The reactions of 2-formyl-5,10,15,20-tetraphenylporphyrin (Ia) with nitromethane and of its Cu complex (Ib) with nitromethane, malonic acid, and its esters have been investigated. On interacting porphyrins (Ia,b) with nitromethane in AcOH/BuNH₂ the 2-(2-nitrovinyl)porphyrins (IIa,b) were formed, in liquid NH₃ the nitroalcohols (IIa,b) were formed, and in DMF/BuNH₂ the dinitro derivatives (IVA,b) were formed. The interaction of porphyrin (Ib) with malonic acid and its esters led to the corresponding condensation products in high yield.

The substance 5,10,15,20-tetraphenylporphyrin is one of the simplest and most widely investigated porphyrins in numerous catalytic processes. With the aim of designing accessible catalysts containing immobilized metalloporphyrin we have effected the synthesis of functionally substituted derivatives of tetraphenylporphyrin which may be used for immobilization on various carriers.

We consider the following route the most promising for obtaining functional derivatives of tetraphenylporphyrin. First, a formyl group was introduced into the tetraphenylporphyrin in the β-pyrole position, and then various reactions were effected on it which led to a compound with an active functional group such as carboxyl. Such compounds may readily be used for covalent addition to various carriers.

The introduction of a formyl group into the tetraphenylporphyrin molecule by the Vilsmeier reaction has been investigated in sufficient detail and occurs in practically quantitative yield. It was shown in [2, 3] that 2-formyl-5,10,15,20-tetraphenylporphyrin (Ia) interacted readily with phosphoranes by the Wittig reaction forming derivatives of acrylic acid. It was established in the present study that porphyrin (Ia) and its Cu complex (Ib) reacted readily with CH acids with the formation of various functionally substituted derivatives of tetraphenylporphyrin.

For Communication 19 see [1].

At first we investigated the interaction of compounds (Ia) and (Ib) with the classical CH acid nitromethane. It was assumed that 2-(2-nitrovinyl)-5,10,15,20-tetraphenylporphyrin (IIa) and its Cu complex (IIb) could be obtained in this way. Previously nitrovinylporphyrins were obtained by the nitration of the corresponding \( \beta \)-vinylporphyrins [4]. It turned out that different compounds were formed depending on the reaction conditions. Nitroalcohols (IIIA, b) were formed on condensation of porphyrins (Ia, b) in liquid ammonia. Since demetallation of complex (IIIB) by the usual method (by treatment with concentrated \( \text{H}_2\text{SO}_4 \)) led to decomposition of the substance, the new method of demetallation from [5] was used, viz., solution of complex (IIIB) in phosphorus oxychloride previously treated with a small quantity of water. Porphyrin (IIIB) was obtained by this method in 50% yield. Derivatives (IIIA, b) were converted into porphyrin (IIIA) in 40% yield on heating in \( \text{POCl}_3/\text{H}_2\text{O} \).

Nitrovinyl derivatives (IIIA, b) were readily formed on condensing porphyrins (Ia, b) with nitromethane in AcOH.

Carrying out the reaction of porphyrins (Ia, b) with nitromethane by heating in DMF led to the dinitro derivatives (IVa, b) also in high yield. These experiments showed that porphyrin (Ia) possessed the classical properties of aromatic aldehydes.

On interacting complex (Ib) with malonic acid and its methyl and ethyl esters, the Cu complexes of 2-(2,2-dicarboxyvinyl)-5,10,15,20-tetraphenylporphyrin (Vb), 2-(2,2-dimethoxycarbonylvinyl)-5,10,15,20-tetraphenylporphyrin (VIIb), and 2-(2,2-diethoxycarbonylvinyl)-5,10,15,20-tetraphenylporphyrin (VIIIb) were obtained, the demetallation of which gave the corresponding porphyrins (Va-VIIa).

Under the conditions of the condensation 2-(2-carboxyvinyl)-5,10,15,20-tetraphenylporphyrin (VIIIb) was not formed.

It was discovered by us that dicarbalkoxyvinyl derivatives (VIIb) and (VIIIb) were readily reduced by LiAlH\(_4\) in THF at -10°C to the Cu complex of 2-(2,2-dimethoxycarbonylvinyl)-5,10,15,20-tetraphenylporphyrin (IXb) and 2-(2,2-diethoxycarbonylvinyl)-5,10,15,20-tetraphenylporphyrin (Xb), the demetallation of which gave 2-(2,2-dimethoxycarbonylvinyl)-5,10,15,20-tetraphenylporphyrin (IXa) and 2-(2,2-diethoxycarbonylvinyl)-5,10,15,20-tetraphenylporphyrin (Xa), respectively. The saponification of porphyrins (IXa) and (Xa) by boiling with aqueous KOH in pyridine with simultaneous decarboxylation led to 2-(2-carboxyethyl)-5,10,15,20-tetraphenylporphyrin (XIIa).

An alternative synthesis of porphyrin (XIIa) seemed of interest. 2-(2-Methoxycarbonylvinyl)-5,10,15,20-tetraphenylporphyrin (XIIb) was synthesized by the known procedure of [2].