# UNSTABLE 2,2-DIBROMO-2-ETHOXY-4,5-BENZO-1,3,2-DIOXAPHOSPHOLANE IN ADDITION REACTIONS TO CHLORAL AND BENZALDEHYDE

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2,2-Dibromo-2-ethoxy-4,5-benzo-1,3,2-dioxaphospholane (I) adds to chloral with no change in the phosphorus coordination. In contrast to chloral, benzaldehyde is converted to dibromotoluene upon reaction with (I).

Pyrocatecholtribromophosphorane readily adds to chloral with no change in the coordination of the phosphorus atom [1]. Other relatively stable bromo- and chlorophosphoranes are also capable of undergoing such addition reactions [2,3]. We have studied the reaction of unstable 2,2-dibromo-2-ethoxy-4,5-benzo-1,3,2-dioxaphospholane (I), obtained in previous work [4], with aldehydes. This compound is a phosphorane ( $\delta P = -104$  ppm) without any significant contribution of the phosphonium structure and decomposes even at -40°C to give 2-bromo-2-oxo-4,5-benzo-1,3,2-dioxaphospholane. The addition of chloral to two equivalents of phosphorane (I) at from -100 to -110°C led to two products with <sup>31</sup>P NMR chemical signals at -60 (~30%) and 10 ppm (~70%). The product with  $\delta P = -60$  ppm is a pentaalkoxyphosphorane having one phenylenedioxaphospholane ring [3,4], while the product with  $\delta P = 10$  ppm is a phosphate. The phosphorane signal is completely converted to the phosphate signal upon heating to 100°C. The phosphate was isolated by distillation and PMR spectroscopy and elemental analysis indicated that this compound is 2-oxo-2-(1-bromo-2,2,2-trichloroethoxy)-4,5-benzo-1,3,2-dioxaphospholane (II). The phosphorane with  $\delta P = -60$  ppm is the addition product (III) containing two chloral molecules since intermediate phosphorane (A), which is the product of 1:1 addition, was not obtained upon carrying out the reaction with equimolar amounts of the reagents. The only product formed in this case was phosphate (II).



Initially formed bromophosphorane (A) decomposes through quasiphosphonium cation (B) to phosphate (II) with the loss of bromoethane. The removal of the groups with greater electron-

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donor capacity from phosphonium ion B may indicate an  $S_N 1$  mechanism for the loss of bromoethane.

Thus, unstable phosphorane (I) is capable of adding to chloral at a high rate with no change in the coordination of the phosphorus atom. However, intermediate monobromophosphorane (A) decomposes more rapidly to phosphate (II) than it adds to a second chloral molecule. We should also note that the bulky, electron-withdrawing OCHBrCCl<sub>3</sub> substituent provides some stabilization of phosphorane (A).

Unexpected results were obtained upon carrying out the reaction of phosphorane (I) with benzaldehyde containing the less electron-withdrawing phenyl substituent. Phosphate (IV) was obtained independently of the ratio of the starting compounds (1:1 or 1:2). This product is obtained by loss of the bromobenzyl group. No compounds with retention of P(V) coordination were observed. The OCHBrPh substituent apparently does not stabilize phosphorane (C). There is probably a greater contribution of structure (D) in the equilibrium than in the case of phosphorane (A). In light of the high tendency of benzyl derivatives to undergo  $S_N$ l substituent reactions [5], we should assume this mechanism in the loss of the benzyl group from phosphonium ion (D), which is similar to the elimination step in the Arbuzov reaction with halogens [6].



Thus, the rate of loss of the bromobenzyl group is significantly greater than the rate of addition of a second benzaldehyde molecule. Thus, phosphoranes are not formed in the case of the latter.

#### EXPERIMENTAL

The PMR spectra were taken on a Tesla BS 467A spectrometer at 60 MHz relative to TMS. The  $^{31}P - (^{1}H)$  NMR spectra were taken an RYa 2308 spectrometer at 8 MHz relative to  $H_{3}PO_{4}$ .

Reaction of 2.2-Dibromo-2-ethoxy-4.5-benzo-1.3.2-dioxaphospholane with Chloral. a. 1:1 Reaction. A sample of 1 ml bromine in 5 ml  $CH_2Cl_2$  was added dropwise with stirring to 3.7 g 2-ethoxy-4,5-benzo-1,3,2-dioxaphospholane in 30 ml  $CH_2Cl_2$  at -100°C. Then, 1.94 ml chloral in 5 ml  $CH_2Cl_2$  was added. The reaction mixture was maintained for 4 h with warming to 20°C and then fractionated to give 2-oxo-2-(1-bromo-2,2,2-trichloroethoxy)-4,5-benzo-1,3,2-dioxaphospholane (II) in 87% yield, bp 129-132°C (0.03 mm). PMR spectrum in  $CD_2Cl_2$ ( $\delta$ , ppm, J, Hz): 6.80 d (POCHBr, 1H,  $^{3}J_{POCH} = 10$ ), 7.10 br.s ( $C_6H_4$ , 4H). Found: C, 25.11; H, 1.57; Br, 21.04; Cl, 27.29%. Calculated for  $C_8H_5BrCl_3O_4P$ : C, 25.09; H, 1.30; Br, 20.88; Cl, 27.84%. Bromoethane was obtained in the liquid nitrogen trap.

b. 1:2 Reaction. This reaction was carried out by analogy to the previous experiment at from -100 to -110°C. Distillation gave phosphate (II) in 80% yield.

<u>Reaction of Phosphorane (I) with Benzaldehyde.</u> This reaction was carried out by analogy to the previous procedures. Removal of the solvent and benzaldehyde by distillation gave  $\alpha, \alpha$ -dibromotoluene in 61% yield, bp 58-60°C (0.06 mm). PMR spectrum in CCl<sub>4</sub> ( $\delta$ , ppm): 7.20 m (C<sub>6</sub>H<sub>5</sub>), 6.50 s (CHBr<sub>2</sub>). The other product was 2-oxo-2-ethoxy-4,5-benzo-1,3,2-dioxaphospholane (IV), bp 90-92°C (0.05 mm),  $\delta$ P 8 ppm. PMR spectrum in CCl<sub>4</sub> ( $\delta$ , ppm, J, Hz): 1.38 t (CH<sub>3</sub>, 3H, <sup>3</sup>J<sub>HH</sub> = 7), 4.20 d.q (POCH, <sup>3</sup>J<sub>HH</sub> = 7, <sup>3</sup>J<sub>POCH</sub> = 10) [7].

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ELECTROCHEMICAL REDUCTION OF Fe(III), Cr(III), AND Mn(III) PORPHYRIN COMPLEXES IN DMSO

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The half-wave potentials are given for the electrochemical reduction of Fe(III), Cr(III), and Mn(III) porphyrin complexes. Cyclic voltamperometry was used to study the reversibility of these reactions. An effect was demonstrated for the structure of the porphyrin ligand on the half-wave potentials for the reduction of the Mn(III) complexes.

The reduced forms of metalloporphyrins are electron donors in biological and industrial catalysis. Electrochemical methods have been used to study the reactions leading to the formation of such compounds [1,2]. The possibility of monitoring the charge transferred is an advantage of the electrochemical method for the generation of reduced forms of the catalyst since the corresponding potential is applied on the working electrode for obtaining the required intermediate species. In the present study, the formation of various reduced forms of Fe(III), Cr(III), and Mn(III) porphyrin complexes was investigated by cyclic and differential pulse voltamperometry.

## EXPERIMENTAL

The voltamperometric methods were carried out using the ESM-700 electrochemical system manufactured in the German Democratic Republic on a platinum electrode in a cell held at 25°C in a nitrogen atmosphere. A standard calomel electrode was used as the reference electrode and 0.1 M  $Et_4NClO_4$  was used as the base electrolyte.

The complexes were synthesized by the coordination of porphyrins with the corresponding metal acetates in DMF. The porphyrins were tetraphenylporphin (H<sub>2</sub>TPP), tetra(pentafluoro)phenylporphin (H\_TPFPP), tetra(2-thienyl)porphin (H\_TTP(2)), tetra(5-amyl-2-thienyl)porphin ( $H_2TATP(5,2)$ ), tetra(7-quinolinyl)porphin ( $H_2TQP(7)$ ), and dimethyl ether of deuteroporphyrin (H<sub>2</sub>DP, d.m.e).

## RESULTS AND DISCUSSION

The reduction of these complexes in DMSO may be approximated by the following scheme:

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$$\mathbf{M}^{\mathbf{I}\mathbf{I}} \mathbf{P}^{+} + e \stackrel{\prime}{\rightleftharpoons} \mathbf{M}^{\mathbf{I}\mathbf{I}} \mathbf{P} + e \stackrel{2}{\rightleftharpoons} \mathbf{M}^{\mathbf{I}\mathbf{I}} \mathbf{P}^{-} + e \stackrel{3}{\rightleftharpoons} \mathbf{M}^{\mathbf{I}\mathbf{I}} \mathbf{P}^{2-}$$
(1)

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