INTRAMOLECULAR CYCLIZATION OF THE PRODUCTS OF FORMYLATION OF THE COPPER COMPLEX OF ETIOPORPHYRIN-I

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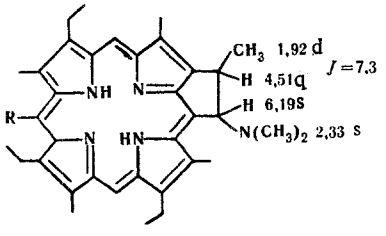
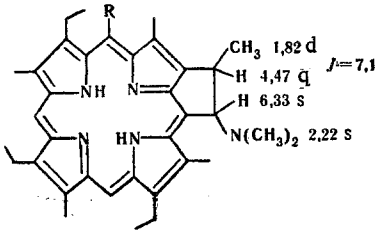
Polyformylation [1] of the Cu complex of etioporphyrin-I and subsequent treatment of the reaction mixture with sodium acetate solution leads primarily to isomers of meso-diformyletioporphyrin-I; however, heating with aqueous alkali makes it possible to obtain new compounds, one of which (the principal product) we isolated in chromatographically pure form. According to the electronic (shoulder at 650 nm) and IR (ν_{CO} 1700 cm^{-1}) spectral data, it contains a meso-formyl group. The most characteristic peaks in the mass spectrum* were fragment peaks at 622 (18), 577 (100), 562 (10), and 549 (16). Demetalation of the complex does not lead to a change in the structure of the ligand; this was confirmed by reintroduction of copper and comparison with the original Cu complex. Analysis of the mass spectrum of the porphyrin obtained by treatment of the starting complex with concentrated sulfuric acid [561 (14), 546 (5), 517 (76), 516 (100), 489 (17), and 488 (15)] makes it possible to conclude unambiguously that the peak at 561 is due to the molecular ion, the composition of which is $C_{36}H_{43}N_5O$ according to the high-resolution mass-spectral data. The most intense ion peaks at 516 and 517 correspond to $[C_{34}H_{36}N_4O]^{+\cdot}$ and $[C_{34}H_{37}N_4O]^{+}$ fragments and detachment of C_2H_7N and $C_2H_6N^{\cdot}$ fragments from the molecular ion, i.e., to the presence of an $(CH_3)_2N$ group in the unknown porphyrin. The $C_{34}H_{37}N_4O$ fragment differs from the mono-meso-formyletioporphyrin ($C_{33}H_{38}N_4O$) with respect to the presence of an additional carbon atom and the absence of a hydrogen atom; this can be explained by intramolecular cyclization during hydrolysis of the formylation products and by the formation of a cylopentane ring. It follows from the PMR spectrum of the porphyrin that it is a mixture of two isomers. This fact was not surprising, since two meso-diformyletioporphyrin isomers are formed in the usual method of isolation. After reduction of the formyl group to a hydroxymethyl group with sodium borohydride we were able to separate the corresponding isomers of the porphyrins by thin-layer chromatography (TLC) on silica gel and were able to establish by PMR spectroscopy that the ethyl group adjacent to the meso position participates in the cyclization. Data on the chemical shifts on the δ scale and the J values in Hertz are presented below for isomers I and II. The porphyrin that we isolated in 20-25% yield is consequently a mixture of isomers III and IV, the ratio of which corresponds to the ratio of the meso-diformylporphyrins [1].

Intramolecular cyclization with the participation of the meso substituent and the alkyl substituent of the porphyrin ring, which we observed for the first time in this research, explains the formation of numerous products with porphyrin character during polyformylation. A detailed description of the experiment and a possible mechanism of the cyclization will be presented in our next paper.



I, III



II, IV

I, II R=CH_2OH; III, IV R=CHO

*Here and subsequently, the m/e values (and intensities in percent of the maximum ion peak) are given for the ion peaks.

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SYNTHESIS OF 3,4-BIS(3-R-4-SYDNONOYL)FUROXANES

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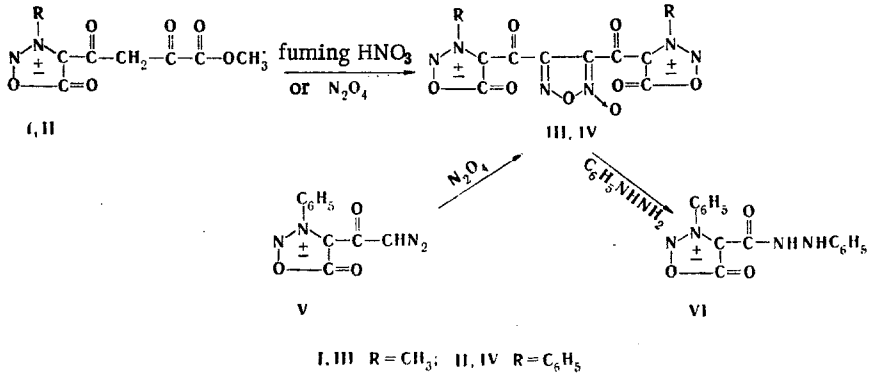
We have observed that an oxalyl residue is split out in the reaction of methyl 4-(3-R-sydnonyl)-2,4-dioxobutanoates (I, II) with fuming nitric acid to give 3,4-bis(3-R-4-sydnonoyl)-furoxanes (III, IV). Thus 2.3 g (0.3 mmole) of fuming nitric acid was added with stirring at 30-35°C to a solution of 5 g (0.15 mmole) of II in 40 ml of chloroform, 2 h after which the solvent was removed, and the residue was washed with ether and recrystallized from chloroform to give 4.53 g (57%) of 3,4-bis(3-phenyl-4-sydnonoyl)furoxane (IV) with mp 198-199°C. Compound III (in 51% yield), with mp 212-214°C (dec.), was similarly obtained. Furoxane IV was also obtained by reaction of II and 3-phenyl-4-diazoacetylsydnone (V) with nitrogen tetroxide.

Compound IV reacts with phenylhydrazine to give N-phenyl-N'-(3-phenyl-4-sydnonoyl)-hydrazine (VI); this is characteristic for furoxanes.



I, II III, IV V VI

I, III R = CH_3; II, IV R = C_6H_5

A 1-g (0.021 mmole) sample of IV was sprinkled into a solution of 2.3 g (0.21 mmole) of phenylhydrazine in 10 ml of ether, and the mixture was stirred until an exothermic reaction commenced. After 2 h, the solvent was removed, and the residue was washed with ether and recrystallized from ethanol to give 0.3 g (47%) of VI with mp > 230°C (dec.).

The IR spectra of furoxanes III and IV contain absorption bands at 1790-1805 (sydnone ring CO group), 1660-1665 (keto group), 1610-1620 (C=N), 730-915, 790-955, and 1060-1080 cm^{-1} (furoxane ring system). The IR spectrum of VI contains absorption bands at 1720 (sydnone ring CO), 1645 (keto group), and 3319 cm^{-1} (NH). UV spectra of furoxanes in chloroform, λ_{max} (log ε): III, 258 (3.32) and 342 (4.21); IV, 268 (3.96) and 350 nm (4.38).

The results of elementary analysis of III, IV, and VI for C, H, and N are in agreement with the calculated values.

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