priate fractions afforded 200 mg of product **6c** containing a trace of a slightly more polar impurity and 150 mg of pure **6c**: $R_f \simeq$ 0.36 in 1:3 ethyl acetate–hexane; NMR (CDCl$_3$) δ 1.33 (CH$_3$), 1.46 (CH$_3$), 2.54 (H$_a$), 1.94 (H$_b$), 2.70 (H$_x$), 2.60 (H$_y$), 3.05 (H$_w$), 3.74 (CH$_2$O), 4.50 (H$_d$), 5.20 (H$_c$); J values in Hz, J_{ab} = 15.0, J_{bd} = 5.0, J_{bc} = 6.5, J_{ac} = 7.5, J_{ad} = 0.0, J_{xy} = 18.0, J_{wy} = 10.0, J_{wx} = 0.0, J_{cw} = 6.5; mass spectrum m/e 285.1163 (M$^+$ – CH$_3$; Calcd for C$_{13}$H$_{21}$O$_5$Si 285.1158) and other ions of decreasing intensity at 73, 75, 197, 43, 225, 59, 135, 55, 183.

Conversion of 2 to 5a and 6a. Following the procedure described above for the preparation of **3** and **4**, 1.5 g of **2**, 15 mL of acetone, 1.8 mL of water, and 20 mg of osmium tetroxide in 1 mL of *tert*-butyl alcohol was stirred with 0.81 g of *N*-methylmorpholine *N*-oxide and 1.2 mL of water for 1.5 h and then worked up as described above to yield 2.1 g of a crude mixture of **3** and **4**. This mixture, in 25 mL of acetone, was treated with 2 drops of 70% perchloric acid for 40 min and was then worked up as described above to give 2.1 g of a mixture of acetonides **5a** and **6a** which was chromatographed in a column of 250 g of silica gel. The column was eluted with 1:1 ethyl acetate–hexane and fractions of about 17 mL each were collected. Fractions 15–21 afforded 0.48 g (26%) of isomer **6a**, mp 129–130.5 °C, while fractions 38–55 afforded 1.46 g of **5a** which, on trituration with benzene, gave 1.53 g (70%) of **5a** benzene solvate, mp 82.5–90 °C. The infrared and NMR spectra of these samples of **5a** and **6a** are essentially identical with those reported above.

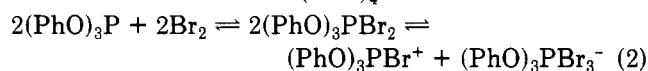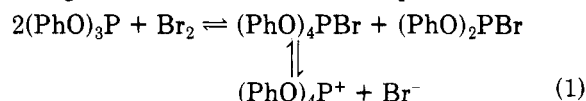# Reinvestigation of Dihalotriphenoxyphosphoranes

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In 1883, Noack[1] was the first to prepare dibromotriphenoxyphosphorane, (PhO)$_3$PBr$_2$, by the addition of bromine to triphenyl phosphite. Since then, many dihalophosphoranes of this type have been prepared and studied.[2-6] The characterization of the above adducts has been based primarily on hydrolytic and elemental analysis data. Recently, Ramirez and co-workers[6] applied ^{31}P NMR to study the product derived from the reaction of chlorine with triphenyl phosphite. Attempts to prepare highly purified samples of these dihalo adducts by Rydon and Tonge[5] were unsuccessful. In the case of the dibromo adduct, elemental analysis was consistent with a structure corresponding to bromotetraphenoxyphosphorane rather than the expected dibromotriphenoxyphosphorane. A conductometric study of the reaction of triphenyl phosphite with bromine in acetonitrile was carried out by Harris and Payne.[4] They postulated that the reaction between triphenyl phosphite and bromine proceeded in

two well-defined stages (eq 1 and 2). In the first step, a steep rise in the conductance was observed, whereas no such change occurred in the second step.

$$2(PhO)_3P + Br_2 \rightleftharpoons (PhO)_4PBr + (PhO)_2PBr$$
$$\Updownarrow$$
$$(PhO)_4P^+ + Br^- \qquad (1)$$
$$2(PhO)_3P + 2Br_2 \rightleftharpoons 2(PhO)_3PBr_2 \rightleftharpoons$$
$$(PhO)_3PBr^+ + (PhO)_3PBr_3^- \quad (2)$$

We have reinvestigated the reaction of triphenyl phosphite with halogens utilizing ^{31}P NMR spectroscopy. The results of this study are reported herein.

Experimental Section

All ^{31}P NMR spectra were obtained on a Varian CFT-20 NMR spectrometer operating at 32.19 MHz. Chemical shifts are reported in terms of the δ scale relative to 85% phosphoric acid as the external reference. All spectra were recorded by using deuterated chloroform as the solvent with and without the use of the external reference. Triphenyl phosphite was purchased from Eastman Organic Chemicals.

Reaction and Discussion

I. Reaction of Triphenyl Phosphite and Bromine. Following the procedure of Rydon and Tonge,[5] a white solid and a pale yellow solid were obtained from the reaction of triphenyl phosphite with a 0.5 molar and a 1 molar equiv of bromine, respectively, in chlorobenzene. The ^{31}P NMR chemical shifts[7] of the white solid and the pale yellow solid are +22.5 and –4.5 ppm, respectively, relative to 85% phosphoric acid. The former chemical shift corresponds to bromotetraphenoxyphosphorane and the latter to dibromotriphenoxyphosphorane. The ^{31}P NMR shift of bromotetraphenoxyphosphorane was previously reported at +26 ppm by Nesterov et al.[8] The assignment of the resonance at –4.5 ppm to dibromotriphenoxyphosphorane was based on the fact that when a limiting amount of triphenyl phosphite was added into the solution containing the pale yellow solid, the peak at –4.5 ppm decreased, and two new peaks at –228.2 and +22.4 ppm corresponding to phosphorus tribromide[9] and bromotetraphenoxyphosphorane appeared in approximately a 1:3 ratio. A slight excess of triphenyl phosphite caused the peak at –4.5 ppm to disappear and resulted in a spectrum exhibiting peaks at –199.4, –175.3, –128.2, and +22.5 ppm corresponding to phenyl phosphorodibromidite,[9,10] diphenyl phosphorobromidite,[9,10] triphenyl phosphite, and bromotetraphenoxyphosphorane, respectively.

Table I presents the results of ^{31}P NMR studies of triphenyl phosphite with 0.25, 0.5, 0.75, and 1 molar equiv amounts of bromine. When 0.25 molar equiv of bromine was added to triphenyl phosphite, bromotetraphenoxyphosphorane, diphenyl phosphorobromidite, and unreacted triphenyl phosphite were observed. When 0.5 molar equiv of bromine was added to triphenyl phosphite, phenyl phosphorodibromidite was observed in addition to the aforementioned compounds. When 0.75 molar equiv of bromine was added to triphenyl phosphite, the phosphorus compounds observed were bromotetraphenoxyphosphorane, diphenyl phosphorobromidite, phenyl phosphoro-

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(3) J. P. Foroman and D. Lipkin, *J. Am. Chem. Soc.*, **75**, 3145 (1953).
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(6) F. Ramirez, J. A. Bigler, and C. P. Smith, *J. Am. Chem. Soc.*, **90**, 3507 (1968).

(7) Since the white solid and the pale yellow solid fumed in air and became liquid on standing, the preparation of samples for NMR measurements must be swift and preferably done in a dry atmosphere.
(8) L. V. Nesterov, R. I. Mutalapova, S. G. Salikhov, and E. I. Loginova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 414 (1971).
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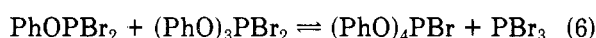(10) R. A. Y. Jones and A. R. Katritzky, *Angew. Chem.*, **74**, 60 (1962).
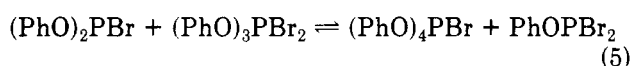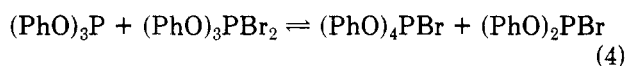
Table I. Products from the Reaction of Triphenyl Phosphite and Bromine[a]

concn, mol		compd obsd,[b] %					
$(PhO)_3P$	Br_2	$(PhO)_3P$	$(PhO)_2PBr$	$PhOPBr_2$	PBr_3	$(PhO)_4PBr$	$(PhO)_3PBr_2$
0.01	0.0025	39	12			49	
0.01	0.0050	9	15	4		72	
0.01	0.0075		10	18	12	60	
0.01	0.01[c]				11	23	66
0.01	0.01[d]				28	72	

[a] The reaction was carried out in deuterated chloroform. [b] The relative percentages of the products are based on the phosphorus integration ratio. [c] Triphenyl phosphite was added immediately into a bromine solution. [d] Bromine was added slowly into a triphenyl phosphite solution.

dibromidite, and phosphorus tribromide. It is interesting to note that when 1 molar equiv of bromine was added slowly into a chloroform solution of triphenyl phosphite, only bromotetraphenoxyphosphorane and phosphorus tribromide were observed. However, when 1 molar equiv of triphenyl phosphite was added quickly into the bromine solution, the major product observed was dibromotriphenoxyphosphorane in addition to two minor products, bromotetraphenoxyphosphorane and phosphorus tribromide. Attempts to detect the presence of the sextuply coordinated phosphorus ion proposed by Harris and Payne[4] were unsuccessful. No new phosphorus-containing compound was observed with the addition of excess bromine.

On the basis of the data in Table I, the reaction between triphenyl phosphite and bromine can be explained by the series of equilibria in eq 3-6.

$$(PhO)_3P + Br_2 \rightleftharpoons (PhO)_3PBr_2 \quad (3)$$

$$(PhO)_3P + (PhO)_3PBr_2 \rightleftharpoons (PhO)_4PBr + (PhO)_2PBr \quad (4)$$

$$(PhO)_2PBr + (PhO)_3PBr_2 \rightleftharpoons (PhO)_4PBr + PhOPBr_2 \quad (5)$$

$$PhOPBr_2 + (PhO)_3PBr_2 \rightleftharpoons (PhO)_4PBr + PBr_3 \quad (6)$$

II. Reaction of Triphenyl Phosphite and Chlorine.

When chlorine was passed slowly into triphenyl phosphite according to the method described by Rydon and Tonge,[5] a white solid was obtained after purification. The white solid exhibited a ^{31}P NMR shift of +22.5 ppm relative to 85% phosphoric acid. When triphenyl phosphite was added slowly into an ice-cooled solution of chlorine in n-hexane, a pale green solid was obtained. The pale green solid exhibited a ^{31}P NMR shift of -7.7 ppm with a small amount of impurities at +17.7 (triphenyl phosphate) and +22.5 ppm. It is likely that the white solid having the ^{31}P shift of +22.5 ppm is chlorotetraphenoxyphosphorane, and the pale green solid having a shift of -7.7 ppm is dichlorotriphenoxyphosphorane. Both chlorotetraphenoxyphosphorane and dichlorotriphenoxyphosphorane give triphenyl phosphate upon addition of water. Ramirez et al.[6] reported dichlorotriphenoxyphosphorane to have a ^{31}P NMR shift of +22.8 ppm in methylene chloride. It is felt that the solid isolated by these authors was chlorotetraphenoxyphosphorane and not dichlorotriphenoxyphosphorane. Nesterov et al.[8] reported the ^{31}P shift of chlorotetraphenoxyphosphorane was +24 ppm. In our laboratory, when bromotetraphenoxyphosphorane was added to the solution of chlorotetraphenoxyphosphorane, only one ^{31}P signal at +22.5 ppm was observed.[11]

Similar to the case for dibromotriphenoxyphosphorane, addition of a small amount of triphenyl phosphite to the solution of dichlorotriphenoxyphosphorane caused the

formation of phosphorus trichloride (-218.6 ppm) and chlorotetraphenoxyphosphorane. Further addition of triphenyl phosphite reduced the peak at -7.7 ppm significantly, accompanied by the formation of a new peak at -177.3 ppm corresponding to phenyl phosphorodichloridite. Excess of triphenyl phosphite diminished the peaks at -7.7 and -218.6 ppm and the phosphorus compounds observed were phenyl phosphorodichloridite (-177.3 ppm), diphenyl phosphorochloridite (-158.3 ppm), chlorotetraphenoxyphosphorane (+22.5 ppm), unreacted triphenyl phosphite (-128.1 ppm), and a trace amount of triphenyl phosphate (+17.8 ppm). The formation of triphenyl phosphate was possibly due to the reaction of dichlorotriphenoxyphosphorane with moisture in the air.

Fluck et al.[9] reported that phosphorus trichloride and triphenyl phosphite could reorganize to form phenyl phosphorodichloridite and diphenyl phosphorochloridite at 180 °C. No reorganization reaction took place at ambient temperature. However, if a trace amount of chlorotetraphenoxyphosphorane was added into the mixture of triphenyl phosphite and phosphorus trichloride, the reorganization reaction took place at ambient temperature. It is believed that dichlorotriphenoxyphosphorane will also cause the reorganization reaction to take place at ambient temperature.

An Improved Synthesis of 1,3:2,4:5,6-Trimethylenesorbitol and 1,3:2,5:4,6-Trimethylenemannitol

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The improved synthesis of 2,4,8,10-tetraoxaspiro[5.5]-undecane from paraformaldehyde and pentaerythritol[2] led me to consider whether polyformals could be prepared with equal facility from vicinal polyhydroxylic compounds such as alcohols derived from sugars. The promise of obtaining polyhydroxylic compounds as aphrogenic pyrostats[3] was

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(11) This would seem to indicate that bromo- and chlorotetraphenoxyphosphorane might exist as ionic species in the form of $(PhO)_4P^+X^-$.

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