SYNTHESIS AND PROPERTIES OF SCHIFF BASES OF MESOFORMYLPOPHYRINS (REVIEW)∗

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A summary is presented on the use of intermediate immonium salts formed in the Vilsmeier reaction in porphyrin chemistry for the synthesis of various Schiff bases of mesoporphyrins. Special attention is given to the formation and properties of porphyrins with a five-membered exocycle.

This review is a logical extension of our recent review of the chemistry of formylporphyrins [1]. Intermediate immonium salts, which have been designated "phosphoric complexes" (PC), are formed in the Vilsmeier reaction. These species are usually not isolated and the reaction mixture is hydrolyzed to the corresponding formylporphyrin. However, the author was able to establish that not only may stable and, sometimes, even crystalline PC be isolated, but these intermediates may be used for various chemical transformations. While the chemistry of formylporphyrins formed by mild basic hydrolysis of PC was the subject of our previous review [1], the chemistry of the Schiff bases of meso- and β-formylporphyrins obtained treating PC with primary amines or ammonia and the use of these compounds in various new reactions are examined in the present review. The term "Schiff bases" implies all azomethines, which formally can be considered products of the reaction of formylporphyrins with any primary amines. In order to compare the scope for the use of PC relative to formylporphyrins, some information is given on the reactions of formylporphyrins with various amino compounds.

1. AZOMETHINES FROM FORMYLPOPHYRINS

1.1. Oximes and Hydrazones from β- and Mesoformylporphyrins and Chlorines

The classical reactions involving the aldehyde group, namely, the reactions with hydroxylamine and hydrazine hydrate to form the corresponding oximes and hydrazones, are characteristics for porphyrins and chlorines regardless of whether the formyl group is in the β- or meso position. Oximes are usually formed in rather high yield upon heating of the corresponding formyl derivative with hydroxylamine from several minutes to 2-3 h in aqueous pyridine often at reflux.

A series of oximes is given below derived from mesoformyltetramethyltetracarboethoxyporphyrin I [2], etioporphyrin-1 II, III [3, 4], octaethylporphyrin IV [5, 6], and its derivatives V-VII [7, 8], tetraphenylporphyrin VIII [9], mesotetra(ρ-tolyl)porphyrin IX, X [10], 2-desvinyl-γ-formyl-2-methoxycarbonylpyrrochlorine XI and the trimethyl ester of rhodine XII [11]. According to our data, di- and triformylporphyrins [12, 13] form the corresponding bis and trisoximes XIII-XVI without any difficulty.

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III, M = Cu; VI, VIII, XIII, R = CH - NOH; VII, XIV, R¹ = CH - NOH; XV, R = R¹ = CH - NOH; XVIII, R = CH - NOAc; XIX, R = CN