PORPHYRINS.

19.* INTRAMOLECULAR REARRANGEMENT OF meso-BUTYLOXYMETHYLPORPHYRINS IN SULFURIC ACID

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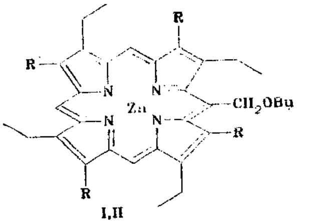
It was established by the methods of PMR and mass spectrometry that zinc complexes of meso-butyloxymethyletio- and -octaethylporphyrin, when heated in conc. H_2SO_4, are converted to products of the cationic addition of butylene to carbonium ions of the porphyrins. A possible scheme of formation of the new porphyrins and the significance of the reaction discovered for the chemistry of meso-substituted porphyrins are discussed.

It is known that meso-hydroxymethylporphyrins, when dissolved in conc. H_2SO_4, form the corresponding carbonium ions of the type of meso-methyleneporphyrin, which is judged according to the specific yellow-brown color of the solution and according to the appearance of two new bands in the electronic absorption spectra in the region of 450 and 880 nm in comparison with the spectra of dications of the porphyrins [2]. The carbonium ions gradually break down (especially rapidly in the case of heating), forming a large number of products, among which only meso-unsubstituted porphyrins and meso-methylporphyrins were isolated with a low yield [3].

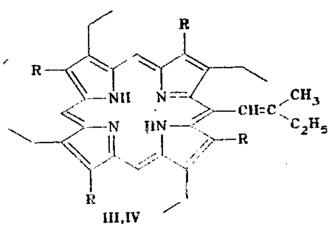
We found that when a whole series of meso-alkoxymethylporphyrins are dissolved in conc. H_2SO_4, the carbonium ion formed is converted after several minutes of heating at 50-60°C to several new porphyrins, the establishment of the structure of which was the purpose of the present investigation.

We selected zinc complexes of meso-butyloxymethylporphyrins I and II as the objects of investigation, since for these compounds the yield of the final product of the reaction was the highest. Since zinc complexes are instantaneously demetallated in sulfuric acid, it can be considered that the reaction studied proceeds with the free base.

When complex I was heated for 2-3 min in conc. H_2SO_4, after chromatographic separation of the reaction products, etioporphyrin-I and meso-methyletioporphyrin-I were isolated with yields of 5-10% each, along with an unknown porphyrin with a yield of 25-30%. In the mass spectrum of this compound (see the experimental section), in addition to the most intense peak of the molecular ion (M^+) at m/z 546, peaks of the ions $[M - CH_3]^+$, $[M - C_2H_5]^+$, $[M - C_4H_9]^+$, and $[M - C_4H_{10}]^+$ are observed. Elimination of the C_4H_{10} molecule is also characteristic of the doubly charged molecular ion (M^{2+}); moreover, the peaks of the ions $[M - C_4H_{10}]^{2+}$ are more intense than the peak of M^{2+}. From this fact it follows that the rearrangement processes result in the formation of a porphyrin with a meso-substituent such that decomposition with stripping of alkyl radicals or a butane molecule becomes the most profitable for M^+.



I,II



III,IV

I,III R=Me; II,IV R=Et

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*For Communication 18, see [1].

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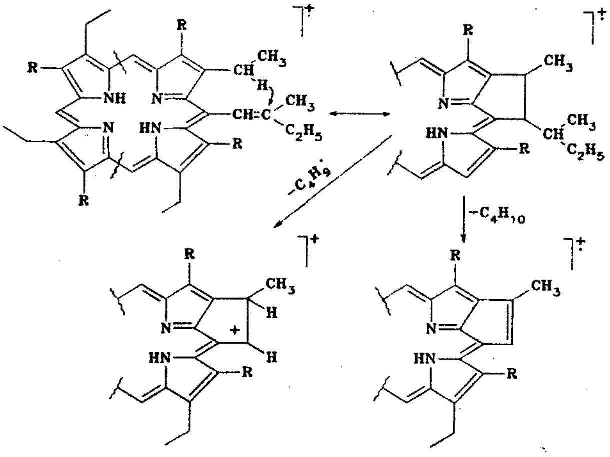
According to the data of the high-resolution mass spectrum, the gross formula $C_{37}H_{46}N_4$ corresponds to this compound (M^+ found 546.3707; M^+ calculated 546.3692); it differs from the gross formula of the initial meso-butyloxymethyleticporphyrin-I ($C_{37}H_{48}N_4O$) by a group of atoms H_2O, and the end result of the process can be defined as the loss of a water molecule by the original porphyrin. From an analysis of the PMR spectra it follows that the structure III corresponds to this porphyrin.

The presence of a double bond in the substituent predetermines the possibility of existence of the porphyrin in the form of two isomers. And actually, when the PMR spectrum of the porphyrin was recorded in the presence of trifluoroacetic acid, two isomers in a 5:1 ratio were detected. The isomer present in a smaller amount was characterized by a more shielded arrangement of the ethyl group of the meso-substituent, i.e., its close approach to the plane of the porphyrin ring.

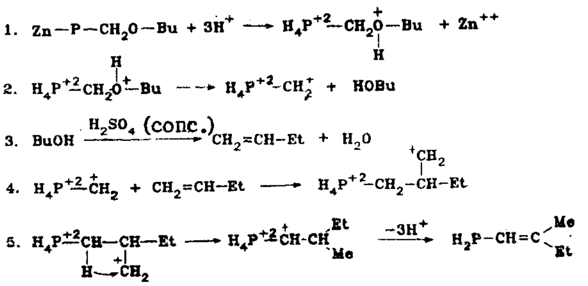
When complex II was treated with sulfuric acid, the porphyrin IV, in which the structure of the meso-substituent was analogous to its structure in the porphyrin III, was isolated. According to the data of the high-resolution mass spectrum, the composition of compound IV corresponded to the formula $C_{41}H_{54}N_4$ (M^+ found 602.4356; M^+ calculated 602.4348). The nature of the fragmentation of the porphyrin IV was practically the same as that of the porphyrin III, i.e., there was a predominant elimination of alkyl radicals and a butane molecule.

On the basis of the structure established for the porphyrins III and IV we can explain the elimination of a butyl substituent in the mass spectrometric decomposition of these compounds by a rearrangement process, which we investigated in the decomposition of the Schiff bases of mesoformylporphyrins [5], which proceeds according to the scheme:



An analogous decomposition is also undergone by M^{2+}.

The formation of the porphyrins III and IV can be represented by the following chain of successive reactions:



$$1.\ \mathrm{Zn{-}P{-}CH_2O{-}Bu} + 3H^+ \longrightarrow \mathrm{H_4P^{+2}{-}CH_2\overset{+}{O}(H){-}Bu} + \mathrm{Zn^{++}}$$

$$2.\ \mathrm{H_4P^{+2}{-}CH_2\overset{+}{O}(H){-}Bu} \dashrightarrow \mathrm{H_4P^{+2}{-}CH_2^+} + \mathrm{HOBu}$$

$$3.\ \mathrm{BuOH} \xrightarrow{H_2SO_4\ (conc.)} \mathrm{CH_2{=}CH{-}Et} + \mathrm{H_2O}$$

$$4.\ \mathrm{H_4P^{+2}{-}\overset{+}{C}H_2} + \mathrm{CH_2{=}CH{-}Et} \longrightarrow \mathrm{H_4P^{+2}{-}CH_2{-}CH(^+CH_2){-}Et}$$

$$5.\ \mathrm{H_4P^{+2}{-}CH(H){-}CH(\overset{+}{C}H_2){-}Et} \longrightarrow \mathrm{H_4P^{+2}{-}\overset{+}{C}H{-}CH(Et)(Me)} \xrightarrow{-3H^+} \mathrm{H_2P{-}CH{=}C(Me)(Et)}$$

The detected conversion of meso-butoxymethylporphyrins is a particular case of a general reaction of carbonium ions of porphyrins with unsaturated compounds at the multiple bonds, as yet undescribed in porphyrin chemistry. The study of this reaction will undoubtedly lead to the production of a large number of quite varied new compounds of the porphyrin class.

EXPERIMENTAL*

The electronic spectra were recorded on a Hitachi model 320 instrument; the PMR spectra were recorded on Bruker WM-360 and WM-250 instruments, with internal standard TMS, solution in $CDCl_3$; the mass spectra were obtained on a Varian MAT-311 instrument; chromatographic purification and separation of the porphyrins was carried out on 20 × 20 cm plates with a fixed layer of brand CF-254 silica gel from Merck, layer thickness 1 cm.

Zinc Complex of meso-Butoxymethyletioporphyrin-I (I). Produced from meso-dimethylaminomethyletioporphyrin-I with a quantitative yield according to the method of [4]. PMR spectrum: 9.90, 9.83 and 9.78 (3H, all s, meso-H); 6.21 (2H, c, $\mathbf{CH}_2$–O); 4.12 (2H, t, O–$\mathbf{CH}_2$); 3.98 (8 H, k, $\mathbf{CH}_2CH_3$ of ring); 3.61, 3.59, 3.52, 3.51 (12H, all s, CH_3 of ring); 1.98 (2H, m, $OCH_2\mathbf{CH}_2$); 1.82, 1.85, 1.80 and 1.77 (12H, all t, $CH_2\mathbf{CH}_3$ of ring); 1.72 (2H, m, $OCH_2CH_2\mathbf{CH}_2$); 1.08 ppm (3H, t, CH_3 of meso-substituent).

Zinc Complex of meso-Butoxymethyloctaethylporphyrin (II). Produced from meso-dimethylaminomethyloctaethylporphyrin according to the method of [4] with a quantitative yield. PMR spectrum: 10.07 and 9.98 (2H and 1H, all s, meso-H); 6.46 (2H, s, $\mathbf{CH}_2$–O); 4.12–4.03 (18H, $\mathbf{CH}_2CH_3$ of ring, and O-CH_2); 1.90 (24H, overlapping t, $CH_2\mathbf{CH}_3$ of ring); 1.66 (m), 1.44 (m), 1.03 (t, 7H, $OCH_2\mathbf{CH}_2\mathbf{CH}_2\mathbf{CH}_3$).

meso-(2-Methylbutenyl-1)etioporphyrin-I (III). A 100 mg portion of the zinc complex I was dissolved with heating in 10 ml of chloroform and evaporated in a 100 ml round-bottomed flask so that the substance was distributed in a uniform thin layer over the surface of the flask. (It is not recommended that a crystalline powdered zinc complex be used for the reaction on account of the slow dissolution of the complex in concentrated sulfuric acid, while increasing the reaction time leads to a sharp decrease in the yield of the end product and to the formation of new compounds of unknown structure.) A 10 ml portion of conc. H_2SO_4 was added, and the mixture was exposed with vigorous mixing for 3 min at 60-70°C. The solution was poured out onto ice, neutralized with ammonia, the substance extracted with chloroform, evaporated to a small volume, filtered through a 1 cm layer of aluminum oxide to remove the red polar porphyrin (most likely the sulfate), and chromatographed with chloroform on plates with silica gel. The main substance was removed, crystallized from a chloroform–methanol mixture, and 28 mg (29%) of the porphyrin III was obtained. Mass spectrum, m/z (%): 546 (M^+, 100), 531 (6), 517 (22), 502 (10), 489 (21), 488 (16), 473 (10), 273 (M^{2+}, 15), 259 (7), 251 (14), 244 (22). PMR spectrum: 10.08 and 9.89 (2H and 1H, all s, meso-H); 8.56 (1H, narrow m, J = 1.1 Hz, $\mathbf{CH}$=C); 4.07, 4.04, 4.02, 4.01 (8H, all k, CH_2CH_3 of ring); 3.63, 3.61, 3.51, 3.37 (12H, all s, CH_3 of ring); 1.86, 1.85, 1.79, 1.59 (12H, all t, $CH_2\mathbf{CH}_3$ of ring); 2.69 (k) and 1.57 (t, 5H, C_2H_5 of meso-substituent); 0.97 ppm (3H, d, J = 1.1 Hz, CH_3 of meso-substituent); PMR spectrum ($CDCl_3$ + 1% CF_3COOH): 10.30, 10.29, 10.15 (all s, meso-H); 8.76 (d, $\mathbf{CH}$=C); 4.01, 3.99, 3.80, 3.64 (all k, $\mathbf{CH}_2CH_3$ of ring); 3.53, 3.51, 3.33 and 3.07 (all s, CH_3 of ring); 2.88 (k), 1.62 (t, C_2H_5 of meso-substituent); 1.704 (d, CH_3 of meso-substituent); 1.70, 1.67, 1.51, 1.33 (all t, $CH_2\mathbf{CH}_3$ of ring); –2.45 (1H), –2.53 (1H), 3.49 ppm (2H, all narrow s, NH); in addition, signals of another isomer are observed in the spectrum at 8.73 (m, $\mathbf{CH}$=C), 3.10 (CH_3 of ring); 2.60 (d, CH_3 of meso-substituent), 2.04, 0.85 ppm (k, t, C_2H_5 of meso-substituent), the intensity of which is approximately 15-20% of the intensity of the signals of the main isomer. UV spectrum ($CHCl_3$) λ_{max} ($\varepsilon \cdot 10^{-3}$): 409 (217), 507 (14.7), 541 (6.45), 579 (6.45), 630 nm (2.21).

meso-(2-Methylbutenyl-1)octaethylporphyrin (IV). Produced analogously from the complex II with a 25% yield. Mass spectrum, m/z (%): 602 (M^+, 100), 597 (2), 573 (18), 559 (3), 558 (4), 545 (20), 544 (7), 301 (M^{2+}, 13), 286 (5), 279 (6), 272 (20). PMR spectrum: 10.08 (2H) and 9.88 (1H, all s, meso-H); 8.71 (2H, narrow s, $\mathbf{CH}$=C); 4.07 (16H, m $\mathbf{CH}_2CH_3$ of ring); 2.66 (k) and 1.07 (t, 5H, C_2H_5 of meso-substituent); 1.80 (24H, overlapping t, CH_2CH_3 of ring), 0.89 (3H, d, J = 1.1 Hz, CH_3 of meso-substituent); –3.09 ppm (2H, NH). UV spectrum ($CHCl_3$), λ_{max} ($\varepsilon \cdot 10^{-3}$): 411 (197), 509 (13.9), 543 (6.35), 578 (6.00), 628 nm (1.75).

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KINETIC STABILITY OF TETRAZAPORPHIN IN BINARY H_2SO_4–AcOH AND H_2SO_4–DMSO SOLUTIONS

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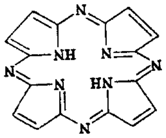
The state and kinetic stability of tetrazaporphin (I) in acetic acid and in dimethyl sulfoxide (DMSO) in the presence of H_2SO_4 were investigated. Partial protonation of I to give I-$AcOH_2^+$ associates occurs in acetic acid. The kinetic parameters of the reaction involving the destruction of tetrazaporphin in the presence of H_2SO_4 in acetic acid and DMSO solutions were determined. The mechanism of the destruction is discussed.

Tetrazaporphin (I) is a structural analog of both porphin itself and phthalocyanine. The aim of the present research was to establish the effect of tetrasubstitution in porphyrins on their stability in proton-donor media.

I



In a preceding communication [1] the state and kinetic stability of tetrazaporphin in sulfuric acid were investigated. In the present research, the kinetics of the destruction of tetrazaporphin under the influence of H_2SO_4 in acetic acid and DMSO solutions, i.e., in solvents that are widely used in the chemistry of porphyrins, were investigated.

In contrast to many porphyrins, in glacial acetic acid tetrazaporphin is not protonated and does not undergo destruction, as does phthalocyanine [2]. The electronic absorption spectrum of I in AcOH does not differ from its absorption spectrum in other organic solvents.

As in the case of phthalocyanine [2], a shift of the spectrum to the long-wave region with a simultaneous decrease in the intensity of the absorption bands of I and II is observed when anhydrous acid is added to a solution of I in glacial acetic acid (in the spectra of porphyrins we have adopted numbering of the absorption bands commencing with the long-wave band). An increase in the bathochromic shift (Table 1); the absorption bands of I and II have a maximum shift at ~15 nm in this case. The shift may be a consequence of partial protonation without complete ionization to give an associate of the I•••H_2SO_4 or I•••$AcOH_2^+$ type, since in a medium with a low dielectric constant the interaction of porphyrin with a strong acid may stop at the stage involving the formation of a hydrogen bond [2].

The shift of the first band in the electronic absorption spectrum is bathochromic, and therefore one should expect protonation at the meso nitrogen atoms of tetrazaporphin.

At H_2SO_4 concentrations on the order of 4 M, virtually no further bathochromic shift of the spectrum is observed. At this concentration of H_2SO_4, tetrazaporphin begins to undergo appreciable destruction. The destruction is accompanied by a change in the color from blue violet to light yellow; in the process one observes a disappearance of the absorption bands of I and II (Fig. 1).

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