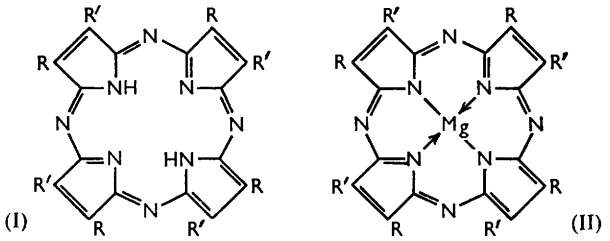
Hydrogenation of tetrazaporphins in the presence of very active catalysts gave substances easily decomposed to the imides of dibasic acids. With palladium black as catalyst, tetrazaporphin (I; R = R′ = H) and three of its alkyl derivatives gave reasonably stable, coloured tetrahydro-derivatives. The hydrogenation level of these substances was established by degradation to saturated imides, by quantitative dehydrogenation, and by spectral evidence.

The dehydrogenation of tetra*cyclo*hexenotetrazaporphin (I; RR′ = $-[CH_2]_4-$) with quinones is described.

Catalytic hydrogenation of tetrazaporphin [1] (I; R = R′ = H) (now more accessible because of an improved method for preparation of maleinitrile [2]), of its tetramethyl [3] (I; R = H, R′ = Me), octamethyl [4] (I; R = R′ = Me), and tetra*cyclo*hexeno- [5] (I; RR′ = $-[CH_2]_4-$) derivatives and of the corresponding magnesium complexes (II) has been



investigated. The metal-free pigments in pyridine, chlorobenzene, or 2-ethoxyethanol and the magnesium pigments in pyridine were rapidly destroyed over active catalysts such as Adams platinum oxide or W-4 Raney nickel. It seems likely that hydrogenation at

* Part XXX, *J.*, 1957, 2882.

† A preliminary account appeared in Special Publication No. 3, The Chemical Society, 1955, p. 98.

[1] Linstead and Whalley, *J.*, 1952, 4839.

[2] Woods, Imperial Chemical Industries Limited, personal communication; cf. U.S.P. 2,447,810/1948.

[3] Brown, Spiers, and Whalley, *J.*, 1957, 2882.

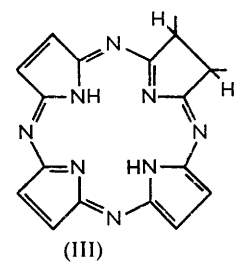
[4] Baguley, France, Linstead, and Whalley, *J.*, 1955, 3521.

[5] Ficken and Linstead, *J.*, 1952, 4846.

the β-positions of the pyrrole rings is accompanied by hydrogenolysis of the macrocycle, the linear, possibly polypyrrolic, intermediates then being hydrolysed. The only products isolated from the magnesium complexes of tetramethyl-, octamethyl-, and tetra*cyclo*hexeno-tetrazaporphin were saturated imides, *viz.*, methylsuccinimide, αα′-dimethylsuccinimide, and *cis*-hexahydrophthalimide. Under similar conditions phthalimide was obtained from magnesium and zinc phthalocyanine.[6]

Controlled hydrogenation was possible by using palladium black.[7] With the metal-free pigments hydrogenation was slow and considerable loss was caused by over-hydrogenation. With the more soluble magnesium pigments in pyridine, preparative hydrogenation was practicable. The magnesium derivatives of tetramethyl-, octamethyl-, and tetra*cyclo*hexeno-tetrazaporphin gave, after 2 mols. of hydrogen had been absorbed, royal-blue solutions which did not show the strong visible and ultraviolet fluorescence characteristic of the parent pigments. The spectra of the blue solutions were of the metal-tetrazaporphin type: in each case hydrogen caused a bathochromic shift of *ca.* 30 mμ in the position of the longest-wavelength band. The blue pigments, either solid or in solution, were readily oxidised in air, to the starting materials contaminated with traces of unidentified pigments which absorbed at longer wavelength (663, 665, and 666 mμ severally). Under the same conditions, hydrogenation of magnesium tetrazaporphin (II; R = R′ = H) gave very small yields of a blue pigment ($\lambda_{max.}$ 608, 454 mμ in pyridine) which was rather more stable to atmospheric oxidation. Magnesium phthalocyanine in dilute solution in pyridine slowly formed a blue pigment ($\lambda_{max.}$ 709, 570 mμ) which in air gave instant and quantitative recovery of magnesium phthalocyanine.

In acetic acid the reduced magnesium pigments from tetramethyl-, octamethyl-, and tetra*cyclo*hexeno-tetrazaporphin gave purple microcrystalline, sparingly soluble (6—8 mg./100 c.c. of chlorobenzene) metal-free compounds. These pigments were reasonably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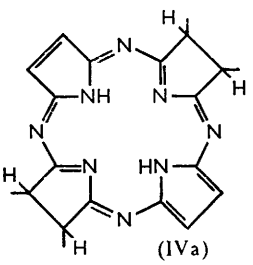
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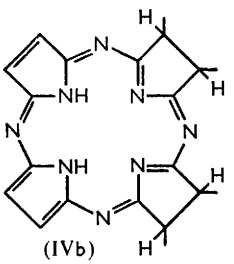
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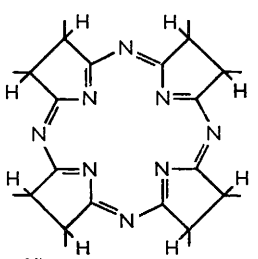
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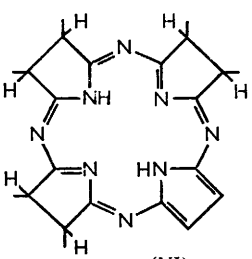
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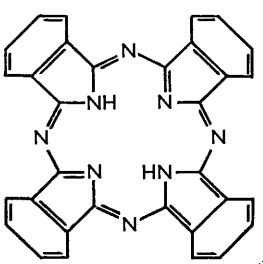

(VII)

stable to oxidation at room temperature but in boiling chlorobenzene or, better, chlorobenzene–nitrobenzene they oxidised to the parent pigment: this made purification by crystallisation impracticable. The number and position of the " extra " hydrogen atoms in these compounds was still to be determined.

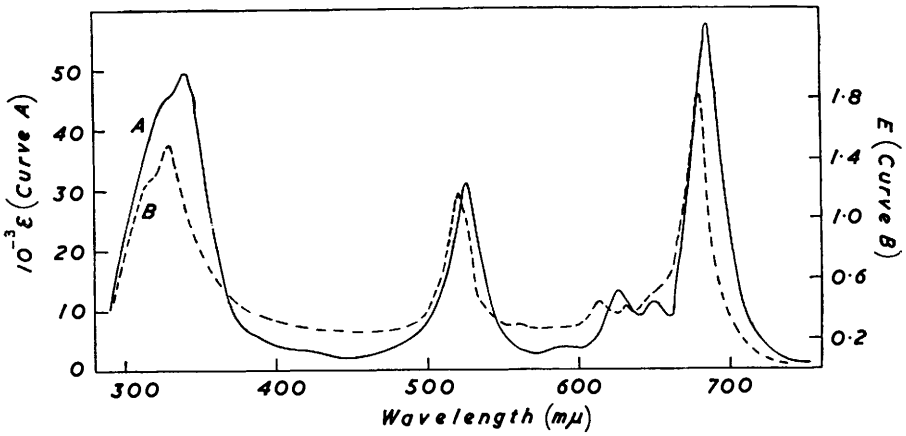
Several coloured hydrotetrazaporphins with the β-positions of one or more pyrrolic

[6] Barrett, Dent, and Linstead, *J.*, 1936, 1719.
[7] Wieland, *Ber.*, 1912, **45**, 489.

corners reduced, are formally possible. The dihydro-form (III) corresponds to the relatively stable chlorin [8] in the porphyrin series. The tetrahydro-compound may be formulated as (IVa) (corresponding to bacteriochlorophyll [9]) or (IVb). Formulæ (V) and (VI) represent possible hexahydro-forms. In (II), (III), (IV), and (V) a large conjugated ring is retained [in (V) by transfer of 2 hydrogen atoms from central nitrogen atoms to β-pyrrolic carbon atoms]. In the hexahydro-compound (VI) the conjugation of the large ring is interrupted.

The more obvious methods for deciding between the possible structures proved unhelpful. Hydrogen uptake figures suggested a tetrahydro-structure for the magnesium hydrotetrazaporphins. This made structure (V) or (VI) unlikely for the metal-free pigments. It was, however, uncertain whether the metal-free pigments were at the tetrahydro- or the dihydro-level because of the possibility of partial dehydrogenation during demetallation. Carbon and hydrogen determinations on the metal-free pigments were inconclusive.

Spectra of (A) tetrahydro-octamethyltetrazaporphin and (B) tetrahydrotetrazaporphin in chlorobenzene.



Vigorous oxidation of a symmetrically substituted tetrazaporphin (cf. refs. 3, 4, 5) yields 4 mols. of the corresponding unsaturated imide. The dihydro-derivative (III) and the tetrahydro-compound (IVa or b) would therefore be expected to yield 1 mol. and 2 mols. of saturated imide respectively. In fact oxidation of hydro-octamethyltetrazaporphin gave αα′-dimethylsuccinimide (0·95 mol.) and dimethylmaleimide (1·77 mols.). Allowing for the (determined) experimental loss the yield of saturated imide becomes 1·19 mols. This still takes no account of the loss (unknown) through dehydrogenation of the pigment before ring scission. It is clear that the true yield of saturated imide is more than 1 mol. and therefore that the hydro-pigment contains more than one reduced pyrrolic corner. The hydro-pigment must therefore be at the tetrahydro-level since a higher level was excluded. This was confirmed by the results of quantitative dehydrogenation described below.

Similar oxidation of hydrotetra*cyclo*hexenotetrazaporphin and of hydrotetramethyltetrazaporphin gave *cis*-hexahydrophthalimide (0·3 mol.) and methylsuccinimide (0·4 mol.). The low yields of saturated imide in these two cases is not unexpected because of the greater ease of dehydrogenation of these hydrogenation products which would greatly increase the extent of dehydrogenation before ring scission. However, the absorption spectra of hydrotetra*cyclo*hexenotetrazaporphin, hydro-octamethyltetrazaporphin and hydrotetrazaporphin ($\lambda_{max.}$ 678, 525 mμ in chlorobenzene; obtained in minute yield from

[8] Cf., *e.g.*, Eisner and Linstead, *J.*, 1955, 3742.
[9] Golden, Linstead, and Whitham, *J.*, 1958, 1725.

magnesium tetrazaporphin) resemble so closely that of tetrahydro-octamethyltetrazaporphin (see Figure) that they too must be tetrahydro-derivatives.

The isolation of succinimide derivatives by degradation of the hydrotetrazaporphins indicated that the extra hydrogen atoms were on the β-positions of two of the pyrrolic corners of the macrocycles. It is of special interest that the αα′-dimethylsuccinimide from tetrahydro-octamethyltetrazaprophin was isolated in the *unstable meso*-form [10] in which the hydrogen atoms are *cis*- with respect to the imide ring. This shows that, as in the mild catalytic hydrogenation of polynuclear aromatic compounds,[11] there is one-sided addition of hydrogen to the molecule. This in turn would correspond with addition to each double bond of both atoms of hydrogen during one period of sorption on the catalyst. There is no evidence from measurements of light absorption during hydrogenation (or during dehydrogenation with air, boiling nitrobenzene, dilute nitric acid, or quinones) for the formation of a dihydro-pigment. If it may be presumed from this that all four atoms of hydrogen are added during a single period of sorption, it may be concluded that the tetrahydride is not only *cis* but *cis-syn-cis*, to apply the nomenclature used [12] for the hydrides of polynuclear aromatic compounds. This is represented diagramatically in (VIII).

H H H H
(VIII)

Indications of the existence of a hexahydro-compound (possibly V or VI) were obtained only in the tetra*cyclo*hexeno-series. The metal-free pigment in pyridine over palladium black gave, after 3 mols. of hydrogen had been absorbed, an olive-green solution ($\lambda_{max.}$ 720 mμ) which was rapidly oxidised in air (with uptake of 0·5 mol. of oxygen) to a solution of tetrahydrotetra*cyclo*hexenotetrazaporphin.

It has not been possible to determine, as yet, whether our products have the structure (IVa) with opposite pyrrolic corners reduced or (IVb) with adjacent corners reduced. The simple absorption spectra, however, suggest that they are not mixtures of the two forms because the two forms of tetrahydroporphins have been shown to have widely differing absorption spectra.[13,14]

The hydrogenation level of the hydrotetrazaporphins was also established by quantitative dehydrogenation. Titration methods using potassium dichromate, hydrogen peroxide, or ferric alum were unsuccessful because ring scission accompanied dehydrogenation; but dehydrogenation with quinones, a method successfully applied to the dehydrogenation of synthetic chlorins,[15] confirmed the tetrahydro-structure for our products: hydro-octamethyltetrazaporphin in *o*-dichlorobenzene at room temperature was 50% dehydrogenated by 1 mol. of 2 : 3-dichloro-5 : 6-dicyano-1 : 4-benzoquinone and 100% dehydrogenated by 2 mols. The product was octamethyltetrazaporphin which was spectroscopically identical with the pigment prepared from dimethylfumaronitrile.[4] The isolation of 2 : 3-dichloro-5 : 6-dicyanoquinol from the reaction indicated that transfer of the " extra " hydrogen atoms to the quinone had in fact occurred. With quinones of lower potential, *e.g.*, tetrachloro-1 : 2-benzoquinone and chloranil, dehydrogenation was slow at 80° and was accompanied by thermal decomposition of both pigment and quinone.

Dehydrogenation of tetrahydrotetra*cyclo*hexenotetrazaporphin with an excess of chloranil at 110° gave nearly complete conversion into the parent pigment (II; RR′ = $-[CH_2]_4-$). With an excess of 2 : 3-dichloro-5 : 6-dicyano-1 : 4-benzoquinone at 80°, the tetrahydro-pigment gave initially the parent tetrazaporphin but then the *cyclo*hexene rings were successively dehydrogenated to yield, finally, phthalocyanine (VII). Two of the intermediate pigments—benzotri*cyclo*hexeno- ($\lambda_{max.}$ 647, 571 mμ) and tribenzo*cyclo*hexenotetrazaporphin ($\lambda_{max.}$ 680, 610 mμ)—were identified by comparison of the absorption

[10] Linstead and Whalley, *J.*, 1954, 3722.
[11] Linstead, Doering, Davis, Levine, and Whetstone, severally, *J. Amer. Chem. Soc.*, 1942, **64**, 1985—2022.
[12] *Idem, ibid.*, p. 1985.
[13] Dorough and Miller, *J. Amer. Chem. Soc.*, 1952, **74**, 6106.
[14] Barnard and Jackman, *J.*, 1956, 1174.
[15] Eisner and Linstead, *J.*, 1955, 3749; Eisner, Linstead, Parkes, and Stephen, *J.*, 1956, 1655.

maxima with those of the known pigments.[16] The third intermediate ($\lambda_{max.}$ 671, 585 mμ) was spectroscopically identical with the pigment obtained by treatment of tetra*cyclo*hexenotetrazaporphin with 6 mols. of dichlorodicyanobenzoquinone at 110° or with an excess of tetrachloro-1 : 2-benzoquinone at 80°. The spectrum and elementary analysis of this pigment suggest that it is dibenzodi*cyclo*hexenotetrazaporphin. Quinones of lower potential, such as 9 : 10-anthraquinone and duroquinone, failed to remove the "extra" hydrogen atoms from tetrahydrotetra*cyclo*hexenotetrazaporphin. The progressive dehydrogenation of the hydro-derivatives of phthalocyanine can be represented in the following scheme where the numbers refer to the extra hydrogen atoms on the four *iso*indole rings: 6.4.6.4 ⟶ 4.4.4.4 ⟶ 4.4.4.0 ⟶ 4.0.4.0 ⟶ 4.0.0.0 ⟶ 0.0.0.0.

Experimental

Microanalyses were carried out in the Microanalytical Laboratory (Mr. F. H. Oliver and Miss J. Cuckney) of this Department.

Maleinitrile.[2]—Fumaronitrile [17] (8·5 g.) was heated with iodine (0·5 g.) at 175—180° for 6·5 hr. The product was dissolved in chloroform (120 c.c.). Sodium thiosulphate (5 g.) was added and the mixture was kept overnight. The chloroform solution was decanted, and the residue was distilled to give fumaronitrile, b. p. 90—95/20 mm. (5·4 g.), and maleinitrile, b. p. 110—120°/20 mm. (2·75 g., 89% on unrecovered fumaronitrile).

Pyridine for Hydrogenations.—Pyridine (from Messrs. Hopkin and Williams, "pure") (500 c.c.) was refluxed for 4 hr. with W-4 Raney nickel (1 teaspoonful) and then redistilled from fresh Raney nickel.

*Tetrahydrotetra*cyclo*hexenotetrazaporphin.*—(i) A suspension of magnesium tetra*cyclo*hexenotetrazaporphin monohydrate monopyridine solvate [5] (222 mg.) in pyridine (100 c.c.) was hydrogenated over palladium black [7] (53 mg.) until 2 mols. of hydrogen had been absorbed. The solution was filtered rapidly under nitrogen and the pyridine was removed under reduced pressure (no air-leak). Filtered acetic acid (20 c.c.) was added and the mixture was kept at room temperature under reduced pressure for 2 hr. Filtered, distilled water was added. *Tetrahydrotetra*cyclo*hexenotetrazaporphin* (140 mg., 76%) separated as a dark purple powder (Found: C, 72·1; H, 6·9; N, 20·8. $C_{32}H_{38}N_8$ requires C, 71·9; H, 7·2; N, 21·0%). (ii) Tetra*cyclo*hexenotetrazaporphin (264 mg.) was suspended in pyridine (50 c.c.) and hydrogenated over palladium black for 7 days: 2·93 mols. of hydrogen were absorbed. The olive-green solution was shaken with air: 0·94 atom of oxygen was absorbed. The purple solution was decanted from the palladium black into 2N-hydrochloric acid (100 c.c.). Tetrahydrotetra*cyclo*hexenotetrazaporphin (217 mg., 82%) spectroscopically identical with that prepared from the magnesium pigment was obtained.

Tetrahydro-octamethyltetrazaporphin.—Magnesium octamethyltetrazaporphin monopentanolate [4] (250 mg.) was hydrogenated in pyridine (100 c.c.) over palladium black (19 mg.). 2·0 Mols. of hydrogen were absorbed. The solution was filtered rapidly and the pyridine was removed under reduced pressure (no air-leak). Acetic acid (20 c.c.) was added, followed, after 2 hr., by water (20 c.c.). *Tetrahydro-octamethyltetrazaporphin* (159 mg., 84%) was precipitated as a purple solid (Found: C, 67·2; H, 6·7; N, 26·3. Calc. for $C_{24}H_{30}N_8$: C, 66·9; H, 7·0; N, 26·0%). The pigment in chlorobenzene passed down kieselguhr or tartaric acid columns as a single band. Alumina caused dehyrogenation to the ground-level pigment.

Tetrahydrotetramethyltetrazaporphin.—This experiment must be completed within 6 hr. Magnesium tetramethyltetrazaporphin monomethanolate [3] (210 mg.) was hydrogenated in pyridine (100 c.c.) over palladium black (55 mg.). The solution became brown and then light green (*ca.* 2 hr.). The reaction was then stopped and the mixture was filtered rapidly under nitrogen. The royal-blue filtrate was evaporated to dryness under reduced pressure and cold acetic acid (20 c.c.) was added to the ice-cold residue. After 2 hr. the acetic acid was removed under reduced pressure and water (20 c.c.) was added. *Tetrahydrotetramethyltetrazaporphin monohydrate* (83 mg., 43%) was obtained as a dark purple solid after drying (room temperature/0·01 mm.) (Found: C, 61·8; H, 5·9; N, 29·1. $C_{20}H_{24}N_8O$ requires C, 61·2; H,

[16] Brown, Linstead, and Whalley, unpublished work.
[17] *Org. Synth.*, **30**, 46.

6·1; N, 28·6%). Drying the pigment at slightly higher temperatures invariably caused dehydrogenation to tetramethyltetrazaporphin.

Oxidation of Tetrahydro-octamethyltetrazaporphin.—The pigment (287 mg.) was dissolved in concentrated sulphuric acid (5 c.c.) at −5° under nitrogen. 0·01N-Potassium dichromate (100 c.c.) was added all at once. After 2 min. ferrous sulphate (3 g.) was added and the solution was filtered to remove octamethyltetrazaporphin ($\lambda_{max.}$ in chlorobenzene 627, 556 mμ) (9 mg., 3%). The filtrate was extracted continuously with ether for 48 hr. The extract was concentrated to *ca.* 10 c.c. (inversion of configuration occurs if the ether extract is evaporated to dryness at this stage or during extraction) and the solution was chromatographed on silica gel loaded with water.[18] The column was eluted with ether. Twenty-four 4-c.c. fractions were collected. Fractions 1—6 yielded dimethylmaleimide (136 mg., 1·7 mols.), m. p. 117—119°, fractions 7 and 8 gave a mixture (6 mg.) and fractions 9—23 contained *meso*-αα′-dimethylsuccinimide (78 mg., 0·95 mol.), m. p. and mixed m. p. 43—45°.[8]

Oxidation and separation as described above of dimethylmaleimide (95 mg.) and dimethylsuccinimide (99 mg.) gave 75 mg. (79% recovery) of the former and 79 mg. (80% recovery) of the latter and 4 mg. of a mixture.

*Oxidation of Tetrahydrotetra*cyclo*hexenotetrazaporphin.*—The pigment (305 mg.) was oxidised as described above. The ether extract was evaporated to dryness, the residue was dissolved in wet benzene, and the solution was chromatographed on silica gel.[18] Fractions 1—17 yielded 3 : 4 : 5 : 6-tetrahydrophthalimide (198 mg., 2·3 mol.), m. p. and mixed m. p. 169—172°, and *cis*-hexahydrophthalimide [19] (27 mg., 0·3 mol.), m. p. and mixed m. p. 133—137°.

Oxidation of Tetrahydrotetramethyltetrazaporphin.—The pigment monohydrate (165 mg.) was dissolved in concentrated sulphuric acid (4 c.c.) at 0° under nitrogen and chromium trioxide (100 mg.) was added in a little water. The mixture was kept at room temperature for 5 min. and excess of ferrous sulphate was then added. The solution was continuously extracted with ether overnight and the extract was chromatographed on silica gel [18] as above. Fractions 1—7 contained citraconimide (69 mg., 1·5 mols.), fractions 8—10 contained no solute, and fractions 11—15 yielded methylsuccinimide (20 mg., 0·4 mol.), m. p. and mixed m. p. 61—64°.

Hydrogenation of Magnesium Phthalocyanine Monohydrate.—Crude magnesium phthalocyanine [6] was crystallised several times from pyridine to give the purple monohydrate (Found: C, 68·7; H, 3·7; N, 19·9; Mg, 4·5. Calc. for $C_{32}H_{16}N_8Mg,H_2O$: C, 69·2; H, 3·3; N, 20·2; Mg, 4·4%). A solution of the pigment in pyridine (0·34 mg./100 c.c.; 20 c.c.) was hydrogenated over palladium black for 16 hr. The blue solution was shaken in the air and immediately reoxidised to a solution of magnesium phthalocyanine (0·34 mg./100 c.c., estimated spectroscopically from the absorption at 674 mμ).

Exhaustive Hydrogenations.—(i) Magnesium tetra*cyclo*hexenotetrazaporphin monohydrate monopyridine solvate (350 mg.) was hydrogenated in pyridine (50 c.c.) over Adams platinum oxide (50 mg.) until no more hydrogen was absorbed. The pyridine was removed under reduced pressure and the dark sticky residue was extracted with light petroleum (b. p. 60—80°). *cis*-Hexahydrophthalimide (21 mg., 0·25 mol.), m. p. and mixed m. p. 133—135°, separated.

(ii) Magnesium octamethyltetrazaporphin monopentanolate (237 mg.) was hydrogenated in pyridine (35 c.c.) over Adams platinum oxide for 3 days. The dark green solution was filtered through charcoal and the filtrate was evaporated to dryness under reduced pressure. The residue was sublimed and the sublimate was crystallised from water to give DL-αα′-dimethylsuccinimide (21 mg., 0·38 mol.), m. p. 99—101°, mixed m. p. 101—102° [8] (no precautions were taken to prevent possible inversion of configuration of the primary product).

(iii) Magnesium phthalocyanine monohydrate (97 mg.) was hydrogenated in pyridine (50 c.c.) over Adams platinum oxide (23 mg.) for 6 days. 11·5 Mols. of hydrogen were absorbed. The brown mixture was shaken with air; magnesium phthalocyanine (6% of the original quantity, estimated spectroscopically) was re-formed. The solution was filtered and the filtrate was evaporated to dryness at room temperature. The residual solid was extracted with light petroleum (b. p. 60—80°), and the extract was evaporated to dryness. Sublimation of the residue gave phthalimide (53 mg., 2·1 mols.), m. p. 224—226° and 229—232° after further sublimation.

(iv) Zinc phthalocyanine monopyridine solvate [4] (188 mg.) was hydrogenated as above.

[18] Elvidge, Linstead, and Whalley, "Modern Techniques of Organic Chemistry," Butterworths, London, 1955, p. 9.

[19] Ficken and Linstead, *J.*, 1954, 3730.

10 Mols. of hydrogen were absorbed. The brown solution was filtered through charcoal, and the filtrate was evaporated to dryness under reduced pressure. The solid was dissolved in a little ethanol and the solution was diluted with benzene (4 vols.). The solution was chromatographed on alumina (Spence H) and gave (*a*) a weakly adsorbed green band containing a trace of zinc phthalocyanine, (*b*) a yellow band which yielded phthalimide (97 mg., 2·1 mols.), m. p. 229—231°, and (*c*) a strongly adsorbed rose-pink band which was eluted with 50% aqueous pyridine and gave no identifiable product.

Dehydrogenation of Tetrahydro-octamethyltetrazaporphin.—(i) The following control experiments showed that Beer's law is obeyed by mixtures of octamethyltetrazaporphin (A) and tetrahydro-octamethyltetrazaporphin (B) in *o*-dichlorobenzene.

	530 mμ		560 mμ		630 mμ		685 mμ	
Concn. (mg./100 c.c.)	$E_{obs.}$	$E_{calc.}$	$E_{obs.}$	$E_{calc.}$	$E_{obs.}$	$E_{calc.}$	$E_{obs.}$	$E_{calc.}$
A 0·2295, B 0·2282	0·232	0·231	0·232	0·235	0·391	0·413	0·416	0·422
A 0·1148, B 0·3400	0·262	0·276	0·121	0·131	0·251	0·252	0·630	0·637
A 0·3440, B 0·1157	0·180	0·189	0·314	0·318	0·540	0·522	0·209	0·213

It was also shown that solutions of octamethyltetrazaporphin and of tetrahydro-octamethyltetrazaporphin in *o*-dichlorobenzene were essentially unchanged after 4 hr. at 80° under nitrogen.

Method A. 5-C.c. portions of a solution of tetrahydro-octamethyltetrazaporphin (2—3 mg./100 c.c. of *o*-dichlorobenzene) were treated with varying molar proportions of 2 : 3-dichloro-5 : 6-dicyano-1 : 4-benzoquinone (11—12 mg. in 25 c.c. of *o*-dichlorobenzene) at 80° for 2·75 hr. (apparatus [20]). Each solution was then withdrawn with a long-necked pipette and the flask was rinsed several times with *o*-dichlorobenzene. The combined solution and washings were made up to 25 c.c. and the resulting solution was examined spectrophotometrically at 530, 560, 630, and 685 mμ.

Method B. 1-C.c. portions of a solution of tetrahydro-octamethyltetrazaporphin (3·4 mg./100 c.c. of dry *o*-dichlorobenzene) were placed in ampoules. To each was added a solution of 2 : 3-dichloro-5 : 6-dicyano-1 : 4-benzoquinone (11·2 mg./100 c.c. of dry *o*-dichlorobenzene: 0·5—2·0 mols.). The ampoules were sealed and kept in the dark at room temperature for 22 hr. The solutions were then made up to 10·0 c.c. with *o*-dichlorobenzene and each was examined spectrophotometrically at 530, 560, 630, and 685 mμ.

Quinone (mols.)	Unchanged hydro-deriv. (%)		Dehydrogenated pigment (%)		Dehydrogn. (%)
	530 mμ	685 mμ	560 mμ	630 mμ	
	Method A				
0·5	77	70	34	32	30
1·0	52	49	49	50	50
1·4	33	32	62	67	67
2·0	6	8	95	97	95

Quinone (mols.)	Unchanged hydro-deriv. (%)		Dehydrogenated pigment (%)		Dehydrogn. (%)
	530 mμ	685 mμ	560 mμ	630 mμ	
	Method B				
0·5	—	70	26	26	27
1·0	—	44	47	50	52
1·25	35	33	60	59	62
1·5	24	29	70	70	72
2·0	3	10	91	94	93

The results tabulated above are each the average of two or more independent experiments.

(ii) Tetrahydro-octamethyltetrazaporphin (14·4 mg.) was heated with 2 : 3-dichloro-5 : 6-dicyano-1 : 4-benzoquinone (180 mg., 3 mols.) in dry *o*-dichlorobenzene (100 c.c.) in the dark for 17 hr. at 80°. The solution was evaporated to small bulk and octamethyltetrazaporphin (13·7 mg., 95%) then separated. It was washed with ether and twice crystallised extractively from *o*-dichlorobenzene (Found: 560 mμ, log ε 4·58; 630 mμ, log ε 4·78. Octamethyltetrazaporphin has log ε 4·58 and 4·78 respectively). The combined filtrate and washings were evaporated and gave 2 : 3-dichloro-5 : 6-dicyanoquinol (10 mg., 55%), m. p. and mixed m. p. 257—259° (Thiele and Gunter [21] give 265°). The product gave the pink colour characteristic for the quinol with aqueous ferric chloride.

[20] Braude, Jackman, and Linstead, *J.*, 1954, 3548.
[21] Thiele and Gunter, *Annalen*, 1906, **349**, 54.

*Dehydrogenation of Tetra*cyclo*hexenotetrazaporphin and its Derivatives.*—(i) A solution of tetra*cyclo*hexenotetrazaporphin or of tetrahydrotetra*cyclo*hexenotetrazaporphin in *o*-dichlorobenzene was boiled with a large excess of 2 : 3-dichloro-5 : 6-dicyano-1 : 4-benzoquinone. Phthalocyanine ($\lambda_{max.}$ 698, 665 mμ) was the only pigment produced.

(ii) Tetra*cyclo*hexenotetrazaporphin (1 mol.) in *o*-dichlorobenzene was heated at 110° with dichlorodicyanobenzoquinone (6 mols.) for 17 hr. in a sealed ampoule. The product was dibenzodi*cyclo*hexenotetrazaporphin ($\lambda_{max.}$ 671, 584 mμ) containing traces of benzotri*cyclo*hexenotetrazaporphin [21] ($\lambda_{max.}$ 647, 571 mμ) and unchanged starting material.

(iii) Tetra*cyclo*hexenotetrazaporphin in chlorobenzene was heated with an excess of tetrachloro-1 : 2-benzoquinone at 80° for 2 days. The solution was diluted and was then chromatographed (alumina, Spence H). Three pigments were eluted with chlorobenzene, *viz.*, (i) blue ($\lambda_{max.}$ 647, 571 mμ), monobenzotri*cyclo*hexenotetrazaporphin [16] (traces), (ii) violet ($\lambda_{max.}$ 671, 586 mμ) main product, and (iii) blue-green ($\lambda_{max.}$ 680, 615 mμ), tribenzo*cyclo*hexenotetrazaporphin [21] (traces). The violet fraction was concentrated and rechromatographed, to give the violet pigment contaminated with traces of the monobenzo-compound. Repeated extractive crystallisation of the pigment from benzene gave dark blue needles of *dibenzodi*cyclo*hexenotetrazaporphin* (Found: C, 72·8; H, 5·1. $C_{32}H_{26}N_8$ requires C, 73·5; H, 5·0%).

(iv) Dibenzodi*cyclo*hexenotetrazaporphin and benzotri*cyclo*hexenotetrazaporphin in *o*-dichlorobenzene with a large excess of dichlorodicyanobenzoquinone at 150° each gave tribenzo*cyclo*hexenotetrazaporphin ($\lambda_{max.}$ 680, 610 mμ) and phthalocyanine.

Absorption Spectra.—For qualitative work a Hilger–Nutting spectrophotometer and a Hartridge reversion spectroscope were used. Quantitative spectra were obtained on a Unicam S.P. 500 (250—400 mμ) and a S.P. 600 (400—1000 mμ) instrument. A reduced pigment (*ca.* 0·5 mg.) was dissolved in the solvent (100 c.c.) at room temperature and intensity measurements were completed within 1 hr.

Absorption spectra (mμ) *and* log ε.

Tetrazaporphin	Solvent							
Tetrahydro-octamethyl	PhCl	333	342	526	626	651	687	
		4·65	4·69	4·48	4·12	4·06	4·75	
	$C_6H_4Cl_2$	331	346	528	625	650	687	
		4·62	4·66	4·57	3·98	4·07	4·78	
Tetrahydrotetra*cyclo*hexeno...	$CHCl_3$	265	328	343	532	628	653	691
		4·03	4·69	4·76	4·45	4·23	4·11	4·78
Tetrahydrotetramethyl	PhCl	333	338	526	624	681		
		4·64	4·65	4·29	4·10	4·61		
Octamethyl	$C_6H_4Cl_2$	343	558	630				
		4·82	4·61	4·82				
Dibenzodi*cyclo*hexeno	$C_6H_4Cl_2$	346	544	586	671			
		4·78	4·31	4·91	4·83			
Magnesium phthalocyanine ...	C_5H_5N	347	568	587	610	647	674	
		4·73	3·59	3·79	4·45	4·39	4·94	

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