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SYNTHESIS OF NEW DEUTEROPORPHYRIN-IX DERIVATIVES BY THE REACTION OF HEMATOPORPHYRIN-IX DIESTER DIETHERS WITH ACETYLACETONE IN THE PRESENCE OF ZINC ACETATE

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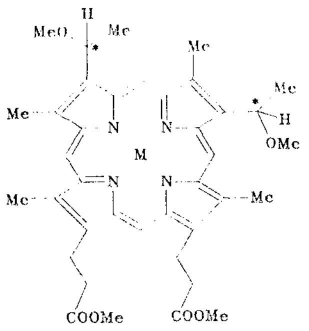
UDC 547.749

meso-Aminomethylporphyrins react with CH acids in the presence of zinc acetate owing to the development of an intermediate zinc complex of the carbonium ion of meso-methyleneporphyrin [1].

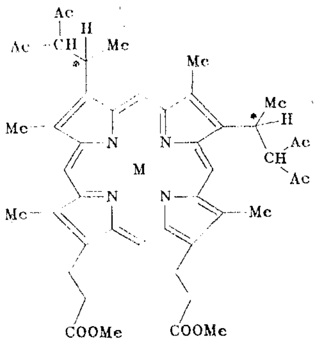
We have established that hematoporphyrin-IX and its alkyl diester diethers [2] also react readily with CH acids under similar conditions.

Thus, for example, heating (for 20-30 min at 110°C) hematoporphyrin-IX dimethyl ester dimethyl ether (I) in acetylacetone in the presence of a tenfold excess (by mass) of zinc acetate leads, through the intermediate Zn complex (II) of porphyrin-I, to Zn complex III, after demetallation of which with HCl porphyrin IV was obtained in quantitative yield based on starting porphyrin I.



I, II

I, IV M=2H; II, III M=Zn



III, IV

The IR spectrum of porphyrin IV contains two intense bands at 1734 and 1700 cm^{-1} ($\nu_{C=O}$ for COOMe and COMe groups). An M^+ peak, which is the most intense peak in the spectrum, and peaks of $[M^+ - CHAc_2]$ and $[M^+ - 2CHAc_2]$ ions are present in the mass spectrum. In the PMR spectrum of porphyrin IV (in $CDCl_3$) the signals of the protons of the $-CH(CH_3)CH(COCH_3)COCH_3$ group are very broad. The spectrum of a solution in CF_3COOD is more informative. Since starting diester diether I is a mixture of diastereomers [the substituents in the 2 and 4 positions have (R) and (S) configurations], doubling of most of the signals in the PMR spectrum (δ, ppm) is also characteristic for porphyrin IV: 11.28, 11.27, 11.25, 11.24, 11.20, 11.19 (3H each, meso-H); 11.01 (1H,

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s, meso-H); 5.78 (2H, broad unresolved m, MeCH); 5.65 and 5.63 (two d, J = 7 Hz) and 5.64 and 5.59 (two d, J = 11 Hz) (2H, $CHAc_2$); 4.71 and 3.30 (8H, two t, CH_2CH_2COO); 4.01, 4.0, 3.97, 3.96, 3.87, 3.80 (12H, all s, ring CH); 3.81 and 3.77 (6H, two s, $COOCH_3$); 2.18, 2.11, 2.05 (6H, all d, J = 6 Hz, side chain CH_3); 2.90, 2.89, 2.89, 2.88, 2.05, 2.03, 1.96, 1.92 (12H, s, 6H, $COCH_3$).

The structure of porphyrin IV opens up completely new prospects for the synthesis of the most diverse and accessible compounds of series of 2,4-disubstituted derivatives of deuteroporphyrin-IX with the goal of their possible use in various areas of medicine.

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DINITROBENZOFURAZAN DERIVATIVES AS SELECTIVE REAGENTS FOR ORGANIC ANALYSIS

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UDC 543.42.063

Dinitro-substituted benzofurazans and their N-oxides are known as active electrophiles in reactions with amines [1].

We have observed the manifestation of high contrast of the spectral properties [2] ($\Delta\lambda_{max}$, the shift of the maximum of the absorption band of the reaction product as compared with the absorption band of the corresponding reagent) in reactions of 5,7-dinitro-4-chlorobenzofurazan, 4,6-dinitro-7-chlorobenzofuroxan, and 4,6-dinitro-5-chlorobenzofurazan with aromatic amines with various degrees of substitution, hydrazides, and hydrazines. Primary amines react with the indicated compounds to give orange and red solutions or spots on TLC plates (λ_{max} 500-520 nm), while secondary and tertiary amines react to give green and blue solutions or spots (λ_{max} 580-670 nm). The reaction of dinitrobenzofurazan derivatives with aryl- and alkylhydrazines and hydrazides also leads to the formation of red (λ_{max} 500-520 nm) reaction products for the hydrazides and green and blue (λ_{max} 630-670 nm) products for the hydrazines. The intensities of the absorption bands of the reaction products (ε 22,000-30,000 at 510 nm and 12,000-18,000 at 650 nm) and the positions of the maxima of the charge-transfer bands are determined by the I and M effects of the substituents.

The high contrast of the electronic spectra of the products of the reaction of halodinitro-substituted benzofurazans and benzofuroxans with amines ($\Delta\lambda_{max}$ reaches 250 nm) makes the indicated compounds effective and selective reagents for the analysis of the components of complex reaction mixtures by HPLC, TLC, and spectrophotometry. When the indicated compounds are used to detect spots in TLC, one can, from the color of the spots, visually evaluate the presence of amines with different degrees of substitution, hydrazides, and hydrazines in reaction mixtures. In some cases it is possible to visually evaluate the presence of substituents and even their position in the aromatic ring in the compound being subjected to the determination. This property of the reagents is important in the analysis of reaction mixtures containing compounds with close R_f values (antioxidants based on dihydroquinolines, some pharmaceutical preparations). The limit of detection of the amines reaches 0.05 μg (TLC) and $5 \cdot 10^{-7}$ mole/liter (photometry).

A dependence of the rate of the analytical reaction on the polarity and donor properties of the solvent, the I and M effects in the substrate, the basicities of the substances subjected to the determination, and the electrophilicity of the reagent is observed. An increase in the selectivity of the determinations is achieved when the indicated parameters are varied. Anomalous reactivity of 4,6-dinitro-7-chlorobenzofuroxan is observed in reactions with dihydroquinoline derivatives and some other secondary amines.

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