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SYNTHESIS OF PORPHYRINS FROM α, α'-DIFORMYL- AND α, α'-DICARBOXYDIPYRRYLMETHANES

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Though synthesis of porphyrins from α, α'-diformyldipyrrylmethanes and dipyrrylmethanes whose α, α'-positions are unsubstituted looks most promising [1], it is not always expedient because of the impossibility of obtaining the unstable alkyl-substituted dipyrrylmethanes. A modification of the method, lacking this disadvantage, serves for synthesis of α, α'-diformyl- and α, α'-dicarboxydipyrrylmethanes. The possibility of achieving such a synthesis for mesoporphyrin III dimethyl ester [1, 4, 5, 8-tetramethyl-2, 3-diethyl-6, 7-di(β-carbomethoxyethyl)porphin] (I) was investigated. 99.1 mg 4, 4'-dimethyl-5, 5'-dicarboxy-3, 3'-di(β-carboxyethyl)dipyrrylmethane (II) [2], and 60.1 mg 4, 4'-dimethyl-3, 3'-diethyl-5, 5'-diformyldipyrrylmethane (III) [3], are condensed together in acetic acid containing hydrogen chloride, for 20 hr, the mixture then neutralized with sodium acetate, oxidized with 63.5 mg chloranil, and poured into water. The precipitate formed was esterified with methanol-sulfuric acid (20: 1) for 24 hr, and a chloroform solution of the ester chromatographed, first on a silica gel column, then on thin plates of silica gel, using chloroform-ethyl acetate (4: 1). The thin plates showed two reddish-brown bands, with R_f 0.8 and 0.4, and these were extracted with chloroform. The band having R_f 0.8 gave 42 mg (33.6%) I, mp 275-276°(from chloroform-methanol). Found: C 72.76; H 7.16; N 9.61%. Calculated for $C_{36}H_{42}N_4O_4$: C 72.70; H 7.12; N 9.42%. λ_{max} 499, 535, 570, 599, 623 mμ; ε 13700, 9760, 6320, 1730, 4800 ($CHCl_3$). IR spectrum (KBr): 3320 cm^{-1} (N—H), 1740 cm^{-1} (C=O). R_f 0.42. [Whatman No. 3 mm, chloroform-isooctane (3 : 7) (system 1)] R_f 0.65, [silica gel-coated plate, chloroform-ethyl acetate (10 : 1) (system 2).] The R_f 0.4 band gave 4.3 mg (4.95%) coproporphyrin tetramethyl ester (IV). λ_{max} 500, 535, 571, 599, 625 mμ; R_f 0.08 (system 1), R_f 0.22 (system 2). Paper chromatography (system 1) showed that the silica gel strips between R_f 1.0 and 0.8, 0.8 and 0.4, contain traces of etioporphyrin (R_f 0.91), and apparently of esterified mono- (R_f 0.67) and tricarboxylic (R_f 0.30) porphyrins.

The same treatment of II gives 6.6% porphyrin, identical with IV when chromatographed in systems 1 and 2. The comparable yield figures shows that in preparation of mesoporphyrin IV, two molecules of II are formed by self-condensation.

76.6 mg 4, 4'-dimethyl-3, 3'-diethyl-5, 5'dicarboxydipyrrylmethane (V) [4] and 62.3 mg III under similar conditions gave 31.1 mg (29.8%) etioporphyrin II (1, 4, 5, 8-tetramethyl-2, 3, 6, 7-tetraethylporphin) (VI). Found: C 80.37; H 8.23; N 11.87%. Calculated for $C_{32}H_{38}N_4$: C 80.29; H 8.00; N 11.70%. λ_{max} 498, 534, 569, 596, 622 mμ; ε 12400, 9350, 6600, 1110, 5050 ($CHCl_3$). IR spectrum (KBr): 3320 cm^{-1} (N—H). R_f 0.91 (system 1), R_f 0.82 (system 2). The same treatment of V gave 36.6% VI.

The method was quite applicable when the main reaction product, e.g., I, could readily be separated from the side reaction product, e.g., IV, or when they were the same.

The present work had been completed when there appeared a paper [5] on the spectroscopic identification of octa- and decamethylporphin in the condensation of diformyl- and dicarboxydipyrrylmethanes. In those experiments, however, it was necessary to take into consideration formation of porphyrins by auto-condensation of dicarboxylic acids too.

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