563. *Conjugated Macrocycles. Part XXX.* Tetramethyltetrazaporphin.*

By P. Margaret Brown, D. B. Spiers, and Margaret Whalley.

Methylmaleinitrile (citraconononitrile) (I) has been prepared in good yield for the first time. It has been converted into a tetramethyltetrazaporphin (VI) which has also been obtained from methylsuccinimidine (VIII). Tetramethyltetrazaporphin has been degraded to citraconimide, and some of its metal derivatives (V; M = Mg, Cu, or Ni) have been prepared. Light absorptions are given.

Tetrazaporphins have been prepared from maleinitrile and its derivatives by treatment with organomagnesium compounds.[1,2,3] We have now achieved a good synthesis of

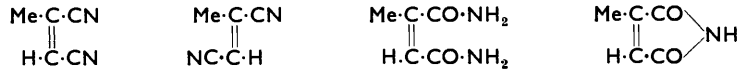
* Part XXIX, *J.*, 1957, 2466.

[1] Linstead and Whalley, *J.*, 1952, 4839.
[2] Ficken and Linstead, *ibid.*, p. 4846.
[3] Baguley, France, Linstead, and Whalley, *J.*, 1955, 3521.

methylmaleinitrile (citraconononitrile) and have effected its conversion with magnesium propoxide into tetramethyltetrazaporphin (VI), in the molecule of which each pyrrolic corner has one free and one methyl-substituted β-carbon atom.

Tetramethyltetrazaporphin has also been obtained from methylsuccinimidine.

There was no good method for the preparation of citraconononitrile (I). It was obtained, in small yield, as one of the products of irradiation of a solution of methylfumaronitrile (II) in acetone with ultraviolet light.[4] The obvious route, by dehydration of methylmaleamide (citraconamide) (III) with phosphoric oxide had given only citraconimide (IV), although dehydration of the *trans*-diamide readily gave methylfumaronitrile [5] (II).



(I) (II) (III) (IV)

The dehydration of citraconamide (III) was now further investigated. It was confirmed that with phosphoric oxide it gave only citraconimide (IV), but with carbonyl chloride in pyridine [6] it gave citraconononitrile (I) as a colourless liquid whose properties corresponded with those reported by Duez.[4] The *cis*-configuration of the product was established by comparison of its physical properties with those of the known *trans*-isomer (II) and by its acid hydrolysis to citraconic acid.

Citraconononitrile (I) reacted with magnesium propoxide in boiling propanol, to give a new blue pigment which is formulated as (V; M = Mg) (or an isomeric form in which the relative positions of the methyl groups are different). Copious evolution of ammonia during the reaction was probably due to propanolysis of the citraconononitrile to the ortho-ester, which would not be a pigment precursor. This would account for the rather low yield of pigment. Magnesium tetramethyltetrazaporphin was isolated as the monomethanolate. This solvate formation is characteristic of the magnesium tetrazaporphins.[1, 2, 3, 7]

The metal-free pigment (VI, or a positional isomer) was obtained from magnesium tetramethyltetrazaporphin (V; M = Mg) by treatment with cold glacial acetic acid. A yield slightly lower than that of the magnesium pigment was given by treatment of the citraconononitrile–propoxide reaction product directly with *cold* glacial acetic acid.

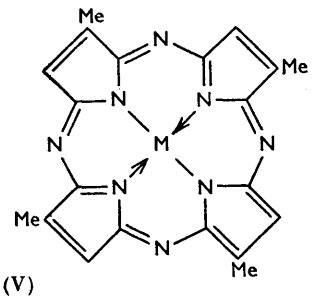
Like the other tetrazaporphins, tetramethyltetrazaporphin forms a series of metallic derivatives, *e.g.* ing *o*-dichlorobenzene with copper bronze the derivative (V; M = Cu) and w drous nickel chloride (but not nickel acetate) the derivative (V; M = Ni). In c zene neither reaction proceeded to completion even on prolonged boiling. Metal exchange was possible with the magnesium pigment (V; M = Mg), which with copper bronze in boiling pyridine gave the derivative (V; M = Cu), but no reaction occurred with anhydrous nickel chloride under these conditions.

The structure (VI or positional isomer) for tetramethyltetrazaporphin is suggested by the analytical data, method of preparation, and physical properties, particularly light absorption, of the metal-free and metal pigments. Conclusive proof is provided by the degradation of the metal-free pigment with chromium trioxide and sulphuric acid at 0° to citraconimide (IV) in 61% yield. This easy degradation to citraconimide contrasts with the porphyrin series : only in a few cases (see, *e.g.*, ref. 8) has citraconimide been detected among the oxidation products of porphyrins which contain monomethylated pyrrole corners.

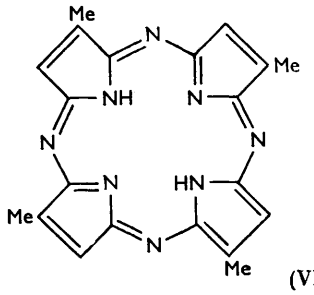
However, the isolation of citraconimide proves only that each pyrrolic corner of the pigment (VI) has one β-methyl group and one β-hydrogen atom. Tetramethyltetrazaporphin can of course exist in four positionally isomeric forms corresponding to the four

[4] Duez, *Bull. Acad. roy. Belg.*, 1939, **25**, 646.
[5] Bruylants and Jennen, *ibid.*, 1936, **22**, 1141; van de Straete, *ibid.*, 1935, **21**, 226.
[6] Ficken, France, and Linstead, *J.*, 1954, 3730.
[7] Linstead and Lowe, *J.*, 1934, 1022.
[8] Fischer and Wenderoth, *Annalen*, 1939, **537**, 170.

*ætio*porphyrins described by Fischer and Stangler.[9] The relative positions of the four methyl groups in the new pigment have not been disclosed and indeed it is not known that our product is a single isomer. No banding was observed during chromatography of the

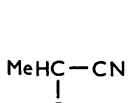


(V)

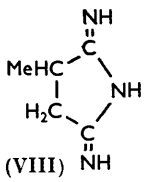


(VI)

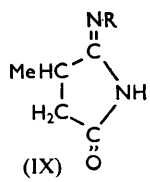
metal-free pigment in chlorobenzene on alumina (Spence H) or on tartaric acid. However the greater solubility of the tetramethyltetrazaporphin and of its metal derivatives than of the corresponding tetrazaporphins (which is unexpected because the octamethyltetrazaporphins [3] are considerably less soluble) suggests that the new pigments are mixtures of isomers.



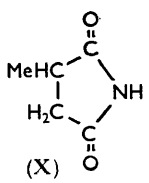
(VII)



(VIII)



(IX)



(X)

The tetramethyltetrazaporphins closely resemble the unsubstituted tetrazaporphins.[1] They are not sufficiently stable thermally to permit sublimation even at low pressures. Solutions of the magnesium pigment in alcohols and in pyridine show a strong fluorescence, crimson in daylight and brilliant orange in ultraviolet light. Solutions of the metal-free compound in benzene or chlorobenzene also show a marked crimson fluorescence. Like other magnesium tetrazaporphins, magnesium tetramethyltetrazaporphin gives a bright red chemiluminescence when it is added to hot tetralin containing peroxide.

The light absorptions (see Table and Figure *) are very similar to those for the tetrazaporphins and octamethyltetrazaporphins.

An alternative route to the preparation of tetramethyltetrazaporphin was suggested by the conversion of dimethylsuccinimidine into octamethyltetrazaporphin [10] and of *cis*-hexahydrophthalimidine into tetra*cyclo*hexenotetrazaporphin.[11]

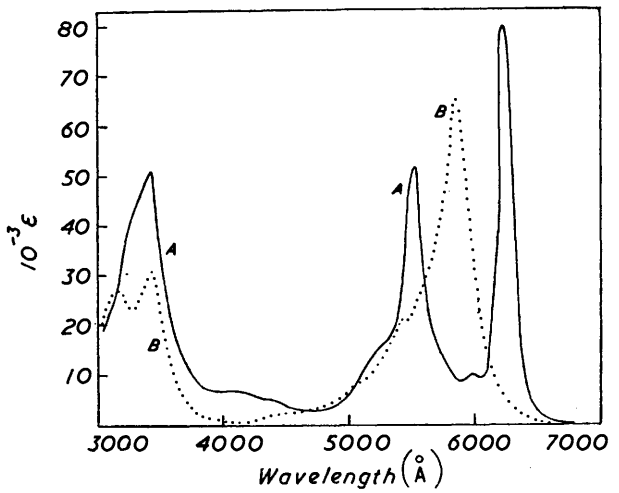
Methylsuccinonitrile (VII), the saturated analogue of citraconontrile, was prepared in good yield by the route : citric acid ⟶ itaconic anhydride ⟶ methylsuccinic acid ⟶ imide ⟶ diamide ⟶ dinitrile. Addition of ammonia to methylsuccinonitrile (VII) yielded methylsuccinimidine (2 : 5-di-imino-3-methylpyrrolidine) (VIII) which was characterised as the picrate and by its stepwise hydrolysis to methylsuccinimide (X). The intermediate imino-imide probably has the orientation (IX; R = H). Under the mild conditions used the methyl substituent would be expected to hinder hydrolysis at the adjacent imino-group. In boiling propanol the imino-imide (IX; R = H) reacted with hydroxylamine to give the hydroxyimino-compound (IX; R = OH).

* Full curves are given because these best characterise the pigments. For tetrazaporphin pigments in general, elementary analyses, and even $\varepsilon_{max.}$ values are not such reliable criteria of purity.

[9] Fischer and Stangler, *Annalen.*, 1927, **459**, 54.
[10] Linstead and Whalley, *J.*, 1955, 3530.
[11] Ficken and Linstead, *J.*, 1955, 3525.

Heating the imidine (VIII) in chlorobenzene with nitrobenzene or better in butanol–nitrobenzene (1 : 1) gave, as principal product, metal-free tetramethyltetrazaporphin. This was spectroscopically identical with the metal-free pigment obtained by the propoxide method. The pigment was contaminated with small amounts of a hydro-derivative ($\lambda_{max.}$ in chlorobenzene 681, 525 mμ).

Absorption of (A) tetramethyltetrazaporphin and (B) nickel tetramethyltetrazaporphin, in chlorobenzene.



Pigment	Solvent	$\lambda_{max.}$ (mμ)	log ε	Pigment	Solvent	$\lambda_{max.}$ (mμ)	log ε
Metal-free (from citraconono-nitrile)	Chloro-benzene	341	4·71	Magnesium	Pyridine	338	4·80
		552	4·71			546	4·21
		596	3·99			596	5·03
		624	4·90		Propanol	264	4·39
						333	4·90
Metal-free (from methylsuccin-imidine)	*o*-Dichloro-benzene	340	4·73			544	4·26
		554	4·52			593	5·09
		595	3·91				
		624	4·73	Copper	Chloro-benzene	339	4·82
						536	4·25
						585	5·03
				Nickel	Chloro-benzene	314	4·43
						342	4·49
						543	4·31
						585	4·81

Experimental

Microanalyses were carried out in the Microanalytical Laboratory (Miss J. Cuckney), and ultraviolet and infrared spectra in the Spectrographic Laboratory (Mrs. A. I. Boston and Mr. R. L. Erskine) of this Department.

Dimethyl Citraconate.—Citraconic anhydride [12] (48 g.) was refluxed overnight with methanol (150 c.c.) containing a little concentrated sulphuric acid. The methanol was removed and the residue was distilled to give dimethyl citraconate (44 g., 66%), b. p. 112—120°/29 mm., n_D^{25} 1·4453.

Citraconamide.—Dimethyl citraconate (98 g.) and aqueous ammonia (*d* 0·880; 150 c.c.) were kept at 0° *in the dark*. Citraconamide (37 g., 50%) slowly separated and, crystallised from ethanol containing a little water, had m. p. 197—199° (decomp.) (Found : C, 46·6; H, 6·3; N, 21·9. Calc. for $C_5H_8O_2N_2$: C, 46·9; H, 6·3; N, 21·9%). (Strecker's product,[13] m. p. 185—191°, probably contained some methylfumaramide.)

[12] *Org. Synth.*, Coll. Vol. II, pp. 368, 140.
[13] Strecker, *Ber.*, 1882, **15**, 1639.

Citraconanitrile.—Citraconamide (40 g.) was suspended in dry pyridine (500 c.c.), and carbonyl chloride (dried by passage through concentrated sulphuric acid) was bubbled into the rapidly stirred suspension. The temperature was maintained at 65—70° by control of the gas flow and by external cooling. When the reaction was complete (*ca.* 1 hr.), the solution was allowed to cool for 3 hr. and it was then poured cautiously on ice. The mixture was made acid (Congo-red) with concentrated hydrochloric acid, and the dark red solution was continuously extracted with ether for 3 days. The ether was removed and the residue was distilled, to give citraconanitrile (24·5 g., 85%), b. p. 66°/0·5 mm., n_D^{24} 1·4587, m. p. 11—13° (methylfumaronitrile has b. p. 71°/15 mm., m. p. −17·6° to −17·2°) (Found : C, 64·7; H, 4·5; N, 30·1. Calc. for $C_5H_4N_2$: C, 65·2; H, 4·4; N, 30·4%), $\lambda_{max.}$ in EtOH 224 mμ (log ε 4·06), principal infrared max. (in Nujol) 3040 (C–H stretching), 2237 (C≡N stretching), 1613 (C=C stretching), 1441 (CH_3–C deformation), 1381, 1176, 1045, 837 (:C–H deformation), 768 cm.$^{-1}$.

Hydrolysis of Citraconanitrile.—Citraconanitrile (200 mg.) was warmed on the steam-bath for 4 hr. with concentrated sulphuric acid (0·5 c.c.), acetic acid (1 c.c.), and water (0·5 c.c.). The mixture was diluted with water (5 c.c.) and extracted with ether (5 × 5 c.c.). The ether solution gave, after evaporation, citraconic acid (50 mg., 18%) which, crystallised from ether–light petroleum (b. p. 60—80°), had m. p. 88—90°.

Citraconylsemicarbazide (N-*Ureidocitraconimide*).[14]—Citraconic anhydride (50 g.), semicarbazide hydrochloride (35 g.), and sodium acetate (40 g.) in a little water, were refluxed in glacial acetic acid (100 c.c.) for 30 min. Citraconylsemicarbazide (48 g., 65%) separated and, crystallised from acetic acid, had m. p. 225—230° (decomp.) (Found : C, 42·7; H, 4·2; N, 25·2. Calc. for $C_6H_7O_2N_3$: C, 42·6; H, 4·2; N, 24·8%).

Citraconimide.—(i) [14] Citraconylsemicarbazide (12 g.) was dissolved in glacial acetic acid, and sodium nitrite (12 g.) in water was added to the cooled solution. The solution was kept at 0—5° for 15 min., heated to 30°, and stirred at this temperature until evolution of gas ceased. The solution was extracted overnight with benzene, the solution was dried (K_2CO_3), and the benzene was allowed to evaporate at room temperature. Citraconimide (1·0 g., 15%), m. p. 109°, was obtained by sublimation of the residue at 20 mm. (Found : C, 54·6; H, 4·8; N, 12·5. Calc. for $C_5H_5O_2N$: C, 54·1; H, 4·5; N, 12·6%).

(ii) Citraconamide (1·0 g.) was heated with an excess of phosphoric oxide at 180—190°/1 mm. Citraconimide (0·12 g., 15%), m. p. 109°, was collected on a cold finger.

Magnesium Tetramethyltetrazaporphin Monomethanolate.—Magnesium (1·5 g.) was dissolved in boiling propanol (60 c.c.) : the reaction was initiated by addition of iodine. Citraconanitrile (3·0 g.) in propanol (20 c.c.) was added during 12—15 min. and refluxing was continued for a further 50 min. Ammonia was evolved at this stage. The propanol was removed under reduced pressure and the solid was then powdered and mixed with an equal volume of kieselguhr to facilitate extraction. The mixture was extracted (Soxhlet) with benzene–methanol (1 : 1), and the extract was filtered twice through alumina (Spence, type H; 15 × 4 cm.) to remove a dark green impurity. Concentration and cooling of the filtrate gave nearly pure pigment (485 mg., 14%) which was crystallised extractively from benzene–methanol (1 : 1) and dried at room temperature/15 mm., to give *magnesium tetramethyltetrazaporphin monomethanolate* (Found : C, 59·1; H, 5·3; N, 26·7; Mg, 5·9. $C_{21}H_{20}ON_8Mg$ requires C, 59·4; H, 4·8; N, 26·4; Mg, 5·7%).

Metal-free Tetramethyltetrazaporphin.—(i) Citraconanitrile (1·0 g.) reacted with magnesium propoxide as above. The propanol was removed under reduced pressure and the dried solid was added in portions to cooled glacial acetic acid (20 c.c.). After 2—3 hr. at room temperature the mixture was diluted with water (20 c.c.), and the solid was filtered off, washed with ethanol, and crystallised extractively several times from benzene, giving purple rods (116 mg., 12%) of *tetramethyltetrazaporphin* (Found : C, 65·1; H, 5·2. $C_{20}H_{18}N_8$ requires C, 64·85; H, 4·9%).

(ii) Magnesium tetramethyltetrazaporphin monomethanolate (5·7 mg.) was treated with glacial acetic acid (15 c.c.) at room temperature for 2 hr. The mixture was diluted with water, and the solid was filtered off, washed with ethanol, and crystallised extractively from benzene, to give tetramethyltetrazaporphin (35 mg., 70%).

Other Metal Derivatives.—The metal-free pigment (90 mg.) was refluxed in *o*-dichlorobenzene (10 c.c.) with copper bronze (1 g.) for 2 hr. The solvent was removed under reduced pressure and the solid was extracted continuously with boiling benzene. The pigment which separated

[14] Cf. Protopopescu and Stancovici, *Chem. Zentr.*, 1943, I, 268.

from the extract was crystallised several times from benzene, to give purple prisms (48 mg., 46%) of *copper tetramethyltetrazaporphin* (Found: C, 55·4; H, 4·0; N, 25·7; Cu, 14·5. $C_{20}H_{16}N_8Cu$ requires C, 55·6; H, 3·7; N, 25·9; Cu, 14·7%).

Tetramethyltetrazaporphin (52 mg.) was extracted into *o*-dichlorobenzene containing anhydrous nickel chloride (1 g.). The solvent was removed under reduced pressure and the solid was washed several times with hot water. The remaining pigment was crystallised extractively several times from benzene, to give *nickel tetramethyltetrazaporphin* (48 mg., 86%) (Found: C, 57·0; H, 4·3; N, 26·8; Ni, 13·0. $C_{20}H_{16}N_8Ni$ requires C, 56·3; H, 3·8; N, 26·2; Ni, 13·7%).

Oxidation of Tetramethyltetrazaporphin.—The pigment (101·8 mg.) was added in portions to concentrated sulphuric acid at 0°. Chromium trioxide (80 mg.) in the minimum of water was added and the mixture was kept at room temperature for 5 min. Ths solution was diluted with water and continuously extracted with ether. The ether extract was filtered to give unchanged pigment (42 mg.). The ether was evaporated and the residue sublimed to give citraconimide (43·9 mg., 61%), m. p. and mixed m. p. 104—105°.

Methylsuccinimide.—Ammonium methylsuccinate was dry distilled to give methylsuccinimide, b. p. 280°, m. p. after recrystallisation from water, 62°.[15]

Methylsuccinamide.—Methylsuccinimide (1·0 g.) was dissolved in aqueous ammonia (*d* 0·880), and the solution was kept at 0° for 24 hr. Methylsuccinamide (0·88 g., 76%), m. p. 222°, was filtered off (Weidel and Roithner [16] give m. p. 225°).

Methylsuccinonitrile.—Methylsuccinamide (37 g.) was suspended in dry pyridine (250 c.c.) and dry carbonyl chloride was passed in. The temperature was maintained at 75—80° for 1 hr. and the mixture was then allowed to cool. The mixture was then worked up as described for citraconontrile, to yield methylsuccinonitrile (20·5 g., 76%), b. p. 135—136°/23 mm. (Euler [17] gives b. p. 130—140°/20 mm.).

Methylsuccinimidine.—Methylsuccinonitrile (2·0 g.) was heated at 143—148° with liquid ammonia (8 c.c.) in methanol (12 c.c.) for 12 hr. The methanol and ammonia were removed at room temperature under reduced pressure. Trituration of the red viscous oil with dry ethyl acetate gave crude methylsuccinimidine (2 : 5-di-imino-3-methylpyrrolidine) (1·73 g., 73%), m. p. 143° (decomp.), contaminated with polymeric material. In absolute ethanol the imidine gave a *picrate*, m. p. 202° (decomp.) (Found: C, 38·8; H, 3·8; N, 24·0. $C_5H_9N_3,C_6H_3O_7N_3$ requires C, 38·8; H, 3·6; N, 24·7%).

Hydrolysis. (i) Methylsuccinimidine (200 mg.) was refluxed with water (2 c.c.) for 1 hr. The solution was evaporated to dryness and the residue was sublimed under reduced pressure, to give methylsuccinimide (104 mg., 51%), m. p. and mixed m. p. 62°.

(ii) A solution of methylsuccinimidine (3·0 g.) in cold water was kept at room temperature overnight. The solution was evaporated to dryness and the brown residue was crystallised from ethanol several times, to yield 2(5?)-*imino*-3-*methyl*-5(2?)-*oxopyrrolidine* (IX; R = H) (377 mg., 12%), m. p. 196° (decomp.) (Found: C, 53·6; H, 7·2; N, 25·1. $C_5H_8ON_2$ requires C, 53·6; H, 7·2; N, 25·0%), $\lambda_{max.}$ in EtOH 228 mμ (ε 19,900). This formed a *picrate*, m. p. 193—194°, from ethanol (Found: C, 38·1; H, 3·5. $C_{11}H_{11}O_8N_5$ requires C, 37·8; H, 3·4%).

2(5?)-*Hydroxyimino*-3-*methyl*-5(2?)-*oxopyrrolidine* (IX; R = OH).—The imino-imide (IX; R = H) (200 mg.) was refluxed for 24 hr. in absolute ethanol (10 c.c.) with hydroxylamine hydrochloride (160 mg.) and anhydrous sodium carbonate (176 mg.). The ethanol was removed under reduced pressure and the solid was extracted with dry ethyl acetate. The solid which separated (205 mg., 89%), m. p. 162°, was recrystallised several times from ethyl acetate, to give 2(5?)-*hydroxyimino*-3-*methyl*-5(2?)-*oxopyrrolidine*, m. p. 172° (Found: C, 47·0; H, 6·4; N, 21·3. $C_5H_8O_2N_2$ requires C, 46·9; H, 6·3; N, 21·9%), $\lambda_{max.}$ in EtOH 223 mμ (ε 9600).

Metal-free Tetramethyltetrazaporphin.—Methylsuccinimidine (202 mg.) was refluxed in nitrobenzene (5 c.c.) and butanol (5 c.c.) for 6·5 hr. The solid (153 mg.) was filtered off and extracted with benzene. The extract was chromatographed on powdered tartaric acid, and the eluate was evaporated to dryness. The residue was crystallised several times from benzene, to give metal-free tetramethyltetrazaporphin (Found: C, 64·3; H, 5·7; N, 29·6. Calc. for $C_{20}H_{18}N_8$: C, 64·85; H, 4·9; N, 30·3%).

Spectra.—Measurements of intensities were made with the Unicam Spectrophotometers

[15] Arppe, *Annalen*, 1853, **87**, 230.
[16] Weidel and Roithner, *Monatsh.*, 1896, **17**, 184.
[17] Euler, *Ber.*, 1895, **28**, 2953.

S.P. 500 and S.P. 600 for the ultraviolet and the visible region respectively. Solutions were prepared by boiling the pigment (*ca.* 0·7 mg.) with the solvent, cooling, and diluting to 100 c.c.

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CHEMISTRY DEPARTMENT,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, LONDON, S.W.7.

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