LETTERS TO THE EDITOR

REACTION OF MESO-DIMETHYLAMINOMETHYLETIOPORPHYRIN WITH CH ACIDS

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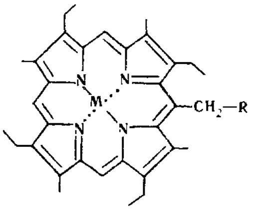
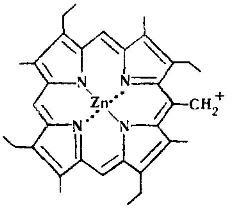
We have observed that meso-dimethylaminomethyletioporphyrin-1 (I) reacts with CH acids in the presence of zinc acetate. Thus reflexing porphyrin I in acetone in the presence of a twofold amount (by weight) of zinc acetate leads, after 12 h, to the formation of a zinc complex (II), from which porphyrin III was obtained in 53% overall yield by treatment with dilute hydrochloric acid.

The reaction with acetylacetone proceeds considerably more rapidly. Thus heating porphyrin I at 50°C for 20 min in the presence of zinc acetate leads, after demetallation of the intermediate zinc complex (IV) and chromatographic purification of the reaction products, to porphyrin V in 62% yield.



I-VI



VII

I M=2H, R=N$(CH_3)_2$; II M=Zn, R=CH_2COCH_3; III M=2H, R=CH_2COCH_3; IV M=Zn, R=$CH(COCH_3)_2$; V M=2H, R=$CH(COCH_3)_2$; VI M=Zn, R=N$(CH_3)_2$

The formation at the first instant of the reaction of an unstable Zn complex of porphyrin I, which in the presence of excess zinc acetate reacts with acetone and acetylacetone with splitting out of dimethylamine, was established spectrally and chromatographically. Complex VI evidently forms carbonium ion VII during the reaction, which also reacts with CH acids.

Intense bands of carbonyl absorption (1720 cm^{-1} for III and 1710 and 1732 cm^{-1} for V) are observed in the IR spectra of III and V. The electronic spectra of porphyrins III and V have a slight bathochromic shift as compared with the spectrum of unsubstituted etioporphyrin, and this constitutes evidence for the absence of long-range interaction between the keto group and the porphyrin ring. Intense peaks corresponding to $[M - CH_2COCH_3]^{+}$ fragments for porphyrin III and $[M - CH(COCH_3)_2]^{+}$ fragments for V are observed in the mass spectra of these compounds in the region of single charged ions, in addition to the molecular ion peaks.

This reaction of porphyrins containing the meso-dimethylaminomethyl group with CH acids opens up prospects for the synthesis of diverse porphyrins.

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