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.

$$(PhO)_3P + Br_2 \rightleftharpoons (PhO)_3PBr_2 \tag{3}$$

$$(PhO)_3P + (PhO)_3PBr_2 \rightleftharpoons (PhO)_4PBr + (PhO)_2PBr \tag{4}$$

$$(PhO)_2PBr + (PhO)_3PBr_2 \rightleftharpoons (PhO)_4PBr + PhOPBr_2 \tag{5}$$

$$PhOPBr_2 + (PhO)_3PBr_2 \rightleftharpoons (PhO)_4PBr + PBr_3 \tag{6}$$

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.

Registry No. $(PhO)_3P$, 101-02-0; Br_2, 7726-95-6; $(PhO)_2PBr$, 70445-76-0; $PhOPBr_2$, 70445-77-1; PBr_3, 7789-60-8; $(PhO)_4PBr$, 32395-00-9; $(PhO)_3PBr_2$, 39943-76-5; chlorine, 7782-50-5; dichlorotriphenoxyphosphorane, 15493-07-9; chlorotetraphenoxyphosphorane, 32394-39-1; phosphorus trichloride, 7719-12-2; phenyl phosphorodichloridite, 3426-89-9; diphenyl phosphorochloridite, 5382-00-3.

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

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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an additional incentive for examining the extension of this reaction to the vicinal polyols. Because sorbitol and mannitol were readily available and their formals are well characterized, they were selected as representative examples for investigation.

Experiments confirm the opinion that the procedure described earlier,[2] i.e., fusion of the reactants neat, is applicable to the two hexitols with equally favorable results and, very likely, to isomeric and homologous polyols. Although here we are concerned with the preparation of the triformals, observations based on the residual oils obtained from the filtrates suggest that mono- and diformals can be synthesized similarly using appropriately less paraformaldehyde.

The triformals of both sorbitol and mannitol were first described by Schulz and Tollens,[4] who prepared them from aqueous formaldehyde and the respective hexitol in a large amount of hydrochloric acid. Later, Ness, Hann, and Hudson[5,6] improved the procedure to get higher yields of both products and determined the structures of the formals from mannitol[5] and sorbitol.[6] Ouchi and So[7] substituted sulfuric for hydrochloric acid in preparing sorbitol triformal according to the procedure recommended by Ness et al.[6] All these syntheses, however, required reactive times from several hours to days and involved large volumes of water.

The synthesis of these formals can be carried out much faster and more conveniently if a dry mixture of the respective hexitol is heated rapidly with a slight excess (5–10%) of paraformaldehyde in the presence of an acidic catalyst, e.g., hydrochloric, sulfuric, or methanesulfonic acid. The solids become a paste at about 70 °C and liquify at about 100 °C, but the clear liquid soon solidifies into a paste at about 110 °C. Continued heating at 115–125 °C converts the paste into a powder. The total heating time is about 10 min. If hydrochloric acid is used, a small amount of zinc chloride is beneficial. Because hydrochloric acid may produce some of the carcinogenic bis(chloromethyl) ether, other acids are preferable catalysts. In such a case a small amount of water (about 1% by weight) is advantageous because then the solids turn into a paste at about 50 °C and stirring becomes easier.

If the reaction is carried out in two stages, the amount of paraformaldehyde can be reduced almost to stoichiometric quantities, i.e., <1% excess; the yield of the triformal is improved, but the total heating time is virtually the same. First, the hexitol is heated with 2 equiv of paraformaldehyde to about 120 °C in 5 min and then cooled to about 75 °C. The third mole equivalent (with 1% excess) of paraformaldehyde is added to the warm mixture and heating continued at 115–125 °C until a solid powder is obtained. This second operation also takes about 5 min. In either case, only 10 min are required to carry out the reaction on 0.1-M quantities.

Whichever preparation is used, the resultant crude white powder is suspended in a small amount of acetone or methanol (the latter is preferable if the filtrate is to be worked up) and the thick paste is filtered. Filtration is surprisingly rapid. The white powders are quite pure with yields in the range of 80–90%. If the filtrate and washings are concentrated, treated with further amounts of paraformaldehyde, and heated as before, the total yields are better than 95%.

Thus, it is clear that this expeditious procedure is a convenient way to make a great variety of cyclic formals from vicinal polyols in any quantity with simple equipment and readily available reagents.

Experimental Section

Sorbitol (97%, mp 93–97 °C), mannitol (mp 164–167 °C), and paraformaldehyde (mp 163–165 °C dec) were obtained from Aldrich Chemical Company. Zinc chloride and acids were reagent-grade chemicals. If necessary, the solids were ground to fine powders. For small amounts (0.1-M lots), the reaction mixtures were stirred with a thermometer and heated in 100-mL beakers over a Bunsen burner flame.

1,3:2,4:5,6-Trimethylenesorbitol. 1. A mixture of 18.2 g (0.1 mol) of sorbitol, 9.5 g (0.317 mol) of paraformaldehyde, 0.5 g of zinc chloride, and 4 mL concentrated hydrochloric acid was heated in 2 min to 90–100 °C. The thin slurry converted into a clear liquid and almost immediately into a paste with evolution of some formaldehyde vapors. Heating and stirring was continued at 110–115 °C until the paste turned into a powder (about 8 min). The tan powder (21.8 g, mp 175–183 °C) was cooled and stirred with 25 mL of acetone and the thick paste was filtered. Filtration proceeded readily. The insoluble powder was washed with acetone (3 × 5 mL) and dried to give 16.7 g of a fine white powder, mp 214–216 °C. Evaporation of the combined filtrate and washings left 5.3 g of a viscous oil or paste; treatment with 1.5 g (0.05 mol) of paraformaldehyde and 1 mL of hydrochloric acid as before gave an additional crop of white powder (3.4 g, mp 214–216 °C) for a combined yield of 95%. The triformal is reported to melt at 212–216 °C.[6]

Similar results were achieved with 5 g of 40% sulfuric acid and washing the crude product with methanol rather than acetone. The product is very soluble in methylene chloride.

2. The mixture of sorbitol (9.1 g 0.05 mol), paraformaldehyde (3.1 g 0.103 mol), and 25% sulfuric acid (1.3 g) was heated in 1.5 min to 100–105 °C and kept at this temperature to get a clear liquid. The temperature was raised to and kept at 110–120 °C for 2.5 min. The liquid was then cooled and 1.6 g (0.053 mol) of paraformaldehyde was added to the soft paste at 75 °C. The temperature was raised to and kept at 105–110 °C for 2 min, during which time the slurry cleared and solidified to a paste. Heating was continued at 110–120 °C for 3 min to obtain 10.9 g of a white powder, mp 178–185 °C. When the product was cold, 20 mL of methanol was added, the slurry was stirred, and then the thick paste was filtered and washed (3 × 5 mL) to leave a white powder (9.1 g, mp 213–215 °C). Concentration of the colorless filtrate and washings left 1.5 g of oily crystals.

1,3:2,5:4,6-Trimethylenemannitol. 1. With mannitol (18.2 g, 0.1 mol) used instead of sorbitol, a 21.7-g yield of crude white powder (mp 183–197 °C) was obtained. The acetone-insoluble white powder (15.4 g) melted at 229–330 °C. A second crop was obtained from the filtrate and washings on treatment with formaldehyde and hydrochloric acid; 5.0 g, mp 228–230 °C. The total yield was 94%. The triformal is reported to melt at 232–233 °C,[5] and its NMR spectrum, consistent with ours, has been studied.[8]

Similar results were found with sulfuric acid and washing the crude reaction product with methanol.

2. In the two-step reaction with mannitol, carried out as described for sorbitol, 10.7 g of the crude white triformal was obtained. Extraction with methanol left 9.1 g of mannitol triformal, mp 230–231 °C. Evaporation of the filtrate and washings left some oily crystals; these were not worked up or characterized further.

Registry No. 1,3:2,4:5,6-Trimethylenesorbitol, 3530-21-0; sorbitol, 50-70-4; paraformaldehyde, 30525-89-4; 1,3:2,5:4,6-trimethylenemannitol, 5434-31-1; mannitol, 69-65-8.

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(3) Unpublished exploratory work carried out at Armstrong Cork Company.

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