## REACTION OF 2-TERT-BUTOXY-4,5-BENZO-1,3,2-DIOXAPHOSPHOLANE WITH TRIBROMOACETALDEHYDE

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The reaction of 2-tert-butoxy-4,5-benzo-1,3,2-dioxaphospholane with tribromoacetaldehyde proceeds by initial halophilic attack on the bromine atom, leading to a product with retention of the P-Br bond (pyrocatechol bromophosphate) and an anion exchange product (pyrocatechol dibromovinylphosphate), and by initial attack at the carbon atom of the C=O group, which is accompanied by the elimination of isobutylene to form an  $\alpha$ -hydroxyphosphonate.

We have recently shown that tribromoacetaldehyde reacts with triphenyl phosphite by a halophilic mechanism to form triphenyl phosphate and tetraphenoxyphosphonium bromide [1]. This bromide is the product of secondary reactions of the initially generated bromophosphonium ion pair, which could not be detected. Secondary ion exchange reactions in the case of phenoxyl radicals lead to tetraphenoxyphosphonium products due to intermolecular processes. In other cases, the final products are vinyloxy derivatives.

The preparation of products containing a phosphorus-halogen bond requires the introduction of a new rapid reaction not affecting this bond. The dealkylation of tert-butyl radicals proceeding rapidly through an  $S_N$ l mechanism in the Arbuzov and Perkov reactions may be such a reaction [2].

The idea of using tert-butyl P(III) derivatives in order to determine products of the halophilic attack with a P-Br bond appeared promising for proving a halophilic mechanism in the reaction with bromal. Bromophosphonium ion pair (A) should be formed in the case of a halophilic attack. The decomposition of an ion pair should proceed by two pathways. If the rate constant for the formation of the tert-butyl cation,  $k_{-Br}$ , is greater than that for ion exchange,  $k_{exc}$ , then we should obtain bromophosphate and tert-butyl dibromovinyl ether (or its elimination products, isobutylene and dibromoacetaldehyde) in pure form. If the  $k_{-Br}/k_{exc}$  ratio is less than unity, the Perkov reaction product, namely, dibromovinyl phosphate, should be obtained in pure form



V. I. Ul'yanov-Lenin Kazan State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1909-1912, August, 1989. Original article submitted July 27, 1988. In order to resolve these questions, we studied the reaction of pyrocatechol tertbutyl phosphite (I) with bromal under various conditions. The ratio and composition of the products formed were found to depend on the order of introducing the reagents and the temperature conditions. On the whole, the reaction proceeds in a more complex manner than represented in Scheme 1. If bromal is slowly added to phosphite (I) in  $CH_2Cl_2$  at 20°C, we obtain bromophosphate (II) and vinyl phosphate (III) in almost equal amounts and also  $\alpha$ hydroxyphosphonate (IV). The reaction products were separated and characterized spectrally. We identified t-BuBr and  $CHBr_2CHO$  in the volatile fractions by spectral methods and comparison with pure authentic samples. These results indicate, firstly, that the generally postulated attack on the C=O group carbon occurs in addition to the halophilic mechanism for phosphite (I) [2]. The formation of  $\alpha$ -hydroxyphosphonate (IV) indicates that the most rapid pathway for the stabilization of the initially formed betaine (Be) is the loss of a tert-butyl cation with its subsequent conversion to isobutylene. Secondly, the formation of phosphates (II) and (III) in approximately equal amounts indicates that k-Br is comparable to  $k_{exc}$ .

Upon altering the order of addition (phosphite to bromal), the only reaction product under the more vigorous reaction conditions  $(CH_2Cl_2 \text{ at reflux})$  is  $\alpha$ -hydroxyphosphonate (IV) (Scheme 2). Product (IV) is extremely hygroscopic and is converted to an ester



of phosphonic acid (V) upon the action of atmospheric moisture or the addition of the required amount of water. Ester (V) was isolated and characterized spectrally



## EXPERIMENTAL

The  ${}^{31}P-{}^{1}H$  NMR spectra were taken on an RYa-2305 spectrometer at 24.8 MHz. The PMR spectra were taken on a Tesla BS-467A spectrometer at 60 MHz relative to HMDS as the internal standard. The IR spectra were taken on a Specord 75 IR spectrometer. Starting bromal was distilled over  $P_2O_5$  and BaO until the distillate was light yellow.

Reaction of Phosphite (I) with Tribromoacetaldehyde. A sample of 0.069 mole (19.39 g)  $Br_3CCHO$  was added dropwise slowly with stirring to 0.069 mole (12.43 g) phosphite (I) in 15 ml  $CH_2CH_2$  at 20°C. Slight heat evolution was noted, and the reaction mixture was left for 24 h at 20°C. A fine crystalline precipitate of 2,3-benzo-1,4-dioxa-5-oxo-6-hydroxy-7,7,7-tribromo-5-phospha[4]heptane (IV) formed, which was filtered, washed with 4:5 pentane-ether at 0°C, and dried in vacuo at 12 mm, mp 123-125°C. Found: C 22.20; H 23; P 6.98%. Calculated

for  $C_8H_6Br_3O_4P$ : C 21.97; H 1.37; P 7.09%. PMR spectrum in  $CD_3COCD_3$  ( $\delta$ , ppm, J, Hz): 5.33 d ( $^2J_{PCH}$  = 11.7, PCH, 1H), 7.06 s ( $C_6H_4$ , 4H), 7.73 s (OH,  $\sim$ 1H). <sup>31</sup>P NMR spectrum ( $\delta$ , ppm, in  $C_6H_5NO_2$ ): 32. IR spectrum ( $cm^{-1}$ ): 725, 815, 990 sh, 1068, 1176 (POC), 1255 (P=O), 1360, 1580 (C=C,  $\delta$ OH), 3160-3190 (OH). The filtrate was evaporated in vacuo and the residue was distilled to give 1) 2-bromo-2-oxo-4,5-benzo-1,3,2-dioxaphospholane (II), bp 90-93°C (0.05 mm),  $\delta_P$  5 ppm [3]; 2) 2-(2',2'-dibromovinyloxy)-2-oxo-4,5-benzo-1,3,2-dioxaphospholane (III), bp 135-140°C (0.05 mm),  $\delta_P$  7 ppm. PMR spectrum in CCl<sub>4</sub> ( $\delta$ , ppm): 7.05 s ( $C_6H_4$ , 4H), 7.30 d (POCH, 1H, <sup>3</sup>J<sub>POCH</sub> = 5 Hz). IR spectrum ( $cm^{-1}$ ): 1610-1630 (C=C), 1280-1330 (P=O); and 3) tert-butyl bromide (isolated in a trap cooled with liquid nitrogen). PMR spectrum in CCl<sub>4</sub> ( $\delta$ , ppm): 1.66. IR spectrum: 1320, 1360, 1435 ( $\delta_{CH}$ ). Dibromoacetaldehyde was detected in small amounts, PMR spectrum in CCl<sub>4</sub> ( $\delta$ , ppm): 8.83 d (CHO), 5.80 d (CHBr<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 4.1 Hz).

<u>Hydrolysis of Phosphonate (IV)</u>. A sample of 15 g phosphonate (IV) was dissolved in 50 ml acetonitrile, and the solution was left in a Petri dish in the air. The precipitate formed after six days was washed with ether and dried to give 14 g 1-hydroxy-2,2,2-tribromo-ethyl-O-(2-hydroxyphenyl)phosphonic acid (V), mp 148-150°C (dec.). Found: C 21.01; H 2.01; Br 54.4; P 6.74%. Calculated for  $C_8H_8Br_3O_5P$ : C 21.8; H 1.82; Br 54.3; P 7.06%. PMR spectrum in CD<sub>3</sub>CN ( $\delta$ , ppm): 4.9 d (PCH, 1H, <sup>2</sup>J<sub>PCH</sub> = 12 Hz), 6.90 m (C<sub>6</sub>H<sub>4</sub>, POH, COH, 7H).

<u>Reaction of Phosphite (I) with Tribromoacetaldehyde.</u> A sample of 2.42 g (0.013 mole) phosphite (I) in 10 ml  $CH_2Cl_2$  was added dropwise over 1.5 h to a solution of 1.41 ml (0.013 mole) bromal in 50 ml  $CH_2Cl_2$  at reflux. The reaction mixture was evaporated in vacuo at 12 mm. The glassy residue was triturated with a glass rod in 20 ml  $CH_2Cl_2$  to give crystalline phosphonate (IV), mp 122-124°C.

<u>Reaction of Phosphonate (IV) with Triethylamine.</u> A sample of 1.88 ml NEt<sub>3</sub> in 10 ml ether was added dropwise to 5.88 g phosphonate (IV) in 100 ml ether at 20°C. The reaction mixture was stirred for 6 h. The precipitated  $Et_3N$ ·HBr was filtered off and the filtrate was evaporated. The residue consisted of spectrally pure phosphate (III).

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