MESOFORMYLATION OF PORPHYRINS CONTAINING CARBONYL SUBSTITUENTS

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We previously showed that copper complexes of porphyrins having ethoxycarbonyl substituents, and with positions 6 and 7 in the porphyrin ring free, readily undergo formylation with dichloromethylethyl ether in the presence of stannic chloride [1].

When the porphyrins have ethoxycarbonyl groups next to free β positions, the latter are not formylated, but reaction occurs at a bridge methine group to give a meso substituted compound. To confirm this, as the starting compound was selected the copper complex of 1, 4, 5, 8-tetramethyl-2, 3, 6, 7-tetraethoxycarbonylporphyrin, i.e. a porphyrin with all the β positions occupied, and it was formylated in the way described [1]. The reaction product isolated melted above 300° C. Found: C 59.86; H 5.27; N 7.84%. Calculated for $C_{37}H_{36}N_4O_9Cu$: C 59.70; H 4.88; N 7.52%. Spectrum in $CHCl_3$ λ_{max}, mμ (ε): 650 (4720), 608 (9190), 565, (5900); in pyridine λ_{max}, mμ (ε): 650 (6130), 612 (12500), 567 (9680); in pyridine the corresponding oxime had λ_{max}, mμ (ε): 612 (14050), 565 (12650).

Treatment with concentrated H_2SO_4 did not result in removal of Cu from this compound, due to its unique stability.

Similar results were obtained on formylating 1, 4, 5, 8-tetramethyl-2, 3, 6-triethoxycarbonylporphyrin, and 1, 4, 5, 8-tetramethyl-2, 7-diethoxycarbonylporphyrin.

REFERENCES

1. G. V. Ponomarev, R. P. Evstigneeva, V. N. Stromnov, and N. A. Preobrazhenskii, KhGS [Chemistry of Heterocyclic Compounds], 628, 1966.

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