LETTERS TO THE EDITOR

A NEW METHOD OF SYNTHESIS OF 1,2-BIS(PORPHYRINYL-5)ETHANES

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The recently discovered spontaneous oxidation of ethane-bisporphyrins into trans-bisporphyrinylethylenes in solutions of acetic and other fatty acids [1-3], followed by isomerization of the trans-dimers into cis-dimers [4], i.e., almost "fact-to-face" porphyrins [5], which are interesting models for the study of the "special pair" in the photosynthesis, gave impetus for an urgent search for suitable and accessible methods of synthesis of the starting porphyrin dimers.

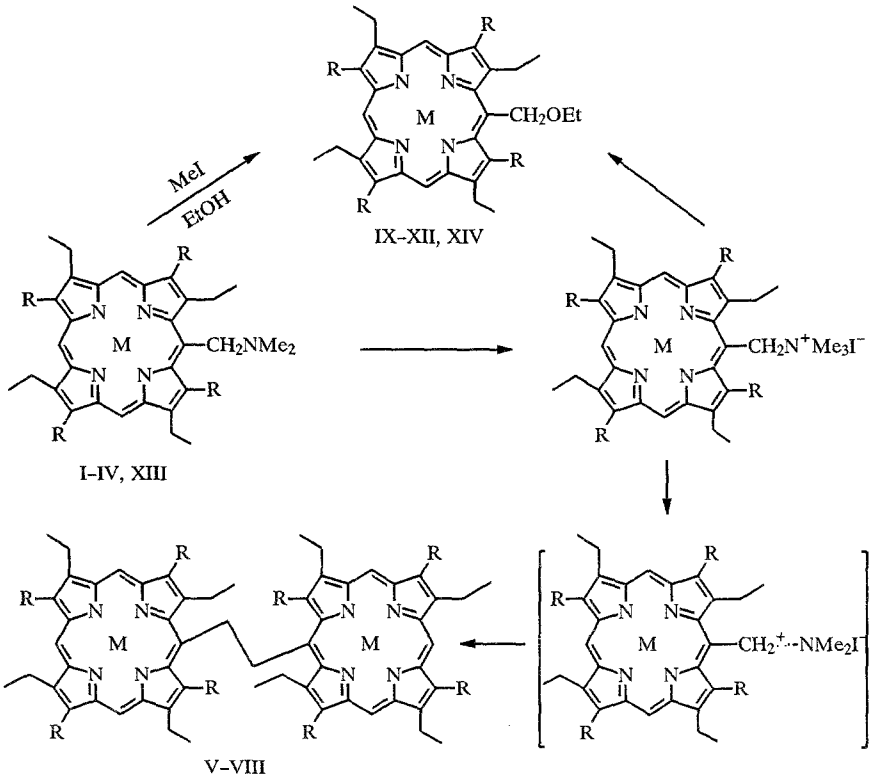
Three variants of synthesis of metal complexes of ethane bisporphyrins are known consisting in the following:

1) heating Cu and Ni-complexes of meso-hydroxymethyloctaethylporphyrin (OEP) in DMFA in the presence of catalytic amounts of conc. H_2SO_4 [6] or holding a Cu-complex of meso-hydroxymethylchlorines in H_2SO_4 in the presence of 10% H_2SO_4 [7];

2) reduction of Cu-complexes of mesoformyl-OEP by means of $LiAlH_4$ in THF;

3) brief treatment of Cu-complexes of meso-hydroxy(alkoxy)methylporphyrins with CF_3COOH [2, 8].

All these methods require an obligatory preparation of complexes of meso-formyl- or meso-hydroxymethylporphyrins, while the dimers formed in yields of 30-45% are contaminated with considerable amounts of impurities with similar chromatographic mobilities.



I, II, V, VI, IX, X R = CH_3; III, IV, VII, VIII, XI—XIV R = C_2H_5; I, III, V, VII, IX, XI M = Cu; II, IV, VI, VIII, X, XII M = Ni; XIII, XIV M = 2H

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We found that Cu- and Ni-complexes of meso-dimethylaminomethyl porphyrins I-IV which are readily obtainable in high yields as the result of carrying out the Vilsmeier reaction by the method described in [9], when heated with MeI for 1 h form bisporphyrins V-VIII in yields not lower than 50-55%. The desired end products are isolated in a crystalline state directly from the reaction mixture. Among the by-products, small amounts (5-10%) of the corresponding metal complexes of meso-ethoxyethylporphyrins IX-XII were found, the formation of which is caused by the reaction of intermediate iodomethylates, which do not enter into the reaction, with ethanol present in chloroform as a stabilizer on carrying out the chromatographic purification on silica gel. A directed synthesis of meso-ethoxymethylporphyrins under similar conditions was previously carried out by us [10].

A brief (15-20 min) heating of the free base of porphyrin XIII in MeI leads to a difficulty separable mixture of reaction products, but in presence of ethanol porphyrin XIV is formed in a yield of 60-70%.

The structure of the compounds obtained was confirmed by mass-spectral data and by comparison with samples synthesized by other methods.

The formation of dimeric porphyrins is brought about by a stepwise dissociation of iodomethylates, which are unstable due to steric factors, through the intermediate carbocations according to a mechanism previously proposed by us [2].

The new method of preparation of ethane-bisporphyrins discovered by us will undoubtedly allow its wide use for the preparation of accessible porphyrin dimers and chlorines even with labile substituents.

REFERENCES

1. G. V. Ponomarev and A. M. Shul'ga, Khim. Geterotsikl. Soed., No. 2, 278 (1986).
2. A. M. Shul'ga and G. V. Ponomarev, Khim. Geterotsikl. Soed., No. 3, 339 (1988).
3. V. V. Borovkov, G. V. Ponomarev, A. Ishida, T. Kaneda, and Y. Sakata, Chem. Lett., 1409 (1993).
4. G. V. Ponomarev, V. V. Borovkov, K. Sugiura, Y. Sakata, and A. M. Shul'ga, Tetrahedr. Lett., **34**, 2153 (1993).
5. M. O. Senge, K. R. Gerzevske, M. G. H. Vicente, T. P. Forsyth, and K. M. Smith, Angew. Chem., Int. Ed. Engl., **32**, 750 (1993).
6. D. Arnold, A. W. Johnson, and M. Winter, J. Chem. Soc. Perkin I, No. 14, 1643 (1977).
7. K. M. Smith, G. M. F. Bisset, and M. J. Bushell, Bioorg. Chem., **9**, 1 (1980).
8. G. V. Ponomarev and A. M. Shul'ga, Inventor's Certificate 1172922 (USSR); Byull. Izobret., No. 30 (1985).
9. G. V. Ponomarev and B. V. Rozynov, Khim. Geterotsikl. Soed., No. 9, 1172 (1973).
10. G. V. Ponomarev, Khim. Geterotsikl. Soedin., No. 1, 90 (1977).