Preparation and Photolysis of 2-Hydroxyalkylcobalt(III) Ætioporphyrins I and 2-Hydroxyethylcobalamin

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THE recent Paper by Schrauzer and Windgassen[1] on the preparation and properties of hydroxyalkylcobalt(III) derivatives in the cobaloxime series prompts us to report that we have prepared similar derivatives from cobalt porphins and also that they can be decomposed to yield carbonyl compounds by processes involving migration of hydrogen. Thus 2-hydroxyethyl- and 2-hydroxypropyl-cobalt(III) ætioporphyrins I have been obtained by reaction of 2-bromoethanol and 2-bromopropanol, respectively, with cobalt(I) ætioporphyrin I,[2] and the products have been characterised by their n.m.r. spectra. Thus in 2-hydroxyethyl cobalt(III) ætioporphyrin I the methylene

protons of the 2-hydroxyethyl group appeared as two multiplets centred at τ 13·45 and 14·85. On the basis of the chemical shifts of alkylcobalt(III) ætioporphyrins I quoted in our Communication[2] and the usual marked downfield shift of the signals associated with the protons of a methylene group adjacent to a hydroxyl group, it would seem that the signal at τ 13·45 should be assigned to the protons of the methylene group adjacent to the hydroxyl and the signal at τ 14·85 to the methylene attached to cobalt. Irradiation of the 2-hydroxyethyl- and 2-hydroxy-n-propyl-cobalt ætioporphyrins I caused the usual[3] homolytic fission of the cobalt–carbon bond and the formation of acetaldehyde and acetone, respectively. Hydrogen transfer in 2-hydroxyalkyl radicals in the manner observed has been reported previously.[4] Acid treatment of the 2-hydroxyalkyl derivatives did not cause these hydrogen transfer reactions. An attempted preparation of 2-hydroxyisopropylcobalt ætioporphyrin I by reaction of 2-bromopropan-1-ol with cobalt(I) ætioporphyrin I[2] gave a product showing doublets centred at τ 11·7 (3 protons) and 15·7 (2 protons), in the n.m.r. spectrum. This indicated that it was the 2-hydroxy-n-propyl derivative and accordingly on photolysis it gave acetone, characterised as the 2,4-dinitrophenylhydrazone. The formation of the 2-hydroxy-n-propyl derivative is presumably due to the production of propylene oxide under the reaction conditions which then reacts at the least hindered carbon atom with the nucleophilic cobalt(I) porphin.

In the cobalamin series, the 2-hydroxyethyl and 2-hydroxy-n-propyl derivatives are known[5,6] although the products of the photolytic decomposition have not been reported. We find that photolysis of 2-hydroxyethylcobalamin yields acetaldehyde as in the porphin and cobaloxime series, thus suggesting that the nature of the nitrogenous ligand is not of primary importance in these non-enzymic rearrangements. We feel it is premature (*cf.* ref. 1) to attempt to draw analogies between these rearrangement reactions and the formally similar enzyme-controlled processes.[7]

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[1] G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, 1967, **89**, 143.
[2] D. A. Clarke, R. Grigg, and A. W. Johnson, *Chem. Comm.*, 1966, 208.
[3] D. Dolphin, A. W. Johnson, and R. Rodrigo, *J. Chem. Soc.*, 1964, 3186.
[4] A. L. Buley, R. O. C. Norman, and R. J. Pritchett, *J. Chem. Soc.* (*B*), 1966, 849.
[5] H. P. C. Hogenkamp, J. E. Rush, and C. A. Swenson, *J. Biol. Chem.*, 1965, **240**, 3641.
[6] R.-H. Yamada, T. Kato, S. Shimizu, and S. Fukui, *Biochem. Biophys. Acta*, 1965, **97**, 353.
[7] R. H. Abeles and B. Zagalak, *J. Biol. Chem.*, 1966, **241**, 1245; B. Zagalak, P. A. Frey, G. L. Karabatsos, and R. H. Abeles, *ibid.*, p. 3028; R. H. Abeles and P. A. Frey, *Fed. Proc.*, 1966, **25**, 1639.