BRIEF COMMUNICATION

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SYNTHESIS OF FORMYL-SUBSTITUTED PORPHYRINS

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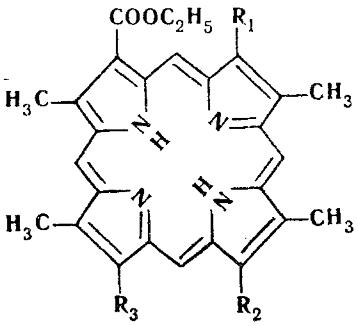
Syntheses of 1, 4, 5, 8-tetramethyl-2-ethoxycarbonyl-6-formylporphyrin and 1, 4, 5, 8-tetramethyl-2, 3-diethoxycarbonyl-6-formylporphyrin from the copper complexes of 1, 4, 5, 8-tetramethyl-2-ethoxycarbonylporphyrin and 1, 4, 5, 8-tetramethyl-2, 3-diethoxycarbonylporphyrin are described.

A previous paper [1] described a method of synthesizing porphyrins containing methyl and ethoxycarbonyl substituents. With a view to further investigating the properties of porphyrins thus prepared, formylation has been studied. The starting porphyrins chosen were 1, 4, 5, 8-tetramethyl-2-ethoxycarbonylporphyrin (I) and 1, 4, 5, 8-tetramethyl-2, 3-diethoxycarbonylporphyrin (II). As positions 6 and 7 in these porphyrins are free, steric hindrance during formylation was excluded.

Formylation was effected with unsymmetrical dichloromethylethyl ether in the presence of stannic chloride. Previously [2], the iron complex has been used to stabilize the porphyrin ring under these conditions. It has been found possible to replace the iron complex by the copper one, which is more convenient, since the porphyrin iron complex is destroyed slowly, and there is partial destruction of the porphyrin formed, while removal of the copper does not give rise to difficulties. On the contrary, it facilitates spectrophotometric control of the reaction, since the absorption bands of the copper complexes of the starting and resultant porphyrins are more clearly defined than the iron ones. Formylation is rapid (about 1 min). Prolongation of the reaction time results in partial destruction of the formylporphyrin formed.

In the case of the monoethoxycarbonylporphyrin I, the formyl group may replace hydrogen at positions 6 or 7, introduction at position 3 is improbable, because of the screening effect of the ethoxylcarbonyl group at position 2. The formylporphyrin obtained has a "rhodo" type of spectrum, indicating insertion of the formyl group at position 6, hence it can be assigned a structure 1, 4, 5, 8-tetramethyl-2-ethoxycarbonyl-6-formylporphyrin (III).

A small amount of 1, 4, 5, 8-tetramethyl-2-ethoxycarbonyl-7-formylporphyrin (IV) is also formed; it has a much lower R_f value, and is separated from III by twice thin-layer chromatographing in chloroform on aluminum oxide (activity 5). Porphyrin IV has an "etio" type of spectrum in chloroform, λ_{max} mμ: 517, 558, 593, 647, and with corresponding band intensities (1 : 0.8 : 0.585 : 0.314); the corresponding oxime had, in pyridine, λ_{max} mμ: 512, 551, 586, 641 (1 : 0.78 : 0.575 : 0.19)



I $R_1 = R_2 = R_3 = H$
II $R_1 = CO_2C_2H_5$, $R_2 = R_3 = H$
III $R_1 = R_3 = H$, $R_2 = CHO$
IV $R_1 = R_2 = H$, $R_3 = CHO$
V $R_1 = CO_2C_2H_5$, $R_2 = CHO$, $R_3 = H$

Porphyrin II was formylated similarly. There the aldehyde group could be introduced only in the equivalent positions 6 and 7. A "rhodo" type spectrum porphyrin was isolated, corresponding to 1, 4, 5, 8-tetramethyl-2, 3-diethoxycarbonyl-6-formylporphyrin (V).

Experimental

Copper complex of 1, 4, 5, 8-tetramethyl-2-ethoxycarbonylporphyrin (I). Prepared by refluxing the porphyrin I with 3 times its weight of $Cu(OAc)_2$. The end of the reaction was observed spectrophotometrically by the absence of the porphyrin's absorption band. The solution of the copper complex was run through aluminum oxide to remove unreacted $Cu(OAc)_2$. Minute plates from $CHCl_3$-petrol ether, mp 157–159° C. Spectrum in $CHCl_3$ λ_{max}, mμ: 538, 579 (I > II). Found: C 64.80; H 5.20; N 11.36%. Calculated for $C_{27}H_{24}N_4O_2Cu$: C 64.86; H 4.84; N 11.20%.

Copper complex of 1, 4, 5, 8-tetramethyl-2, 3-diethoxycarbonylporphyrin (II). Prepared similarly to compound I. Minute needles from $CHCl_3$. Did not melt at 300° C. Spectrum in $CHCl_3$ λ_{max}, mμ: 542, 585 (I > II). Found: C 62.51; H 5.24; N 9.75%. Calculated for $C_{30}H_{28}N_4O_4Cu$: C 62.96; H 4.93; N 9.75%.

1, 4, 5, 8-Tetramethyl-2-ethoxycarbonyl-6-formylporphyrin copper complex (III). 140 mg porphyrin I Cu complex was dissolved in 10 ml dichloromethylethyl ether, and 0.2 ml $SnCl_4$ added with stirring and cooling. After 2 min the solution was poured into 200 ml ice water, the precipitate formed after the ether was decomposed filtered off, washed with water, until the acid reaction disappeared, dissolved in $CHCl_3$, and run through an aluminum oxide column to remove unreacted starting complex (26 mg). The formylporphyrin Cu complex III was eluted with $CHCl_3$–EtOH (99 : 1). The complex was obtained by removing the solvent, yield 94 mg (78%), glistening dark violet plates ex $CHCl_3$–petrol ether. Did not melt up to 300° C. Spectrum in $CHCl_3$ λ_{max}, mμ(ε): 547 (7390), 594 (13 300). Found: C 63.48; H 4.67; N 10.30%. Calculated for $C_{28}H_{24}N_4O_3Cu$: C 63.69; H 4.58; N 10.60%.

1, 4, 5, 8-Tetramethyl-2-ethoxycarbonyl-6-formylporphyrin (III). 46 mg III Cu complex was treated with concentrated H_2SO_4 for 10 min, diluted with water, until precipitation was complete, then neutralized with NH_4OH. Yield 30 mg (75.5%). Recrystallized from $CHCl_3$ it formed plates mp 187–190° C. Spectrum in $CHCl_3$ λ_{max}, mμ (ε): 518 (8900); 561 (11100); 589 (6880); 645 (3280). Found: C 72.15; H 6.11; N 11.92%. Calculated for $C_{28}H_{26}N_4O_3$: C 72.09; H 5.62; N 12.01%.

1, 4, 5, 8-Tetramethyl-2, 3-diethoxycarbonyl-6-formylporphyrin (V). Prepared similarly to porphyrin III, without intermediate separation of the Cu complex, yield 41%. Did not melt at 300° C. Spectrum in $CHCl_3$ λ_{max}, mμ (ε): 523 (9000); 564 (11400); 595 (6290); 658 (3290). Found: C 69.16; H 5.40; N 10.21%. Calculated for $C_{31}H_{30}N_4O_5$: C 69.13; H 5.61; N 10.39%.

REFERENCES

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