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LETTERS TO THE EDITOR

A NEW GENERAL DIMERIZATION OF *meso*-AMINOMETHYLPORPHYRINS TO 1,2-BIS(PORPHYRIN-5-YL)ETHANES

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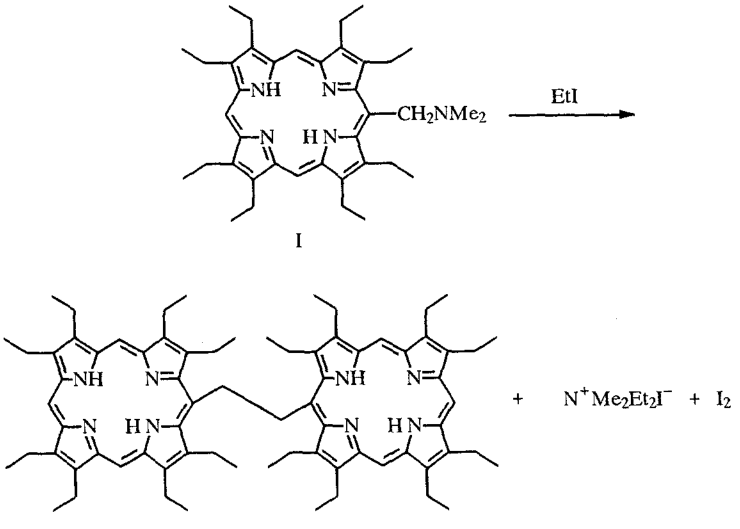
In recent work [1], we found that copper and nickel complexes of *meso*-dimethylaminomethylporphyrins are converted to the corresponding metal complexes of 1,2-bis(porphyrin-5-yl)ethanes in yields above 50-55% upon heating for 1 h. In a study of this method, we found that the dimerization of *meso*-dimethylaminomethylporphyrins is general in nature. We should note that not only the metal complexes of *meso*-dimethylaminomethylporphyrins but also their free bases undergo this reaction. This finding is important since it had been thought that the dimerization is possible only for complexes of porphyrins with transition metals, which undergo oxidation–reduction processes involving free radical formation [2].

Thus, heating porphyrin I, which was prepared according to our previous procedure [3], for 2 h in iodoethane at reflux, removal of the solvent, and chromatographic purification on a silica gel column using 47:3 chloroform–acetone as the eluent lead to bisporphyrin II in 87% yield. The structure of II was demonstrated by comparison with a sample obtained according to our previous procedure [4].



I

II

The use of iodoethane in this specific case instead of iodomethane is dictated in order 1) to eliminate or, at least, minimize the alkylation of the pyrrole nitrogen atoms since the prolonged heating of porphyrins in iodomethane leads to N-methylporphyrins and 2) to reduce the reaction time by significantly increasing the reaction temperature.

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Since two additional products, namely, molecular iodine and the quaternary salt, $N^{+}Me_2Et_2I^{-}$ or $N^{+}Me_4I^{-}$, are formed in this reaction along with dimer II, depending on the alkyl group of the iodide used, the dimerization mechanism may be presented as follows:

1) $M - P\text{-}CH_2NMe_2 + RI \rightarrow M - P\text{-}CH_2\text{—}N^{+}Me_2RI^{-}$
2) $M - P\text{-}CH_2\text{—}N^{+}Me_2RI^{-} \rightarrow M - P\text{-}CH_2\text{-}I + NMe_2R$
3) $NMe_2R + RI \rightarrow N^{+}Me_2R_2I^{-}$
4) $M - P\text{-}CH_2\text{-}I \rightarrow M - P\text{-}CH_2^{\bullet} + I^{\bullet}$
5) $2 \times M - P\text{-}CH_2^{\bullet} \rightarrow M - P\text{-}CH_2\text{-}CH_2\text{-}P\text{-}M$
6) $2 \times I^{\bullet} \rightarrow I_2$,

where $M = 2H$, Cu^{2+}, Ni^{2+}, Zn^{2+}, etc., P is the porphyrin or chlorine dianion, and R = Me, Et, Pr, and, possibly, other lower alkyl groups.

The extremely high yields of the dimeric problems may be explained on the basis of this mechanism. A whole series of ethane-bisporphyrins and chlorines and their metal complexes has already been obtained, including coproporphyrin-I, octaethylporphyrin, and octaethylchlorine. Of course, not only *meso*-dimethylaminomethyl derivatives but also other N-substituted *meso*-aminomethyl derivatives of porphyrins and chlorines may also be used to obtain porphyrin and chlorine dimers with the same degree of success.

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