

crystallized twice from acetone-Skellysolve B to afford 2.42 g (76%) of oxide, mp 125–127°,  $\lambda_{\max}$  282 ( $\epsilon$  26,200).

*Anal.* Calcd for  $C_{19}H_{26}FOP$ : C, 71.22; H, 8.18. Found: C, 71.26; H, 8.21.

[3-(*p*-Fluorophenyl)-6-methyl-3,5-heptadienyl]dimethylphosphine Oxide (18).—The ylide prepared from 3.50 g of the salt 12 was allowed to react with 0.8 ml of acetone. There was obtained on work-up 2.48 g of crude oxide, mp 81–95°. A sample was rechromatographed and recrystallized from moist Skellysolve B to give a sample (320 mg): mp 90–96°;  $\nu_{\max}$  3300  $cm^{-1}$ ; nmr four aromatic protons (multiplets  $\delta$  6.8–7.6), two vinyl protons (multiplets  $\delta$  5.9–6.7), allylic methyl (three-proton singlets at  $\delta$  2.82 and 2.9), P-CH<sub>3</sub> (6 H, doublet about  $\delta$  1.5,  $J = 13$  Hz).

*Anal.* Calcd for  $C_{18}H_{22}FOP \cdot H_2O$ : C, 64.48; H, 8.12. Found: C, 64.61; H, 8.00.

**Registry No.**—2, 24699-83-0; 3, 24728-08-3; 4, 24699-84-1; 5, 24699-85-2; 6, 24699-86-3; 7, 24699-87-

4; 8, 24699-88-5; 9, 24699-89-6; 10, 24699-90-9; 11, 24699-91-0; 12, 24699-92-1; 13, 24699-93-2; 14, 24699-94-3; 15a, 24691-52-9; 15b, 24691-53-0; 15c, 24691-54-1; 15d, 24691-55-2; 15e, 24691-56-3; 15f, 24728-09-4; 15g, 24691-57-4; 15h, *trans,trans*, 24691-58-5; 15h, *trans,cis*, 24691-60-9; 15i, *trans,trans*, 24691-59-6; 15i, *trans,cis*, 4728-00-5; 16, 24699-95-4; 17, 24728-96-5; 18, 24699-96-5.

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## Synthesis of 2,6,7-Trioxa-4-phosphabicyclo[2.2.2]octane Systems

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The formation of  $P(CH_2O)_3P$  from  $P(CH_2OH)_3$  and  $P(OMe)_3$  is shown to be highly dependent on the manner in which the triol is prepared. Neutralization of  $[P(CH_2OH)_4]Cl$  with NaOH produces 1 mol of  $H_2O$  which is difficult to remove and leads to extensive hydrolysis of the  $P(OMe)_3$  when transesterification is attempted. Treating the salt with an equimolar quantity of NaOMe, although eliminating the hydrolysis problem, results in appreciable isomerization of  $P(OMe)_3$  to  $Me(O)P(OMe)_2$ . In neither case does  $P(CH_2O)_3P$  form in consistent or reasonable yields. The isomerization side reaction is shown to be due to small amounts of unneutralized phosphonium salt. A 20% molar excess of NaOMe over salt results in 20–30% yields of  $P(CH_2O)_3P$  and only a trace of  $Me(O)P(OMe)_2$  side product. The synthesis and characterization of the new compounds  $P(CH_2O)_3As$ ,  $OP(CH_2O)_3As$ ,  $P(CH_2O)_3SiMe$ , and  $MeC(CH_2O)_3SiMe$  are also reported.

In 1965 we reported<sup>2</sup> what appeared at the time to be a straightforward synthesis of  $P(CH_2O)_3P$  by the transesterification of  $P(CH_2OH)_3$  with trimethyl phosphite in tetrahydrofuran. Since then we have experienced little success in consistently repeating the synthesis. Moreover, it has come to our attention that several other investigators have had similar difficulties, although there is one published report<sup>3</sup> in which the compound was successfully prepared by our method. We thought it appropriate, therefore, to examine the synthesis more closely in an effort to elucidate the nature of the side products in the reaction of  $P(CH_2OH)_3$  with  $P(OMe)_3$ . Moreover, it was highly desirable to determine the conditions necessary for a more reliable preparation of  $P(CH_2O)_3P$  since this difunctional non-chelating ligand has been found to exhibit interesting coordination properties.<sup>4</sup>

It is not obvious *a priori* why the transesterification of  $P(CH_2OH)_3$  with  $P(OMe)_3$  should be more difficult than the analogous reaction with  $RC(CH_2OH)_3$  or *cis*-1,3,5-cyclohexanetriol. These latter triols with  $P(OMe)_3$  afford  $P(OCH_2)_3CR$  and  $P(OCH)_3(CH_2)_3$ , respectively, in high yields and numerous reports in the literature from other laboratories<sup>5</sup> as well as ours<sup>6</sup> on the use of these bicyclic phosphites in other reactions

attest to the reliability of our syntheses<sup>7</sup> of these compounds.

We show in the present report that the formation of  $P(CH_2O)_3P$  is very sensitive to the manner in which the  $P(CH_2OH)_3$  is prepared from the commercially available  $[P(CH_2OH)_4]Cl$ . It is also demonstrated that  $P(OMe)_3$  undergoes deleterious hydrolysis and rearrangement reactions whereas  $As(OMe)_3$  and  $MeSi(OMe)_3$  are quite stable to rearrangement. The arsenic and silicon esters with  $P(CH_2OH)_3$  lead to the new bicyclic compounds  $P(CH_2O)_3As$  and  $P(CH_2O)_3SiMe$ , respectively. Also reported for the first time are  $OP(CH_2O)_3As$  and  $MeC(CH_2O)_3SiMe$ .

### Experimental Section

Elemental analyses were carried out by Chemalytics, Inc., Tempe, Ariz., or Galbraith Laboratories, Inc., Knoxville, Tenn. Molecular weights were obtained on an atlas CH-4 single-focusing spectrometer at 70 eV. Infrared spectra were obtained on a Perkin-Elmer Model 21 double-beam spectrometer using sodium chloride optics. Proton nmr spectra were obtained on a Varian Associates A-60 spectrometer using tetramethylsilane as an internal standard. Melting points were taken in capillaries and are uncorrected.

**$P(CH_2OH)_3$ .**—To a well-stirred solution of 19.05 g (0.1 mol) of  $[P(CH_2OH)_4]Cl$  in 75 ml of anhydrous methanol, 65 ml of methanolic NaOCH<sub>3</sub> containing 1 g of NaOCH<sub>3</sub> in 10 ml of MeOH was added all at once, the latter being in about a 20% excess of the equimolar amount. The mixture was allowed to stir for 15 min during which time the NaCl precipitated. A small amount of dry ether (about 15 ml) was then added to precipitate the last traces of NaCl, which was subsequently removed by filtration.

(1) NSF Undergraduate Research Participant, 1969.

(2) K. J. Coskran and J. G. Verkade, *Inorg. Chem.*, **4**, 1655 (1965).

(3) W. McFarlane and J. A. Nash, *Chem. Commun.*, 127 (1969).

(4) R. D. Bertrand, D. A. Allison, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 71 (1970).

(5) See, for example, F. Basolo and H. G. Schuster-Woldan, *ibid.*, **88**, 1657 (1966); C. S. Kraihanzel and P. K. Maples, *Inorg. Chem.*, **7**, 1806 (1968).

(6) See, for example, A. C. Vandenbroucke, D. G. Hendriker, R. E. McCarley, and J. G. Verkade, *ibid.*, **7**, 1825 (1968), and references therein.

(7) J. G. Verkade, T. J. Huttemann, M. K. Fung, and R. W. King, *ibid.*, **4**, 83 (1965).

The resulting solution of  $P(CH_2OH)_3$  was strongly basic when tested with moist pH paper and gave no further precipitate upon introduction of a few additional drops of  $NaOCH_3$  solution. Removal of the solvent by evaporation gave the triol as a clear viscous liquid.

$P(CH_2O)_3P$ .—Freshly prepared  $P(CH_2OH)_3$  (0.1 mol) was slowly added with constant stirring to a solution containing 24 ml (0.2 mol) of  $P(OMe)_3$ , an equal volume of methanol, and 1 ml of 10% methanolic  $NaOCH_3$ . The methanol permits a homogeneous reaction mixture but can be omitted giving a two-phase reaction which gives  $P(CH_2O)_3P$  in yields identical with those obtained from the homogeneous reaction mixture. Upon completion of the addition of  $P(CH_2OH)_3$ , the reaction mixture was heated to 90° and held at this temperature for several hours. Methanol, formed as the result of the transesterification reaction



slowly distills from the reaction mixture. When no more methanol was collected, the excess  $P(OMe)_3$  was swept out of the reaction with the aid of a slow  $N_2$  flush. Upon allowing the reaction to cool, a crystalline but oily mass of crude product was obtained. The oily nature of the crude product makes difficult the isolation of pure  $P(CH_2O)_3P$ . Nonetheless, two dissimilar purification procedures have been found to give satisfactory results.

In the first method the crude product was stirred for about 1 hr with 50 ml of dry benzene while the mixture was kept at 70°. After decanting the benzene, the extraction process was repeated three more times. Evaporation of the extracts gave a liquid which solidified on standing. The solid mass was dissolved in 25 ml of benzene and the clear solution was decanted from the oily, insoluble droplets that were also present. Final crystallization was effected by bubbling a slow stream of  $N_2$  through the slightly warmed (30–35°) benzene solution until crystallization commenced, whereupon it was cooled to 0°. The crystalline solid was then separated from the small amount of remaining solvent by rapid filtration. The last traces of solvent were removed under vacuum to give pure  $P(CH_2O)_3P$  in the form of large, clear but soft crystals. The absence of any significant impurities was confirmed by nmr spectroscopy, the spectrum being identical with that previously recorded of pure  $P(CH_2O)_3P$ .<sup>8</sup>

Alternately, purification was accomplished by stirring the crude reaction product in three or four separate portions with excess ice water whereupon the oil dissolved almost immediately, leaving the solid ester behind. The water was quickly drawn off through a coarse frit and the solid was washed with benzene into a stirred mixture of benzene and anhydrous magnesium sulfate (approximately 200 g of  $MgSO_4$  in 400 ml of benzene). These operations were performed quickly as  $P(CH_2O)_3P$  dissolves with hydrolysis quite rapidly in water. The exposure of  $P(CH_2O)_3P$  to water has not been allowed to exceed 30 sec and even minimal exposure to  $H_2O$  undoubtedly has resulted in some loss of yield. *Caution:* Allowing  $P(CH_2O)_3P$  moist with water to stand has occasionally caused the material to burst into flames. After filtration of the benzene to remove  $MgSO_4$ , evaporation of the benzene gave  $P(CH_2O)_3P$  as a dry, crystalline powder which exhibited the expected nmr spectrum.

The purities and yields of  $P(CH_2O)_3P$  have been found to be nearly identical for the two purification procedures but the second method described can be completed in much less time and has been most often, albeit cautiously, used. Consistent yields of 20–30% of the theoretical have been obtained. Calcd: mol wt, 152. Found: mol wt, 152. *Caution:* In this synthesis it is essential that the  $P(CH_2OH)_3$  used be strongly basic. It has been found in the  $^1H$  nmr spectrum of triol which is nearly neutral or even slightly basic (as in the case when the stoichiometric amount of  $NaOCH_3$  is used) that considerable amounts of  $[P(CH_2OH)_4]^+Cl^-$  are present and will, when added to  $P(OCH_3)_3$ , give rise to a violent, exothermic reaction which occasionally takes fire or explodes and from which no  $P(CH_2O)_3P$  can be isolated.

$P(CH_2O)_3As$ .—To 12.4 g (0.100 mol) of  $P(CH_2OH)_3$  was added, with stirring under nitrogen flush at room temperature, 16.9 g (0.100 mol) of  $As(OCH_3)_3$  prepared as reported previously.<sup>9</sup> The mixture immediately formed a solid crystalline mass of crude product. Rapid nitrogen flush was continued for 15 min to remove most of the methanol. Benzene was added and the mixture was stirred until only a small amount of oil remained undissolved. After filtration of the solution, the solvent was removed and the remaining product was sublimed at 40° (2 mm).

(8) K. Moedritzer, *Inorg. Syn.*, **11**, 182 (1968).

A 61.2% yield of product as colorless crystals (mp 91–92°) was realized. The very hygroscopic crystals were stored under dry nitrogen in a desiccator. The dipole moment of 1.58 D in benzene at 25.0° was measured as described previously.<sup>9</sup> Because of a small amount of decomposition noted after the measurements, the experimental moment is probably precise to only  $\pm 0.15$  D. *Anal.* Calcd for  $PC_3H_5O_4As$ : C, 18.38; H, 3.09; mol wt, 196. Found: C, 18.39; H, 2.98; mol wt, 196.

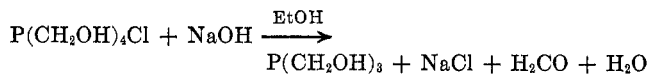
$OP(CH_2O)_3As$ .—To a solution of 3.92 g (20.0 mmol) of  $P(CH_2O)_3As$  in 100 ml of benzene was added 4.64 g (20.0 mmol) of benzoyl peroxide and the mixture was refluxed under nitrogen flush for 2 hr. A yield of 85.5% of product as colorless needles decomposing at 175° separated from the solution. A strong infrared absorbance at 1195  $cm^{-1}$  in  $CDCl_3$  revealed the presence of a  $P=O$  link in the compound. Calcd for  $PC_3H_5O_4As$ : mol wt, 212. Found: mol wt, 212.

$P(CH_2O)_3SiCH_3$ .—To 12.4 g (0.100 mol) of  $P(CH_2OH)_3$  was added under nitrogen flush 13.6 g (0.100 mol) of  $CH_3Si(OCH_3)_3$  prepared as described previously.<sup>10</sup> The reaction was carried out in a 250-ml flask equipped with a mechanical stirrer, distillation condenser, and nitrogen inlet. The mixture was heated with stirring at 90° for 3 hr with a gentle nitrogen flush to remove methanol. After the reaction period the mixture was transferred to a sublimation apparatus and colorless crystals were sublimed from the mixture at 80° (2 mm). Purification was achieved by resublimation under vacuum at room temperature. There was obtained a 41.9% yield of crystals (mp 61–62°). The extremely hygroscopic crystals could be stored for long periods only under vacuum. *Anal.* Calcd for  $PC_4H_9O_3Si$ : C, 29.25; H, 5.52; mol wt, 164. Found: C, 29.02; H, 5.46; mol wt, 164.

$CH_3Si(OCH_2)_2CCH_3$ .—This bicyclic compound was prepared in the same manner as the previous compound except that 12.0 g (0.100 mol) of  $CH_3C(CH_2OH)_3$  was used in place of  $P(CH_2OH)_3$  and 0.50 g of  $NaOCH_3$  was added to catalyze the reaction. The product was sublimed from the reaction mixture at 250° (2 mm). Purification was achieved by resublimation of the colorless crystals at 60°. A 9.75% yield of colorless crystals (mp 106–108°) was obtained. The extremely hygroscopic solid was stored under vacuum. *Anal.* Calcd for  $C_8H_{12}O_3Si$ : C, 44.98; H, 7.56; mol wt, 160. Found: C, 46.11; H, 7.83; mol wt, 160.

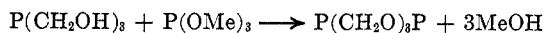
## Results and Discussion

The course of the reaction between  $P(CH_2OH)_3$  and  $P(OMe)_3$  was followed by observing changes in the  $^1H$  nmr spectrum in *t*-butyl alcohol as a solvent. Because the  $P(CH_2OH)_3$  used in our earlier synthesis<sup>2</sup> of  $P(CH_2O)_3P$  was prepared after the manner of Grayson<sup>11</sup> rather than by the procedure given in the Experimental Section, our initial nmr studies were made with  $P(CH_2OH)_3$  obtained by the reaction



The reaction mixture was prepared by adding slightly more than an equimolar amount of  $P(OMe)_3$  to a solution of the triol in *t*-butyl alcohol<sup>12</sup> and the  $^1H$  nmr spectrum of the mixture was periodically scanned.

If the major reaction is the transesterification, then the  $^1H$  spectra of the appropriate compounds in Table I



would show that (a) the integrated area of the  $P(OMe)_3$  peaks would decrease 1.5 times as fast as the area of the  $P(CH_2OH)_3$  methylene proton peaks, and (b) the

(9) A. C. Vandenbroucke, R. W. King, and J. G. Verkade, *Rev. Sci. Instrum.*, **39**, 558 (1968).

(10) D. Seyferth and E. G. Rochow, *J. Org. Chem.*, **20**, 250 (1955).

(11) M. Grayson, German Patent 1151255; *Chem. Abstr.*, **60**, 554g (1964).

(12) Not quite all of the triol dissolves in *t*-butyl alcohol regardless of the preparation used. Thus insoluble side products in minor quantities may form. Indeed  $P(CH_2OH)_3$  has been found [W. J. Vulbo, *J. Org. Chem.*, **33**, 3665 (1968)] to react with the  $CH_2O$  formed in the  $NaOH$  neutralization reaction to give  $HOCH_2OCH_2P(CH_2OH)_2$ .

TABLE I  
<sup>1</sup>H NMR SPECTRAL DATA<sup>a</sup>

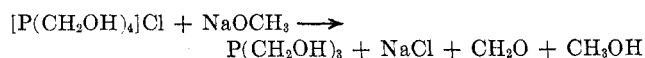
Compd	Registry no.	$\delta$ <sup>1</sup> H (resonance)	<i>J</i> (nuclei)	Solvent
P(CH <sub>2</sub> O) <sub>3</sub> P	4579-03-7	4.54 (CH <sub>2</sub> )	8.8 (PCH) 2.8 (POCH)	CDCl <sub>3</sub> <sup>b</sup>
P(CH <sub>2</sub> O) <sub>3</sub> As	24647-30-1	4.61 (CH <sub>2</sub> )	9.4 (PCH)	CDCl <sub>3</sub>
OP(CH <sub>2</sub> O) <sub>3</sub> As	24647-31-2	4.64 (CH <sub>2</sub> )	7.4 (PCH)	CDCl <sub>3</sub>
P(CH <sub>2</sub> O) <sub>3</sub> SiCH <sub>3</sub>	24647-32-3	4.66 (CH <sub>2</sub> ) 0.11 (CH <sub>3</sub> )	8.9 (PCH) <sup>c</sup>	CDCl <sub>3</sub>
H <sub>3</sub> C-Si(OCH <sub>2</sub> ) <sub>2</sub> CCH <sub>3</sub>	24647-52-7	3.98 (CH <sub>2</sub> ) 0.66 (CCH <sub>3</sub> ) 0.20 (SiCH <sub>3</sub> )		CDCl <sub>3</sub>
(CH <sub>3</sub> ) <sub>3</sub> COH	75-65-0	1.22 (CH <sub>3</sub> ) 4.64 (OH)		<i>d</i>
P(CH <sub>2</sub> OH) <sub>3</sub>	2767-80-8	4.07 (CH <sub>2</sub> )	3.0 (PCH)	(CH <sub>3</sub> ) <sub>3</sub> COH
P(OCH <sub>3</sub> ) <sub>3</sub>	121-45-9	3.44 (CH <sub>3</sub> )	10.6 (POCH)	(CH <sub>3</sub> ) <sub>3</sub> COH
CH <sub>3</sub> OH	67-56-1	3.31 (CH <sub>3</sub> )		(CH <sub>3</sub> ) <sub>3</sub> COH
H(O)P(OCH <sub>3</sub> ) <sub>2</sub>	868-85-9	3.75 (CH <sub>3</sub> ) 6.75 (PH)	11.5 (POCH) 698 (PH)	(CH <sub>3</sub> ) <sub>3</sub> COH
CH <sub>3</sub> (O)P(OCH <sub>3</sub> ) <sub>2</sub>	756-79-6	3.66 (OCH <sub>3</sub> ) 1.44 (PCH <sub>3</sub> )	11.0 (POCH) 17.0 (PCH)	Neat
[P(CH <sub>2</sub> OH) <sub>4</sub> ]Cl	16980-25-9	4.73 (CH <sub>2</sub> )	2.0 (PCH)	D <sub>2</sub> O

<sup>a</sup>  $\delta$  <sup>1</sup>H and *J* values are in parts per million with respect to TMS and in hertz, respectively. <sup>b</sup> See ref 2. <sup>c</sup> <sup>29</sup>Si chemical shifts and couplings will be reported later. <sup>d</sup> The data are for a (CH<sub>3</sub>)<sub>3</sub>COH solution saturated with P(CH<sub>2</sub>OH)<sub>3</sub>. The OH proton absorption is broadened compared with that in the pure solvent.

methyl proton area of MeOH would grow at twice the rate that either member of the P(OMe)<sub>3</sub> proton doublet is decreasing. Using P(CH<sub>2</sub>OH)<sub>3</sub> prepared by Grayson's method,<sup>11</sup> however, it was found that 80% of the P(OMe)<sub>3</sub> disappeared after 1 hr while the P(CH<sub>2</sub>OH)<sub>3</sub> concentration decreased only about 10%. Three new peaks appeared at the expense of the P(OMe)<sub>3</sub> protons: a singlet ( $\delta$  3.31) due to methanol (OCH<sub>3</sub>) and an OCH<sub>3</sub> doublet ( $\delta$  3.75, *J* = 11.5 Hz) shown to arise from H(O)P(OMe)<sub>2</sub> by addition of an authentic sample. The intensity ratio (1:2) of the methanol peak to that of the new doublet showed that only 1 mol of methanol was formed from each mole of reacting P(OMe)<sub>3</sub>. At this point it was suspected that substantial water contamination of the P(CH<sub>2</sub>OH)<sub>3</sub> stemming from its mode of preparation was hydrolyzing the P(OMe)<sub>3</sub> and that H(O)P(OMe)<sub>2</sub> was the source of the new doublet.

Although the liquid P(CH<sub>2</sub>OH)<sub>3</sub> was subjected to prolonged evacuation in an effort to remove water, the strong hydrogen bonding undoubtedly present in P(CH<sub>2</sub>OH)<sub>3</sub>-H<sub>2</sub>O solutions retains the H<sub>2</sub>O in most cases. It is to be noted, however, that P(CH<sub>2</sub>O)<sub>3</sub>P obviously has been obtained<sup>2</sup> in poor to moderate yield from P(CH<sub>2</sub>OH)<sub>3</sub> prepared according to Grayson's method,<sup>11</sup> although the vast majority of attempts since have ended in failure. These successes may indicate that sufficient water can be removed in some instances such as in the case of rotary evacuation where a large and changing surface of water-containing material is exposed to the vacuum.

The most straightforward solution to this problem was to prevent the formation of water by the preparation of P(CH<sub>2</sub>OH)<sub>3</sub> according to the equation



The reaction of P(OMe)<sub>3</sub> with dry P(CH<sub>2</sub>OH)<sub>3</sub> was performed under the same conditions as the reactions just described in which hydrolysis was noted. The absence of water was confirmed by the complete lack

of dimethyl phosphite in spectra of the reaction mixture. It was found, however, that anhydrous conditions were not a sufficient condition for formation of P(CH<sub>2</sub>O)<sub>3</sub>P. In a typical experiment, a violent, exothermic reaction yielding a viscous oil would occur upon mixing the two reactants neat. The gas in the reaction spontaneously inflamed in air indicating the presence of phosphines. Since completely aliphatic triols under the same conditions undergo facile transesterification with P(OMe)<sub>3</sub> to give bicyclic phosphite esters, it was of interest to determine the cause of the uncontrollable exothermic reaction. New features in the <sup>1</sup>H nmr spectra of the viscous product of the reaction included a doublet (*J* = 17 Hz) at 1.44 ppm and a doublet (*J* = 11 Hz) of twice the intensity at 3.66 ppm. Moreover, the P(OMe)<sub>3</sub> doublet was absent while the P(CH<sub>2</sub>OH)<sub>3</sub> methylene proton absorption remained relatively unchanged. These doublets were found to be superimposable with a spectrum of a pure sample of Me(O)P(OMe)<sub>2</sub>, and it is quite reasonable that in the exothermic reaction sufficiently high temperatures were reached (210°)<sup>13</sup> to isomerize P(OMe)<sub>3</sub> thermally to Me(O)P(OMe)<sub>2</sub>.<sup>14</sup> It was also suspected that perhaps unneutralized [P(CH<sub>2</sub>OH)<sub>4</sub>]Cl might catalyze this reaction since small amounts of unreacted phosphonium salt were detected in the nmr spectrum of the reaction mixture even when the mole ratio of NaOMe to salt was 1.05. Indeed a 1:1 mol ratio of [P(CH<sub>2</sub>OH)<sub>4</sub>]Cl and P(OMe)<sub>3</sub> in methanol produced an exothermic reaction in which all of the phosphite reacted. About 40% of the phosphite is converted to Me(O)P(OMe)<sub>2</sub> as shown by the nmr spectrum.

Apparently there are two likely ways in which this isomerization reaction can arise. It is possible that the [P(CH<sub>2</sub>OH)<sub>4</sub>]<sup>+</sup> cation is directly responsible, since it has been observed that P(OMe)<sub>3</sub> behaves similarly in the presence of [MeP(OMe)<sub>3</sub>]BPh<sub>4</sub>.<sup>13</sup> Although the

(13) L. V. Nesterov and A. Ya. Kessel, *Zh. Obshch. Khim.*, **37**, 1171 (1967); *Chem. Abstr.*, **67**, 54215a (1967).

(14) J. R. Van Wazer, "Phosphorus and its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958.

mechanism of this reaction is unknown, the phosphonium salt may provide a nucleophilic site for phosphite attack *via* a phosphorus or an oxygen lone pair. The nucleophilic site in the phosphonium salt could be the phosphorus or a released methylene proton. House<sup>15</sup> notes that the  $\text{Ph}_3\text{P}^+$  substituent will enhance the acidity of an adjacent methylene hydrogen to a greater extent than a carbonyl function. The  $[\text{P}(\text{OMe})_3]^+$  moiety may have a similar effect on the methyl protons in the  $[\text{MeP}(\text{OMe})_3]^+$  cation. Similar arguments might apply to the  $[\text{P}(\text{CH}_2\text{OH})_3]^+$  group and its effect on the methylene protons in the remaining  $\text{CH}_2\text{OH}$  moiety. Although protons do effectively bring about the isomerization of  $\text{P}(\text{OMe})_3$ ,<sup>16</sup> a more likely source of these species in the present reaction stems from the dissociation of  $[\text{P}(\text{CH}_2\text{OH})_4]\text{Cl}$  to  $\text{P}(\text{CH}_2\text{OH})_3$ ,  $\text{CH}_2\text{O}$ , and  $\text{HCl}$ .<sup>17</sup> In any case, a large excess of neutralizing base is to be avoided in the preparation of  $\text{P}(\text{CH}_2\text{O})_3\text{P}$ , however, inasmuch as  $\text{P}(\text{CH}_2\text{OH})_3$  is destroyed under these conditions.<sup>17</sup> The presence of excess phosphonium salt in the reactions carried out with  $\text{P}(\text{CH}_2\text{OH})_3$  prepared by Grayson's method<sup>11</sup> could also account for the extensive hydrolysis of  $\text{P}(\text{OMe})_3$  since this reaction is known<sup>18</sup> to be acid catalyzed.

In sharp contrast to the difficulties encountered in the reaction of  $\text{P}(\text{OMe})_3$  with anhydrous  $\text{P}(\text{CH}_2\text{OH})_3$ , the formation  $\text{P}(\text{CH}_2\text{O})_3\text{As}$  took place rapidly at room temperature and in high yield. Trimethyl arsenite hydrolyzes more readily than  $\text{P}(\text{OMe})_3$  to give solid  $\text{As}_2\text{O}_3$  and  $\text{MeOH}$ ; so the preparation of anhydrous triol is essential. The difference in the two reactions undoubtedly lies in the tendency for  $\text{P}(\text{OMe})_3$  to isomerize to  $\text{Me}(\text{O})\text{P}(\text{OMe})_2$  and the absence of this property in  $\text{As}(\text{OR})_3$  compounds. The greater strength of the  $\text{O}=\text{P}$  link compared with the  $\text{O}=\text{As}$  bond is very likely responsible as the driving force for the  $\text{P}(\text{OMe})_3$  isomerization. Supporting chemical evidence for this reasoning is found in the ease of peroxide oxidation of

(15) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965.

(16) The adverse effect of protons in some triester formations is seen when  $\text{MeOH}$  is treated with  $\text{PCl}_3$  in a 3:1 mol ratio in  $\text{CH}_2\text{Cl}_2$ . Only  $\text{H}(\text{O})\text{P}(\text{OMe})_2$  and  $\text{MeCl}$  in 1:1 mol ratio was produced as shown by  $^1\text{H}$  nmr spectroscopy. It is well known in fact (ref 14) that  $\text{P}(\text{OMe})_3$  in the presence of gaseous  $\text{HCl}$  gives excellent yields of these products. In the presence of 3 mol of pyridine, however,  $3\text{MeOH} + 1\text{PCl}_3$  gives only  $\text{P}(\text{OMe})_3$  as shown from the  $^1\text{H}$  nmr spectrum.

(17) A. Hoffman, *J. Amer. Chem. Soc.*, **43**, 1684 (1921).

(18) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley & Sons, Inc., New York, N. Y., 1950.

$\text{P}(\text{CH}_2\text{O})_3\text{As}$  to  $\text{OP}(\text{CH}_2\text{O})_3\text{As}$ . The formulation of the latter compound as shown was deduced from the presence of an infrared band at  $1195\text{ cm}^{-1}$  assigned to  $\nu_{\text{P}=\text{O}}$  which was absent in the reduced form and which appeared at  $1200\text{ cm}^{-1}$  in  $\text{OP}(\text{CH}_2\text{O})_3\text{CCH}_3$ .<sup>19</sup>

Group dipole moments in polycyclic molecules are quite additive owing to the rigidity and symmetry of the molecules.<sup>20</sup> It is therefore possible to compare the experimental moments of  $\text{P}(\text{CH}_2\text{O})_3\text{As}$  (1.58 D) and  $\text{P}(\text{CH}_2\text{O})_3\text{P}$  (3.10 D)<sup>21</sup> with those obtained by considering the appropriate vectorial sums of the  $\text{P}(\text{CH}_2)_3$ ,  $\text{O}_3\text{As}$ , and  $\text{O}_3\text{P}$  group contributions. The  $\text{P}(\text{CH}_2)_3$  contribution is taken as 1.19 D, the dipole moment of  $\text{P}(\text{CH}_3)_3$ ,<sup>22</sup> while the  $\text{O}_3\text{PAs}$  and  $\text{O}_3\text{P}$  moments of 2.68<sup>23</sup> and 4.13 D,<sup>21</sup> respectively, are the dipole moments of the  $\text{CH}_3\text{C}(\text{CH}_2\text{O})_3\text{As}$  and  $\text{CH}_3(\text{CH}_2\text{O})_3\text{P}$  molecules.<sup>24</sup> Taking appropriate differences (inasmuch as the two group contributions are opposed along the  $\text{C}_3$  axis of the cages), values of 1.49 and 2.94 D are calculated for  $\text{P}(\text{CH}_2\text{O})_3\text{As}$  and  $\text{P}(\text{OCH}_2)_3\text{P}$ , respectively. The reasonable agreement with the experimental values further substantiates the indicated structures of these polycycles.

Polycyclic systems of the type  $\text{P}(\text{CH}_2\text{O})_3\text{CCH}_3$ <sup>19,25</sup> and  $\text{CH}_3\text{C}(\text{OCH}_2)_3\text{CCH}_3$ <sup>25</sup> have been studied previously, and it is therefore not surprising that the silicon analogs  $\text{P}(\text{CH}_2\text{O})_3\text{SiCH}_3$  and  $\text{CH}_3\text{Si}(\text{OCH}_2)_3\text{CCH}_3$  could be synthesized. The relative ease of formation of  $\text{P}(\text{CH}_2\text{O})_3\text{SiCH}_3$ , however, again attests to the normal behavior of  $\text{P}(\text{CH}_2\text{OH})_3$  toward transesterification except with  $\text{P}(\text{OMe})_3$ .

**Registry No.**— $\text{CH}_3\text{Si}(\text{OCH}_2)_3\text{CCH}_3$ , 24647-57-2.

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(24) We assume here that the C-C and C-H moments are negligible.

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