

Contribution from the Department of Chemistry,  
Vanderbilt University, Nashville, Tennessee 37235**Redistribution, Condensation, and Rearrangement Reactions  
Involving Dichloro- and Dimethoxymethylphosphines**

KUZHIKALAIL M. ABRAHAM and JOHN R. VAN WAZER\*

Received April 19, 1974

AIC40258C

Nuclear magnetic resonance spectra supplemented by hydrolysis studies show that the room-temperature reaction between dichloromethylphosphine and dimethoxymethylphosphine involves redistribution, condensation, and rearrangement processes, with the redistribution of chloro and methoxyl groups being the first to dominate the reaction sequence. It appears that the major condensation processes involve rearrangement to give  $\text{CH}_3(\text{O})\text{P}<$  units connected by P-P bonds in the molecules. When an excess of  $\text{CH}_3\text{PCl}_2$  was employed, the crystalline compound  $[\text{CH}_3\text{P}(\text{O})]_x$ , where  $x \approx 8$ , precipitated upon standing. The reaction of dichloromethylphosphine oxide with dimethoxymethylphosphine leads to a rapid exchange of chloro and methoxyl groups, as well as condensation, to give  $[\text{CH}_3(\text{O})\text{PO}]_n$  plus the same products as were obtained from condensation of  $\text{CH}_3\text{PCl}_2$  with  $\text{CH}_3\text{P}(\text{OCH}_3)_2$ . The reverse reaction between dimethyl methylphosphonate (dimethoxymethylphosphine oxide) and dichloromethylphosphine does not exhibit redistribution of chloro and methoxyl groups and undergoes slow condensation to give mixed products apparently based on both the  $\text{CH}_3\text{P}<$  and  $\text{CH}_3\text{P}(\text{O})<$  moieties.

Much of the known chemistry of oligomers and polymers based on the main-group elements involves structures in which these atoms are joined<sup>1</sup> through bridging oxygens or related bridging groups such as S or NH. In spite of widespread interest in the organic chemistry of the triply connected phosphorus atom, we are not aware<sup>2</sup> of any literature dealing with real or attempted preparations of such polyphosphorus compounds in which phosphorus atoms bearing an unshared pair of electrons are bridged by oxygen atoms. One possible method for achieving this end might be found in the gentle condensation, at room temperature or below, of monomers based on triply connected phosphorus. It is also possible that a transfer of some or all of the oxygen atoms from the bridging position to the position formerly occupied by the lone pair on the phosphorus might occur during the reaction. This again is also a relatively little known field in that there appear to be only two publications<sup>2,3</sup> dealing with this matter, and both studies involved heating the reagents. In one of these publications,<sup>3</sup> it is noted that the compounds  $o\text{-C}_6\text{H}_4\text{O}_2\text{PP}(\text{O})(\text{OR})_2$ , which were said to be formed, deposited, upon standing in sealed vessels, the red-to-orange precipitates<sup>4</sup> which are so common in the chemistry of polyphosphorus compounds based on phosphorus in its lower oxidation states.

In the study reported here, we have investigated the condensation of  $\text{CH}_3\text{PCl}_2$  with  $\text{CH}_3\text{P}(\text{OCH}_3)_2$ —a reaction which should be at least formally similar to the condensation of  $\text{CH}_3(\text{O})\text{PCl}_2$  with  $\text{CH}_3(\text{O})\text{P}(\text{OCH}_3)_2$ , which we have described in a previous study.<sup>5</sup> To round out this work, condensation was also investigated in two systems:  $\text{CH}_3(\text{O})\text{PCl}_2$  vs.  $\text{CH}_3\text{-P}(\text{OCH}_3)_2$  and  $\text{CH}_3(\text{O})\text{P}(\text{OCH}_3)_2$  vs.  $\text{CH}_3\text{PCl}_2$ . In all of these reactions the presence of an organic group ( $\text{CH}_3$ ) bonded to the phosphorus eliminates the possibility of branching in any resulting condensation products.

**Experimental Section**

The <sup>31</sup>P and some of the <sup>1</sup>H nuclear magnetic resonance (nmr)

(1) H. R. Allcock, "Heterocyclic Ring Systems and Polymers," Academic Press, New York, N. Y., 1967.

(2) E. Fluck and H. Binder, *Inorg. Nucl. Chem. Lett.*, **3**, 307 (1967).

(3) V. S. Abramov and S. N. Kofanov, *Tr. Kazan. Khim.-Tekhnol. Inst.*, No. 15, 65 (1950).

(4) J. G. Riess and J. R. Van Wazer, *Inorg. Chem.*, **5**, 178 (1966); see pp 182-183.

(5) D. Grant, J. R. Van Wazer, and C. H. Dungan, *J. Polym. Sci., Part A-1*, **5**, 57 (1967).

measurements were carried out using a Varian XL-100-15 spectrometer equipped with Fourier-transform accessories supplied by Transform Technology, Inc. Most of the <sup>1</sup>H nmr studies were run with a JEOLCO JNM-MH-100 spectrometer. The phosphorus spectra were usually obtained in the Fourier-transform mode using an accumulation of 256 passes, while the proton spectra were taken in the continuous-wave mode, often without signal accumulation. Broad-band proton decoupling and homonuclear indor<sup>6</sup> could be employed separately in the <sup>31</sup>P studies, and the chemical shifts for this nucleus were referenced by the tube-interchange method to 85%  $\text{H}_3\text{PO}_4$ , with negative shifts being downfield. Internal tetramethylsilane was used as the <sup>1</sup>H nmr reference standard, again with negative shifts downfield.

The methylchlorophosphine and methylchlorophosphine oxide were obtained from Edgewood Arsenal. The dimethoxymethylphosphine was prepared from its chloride according to the method of Maier.<sup>7</sup> It should be noted that Maier reported -200.8 ppm for the <sup>31</sup>P nmr chemical shift of this compound for which we have consistently found for repeatedly analyzed preparations a shift of -182.5 ppm for the neat liquid. The  $\text{CH}_3(\text{O})\text{P}(\text{OCH}_3)_2$  was obtained from our laboratory stores and had been made from the rearrangement of trimethyl phosphite with methyl iodide. All of these compounds were finally purified by distillation in a nitrogen atmosphere and exhibited the proper boiling and/or melting points. Both the <sup>31</sup>P and <sup>1</sup>H nmr showed no evidence of impurities in them, except for somewhat less than 1% of some phosphorus-free organic compounds in the dimethoxymethylphosphine.

Hydrolysis was carried out by injecting the sample into a large excess of well-stirred water at room temperature in a nitrogen atmosphere, with the water having previously been deaerated by bubbling with nitrogen for ca. 10 min. The products of hydrolysis were analyzed by both <sup>31</sup>P and <sup>1</sup>H nmr.

In the studies reported herein, weighed quantities of the reactants were combined at -78° in an nmr tube which was then sealed before being allowed to warm to room temperature at which the measurements were carried out. Usually, the first nmr determination was made about 10 min after the sample was removed from the Dry Ice cooling bath. Considerable caution was employed throughout these studies to avoid hydrolysis by moisture and oxidation by the air. Predried nitrogen-filled drybags or dryboxes, always containing phosphorus pentoxide as the dehydrating agent, were employed wherever appropriate.

**Crystalline  $[\text{CH}_3\text{P}(\text{O})]_x$ .** In a typical low-chlorine preparation, 0.78 g (7.22 mol) of  $\text{CH}_3\text{P}(\text{OCH}_3)_2$  and 1.29 g (11 mmol) of  $\text{CH}_3\text{-PCl}_2$  were put into a glass tube at -78° and sealed. After warming to room temperature, good mixing was achieved by shaking. A white crystalline solid began to separate after about 4 hr and its formation was complete in about 20 hr. It was filtered under nitrogen, washed three times with 5-ml portions of degassed carbon tetrachloride, and dried under vacuum; yield 0.28 g; mp 115-118°;

(6) T. Glonek, T. C. Myers, P. Z. Hann, and J. R. Van Wazer, *J. Amer. Chem. Soc.*, **92**, 7214 (1970). For technical details, see R. Freeman and W. A. Anderson, *J. Chem. Phys.*, **37**, 2053 (1962).

(7) L. Maier, *Helv. Chim. Acta*, **46**, 2667 (1963).

soluble in chloroform. The  $^{31}\text{P}$  nmr spectrum showed a broad singlet (ca. 50-Hz width at half-height) at  $-17.1$  ppm, whereas in the  $^1\text{H}$  nmr spectrum there was a doublet at  $-1.64$  ppm, with  $J_{\text{HCP}} = 9.1$  Hz. The molecular weight in chloroform by the vapor pressure osmometric method was 460, corresponding to a value of  $x = 7.4$  in the  $(\text{CH}_3\text{PO})_x$  empirical composition.

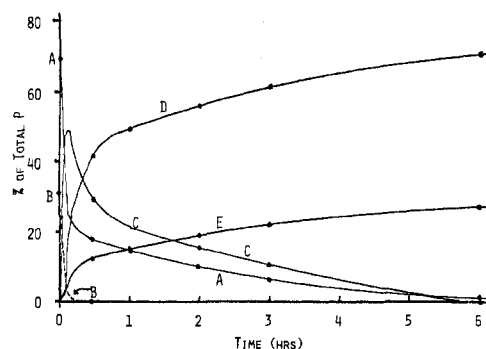
Chlorine analysis showed that the crystalline solid always contained from 3 to 12 wt % Cl depending on its preparation, and careful examination of the  $^1\text{H}$  nmr spectra showed that there were no methoxyl hydrogens ( $<0.2\%$  of total H) and that indeed all of the hydrogens in the sample correspond to the  $\text{CH}_3\text{P}$  moiety. Therefore, we conclude that the chlorine in the product is due to a compound from the family  $\text{Cl}[(\text{CH}_3\text{PO})_m(\text{CH}_3)\text{P}]\text{Cl}$  (without assigning the positions of the oxygen atoms) for  $m \geq 0$ , with the most probable chlorine-contributing contaminant being  $\text{CH}_3\text{P}(\text{OCH}_3)\text{Cl}$ . For a sample low in chlorine, the following data were obtained. *Anal.* Calcd for the empirical formula  $(\text{CH}_3\text{PO})_m(\text{CH}_3\text{P})_n\text{Cl}_2$  for  $n = 31$ : C, 18.85; H, 4.75; P, 48.61; Cl, 3.5. Found: C, 18.6; H, 4.8; P, 48.8; Cl, 3.5.

## Results and Discussion

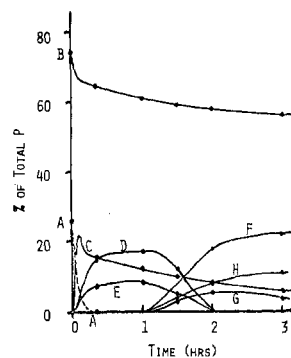
**Reactions of  $\text{CH}_3\text{P}(\text{OCH}_3)_2$  with  $\text{CH}_3\text{P}(\text{OCH}_3)\text{Cl}$ .** Preliminary experiments using various proportions of dichloromethylphosphine with dimethoxymethylphosphine showed that the reaction between these two compounds gives off a noticeable amount of heat at the beginning and that the condensation as measured by methyl chloride elimination progresses substantially within the first hour and is essentially complete in several hours. In the hydrogen-decoupled  $^{31}\text{P}$  nmr spectra, there is a prominent peak appearing at  $-204.5$  ppm which maximizes during the first half hour of the reaction. Without decoupling, the peak is seen to be a septet exhibiting a coupling constant of 13.2 Hz. In the  $^1\text{H}$  spectra, a doublet appearing in the methoxyl region and another in the methylphosphorus region are seen to vary the same way with time and concentration as this  $^{31}\text{P}$  resonance, so that it is fairly certain that this pair of doublets in the  $^1\text{H}$  spectra is associated with the same molecular species. In the  $^1\text{H}$  spectra, the methoxyl doublet exhibits exactly the same area and coupling constant as the methylphosphorus doublet and this coupling constant is identical with the one observed for the septet in the  $^{31}\text{P}$  spectrum. Since HCOP and HCP coupling constants are found to lie in the same range,<sup>8</sup> it is not surprising that they exhibit the very same value in the compound corresponding to these nmr measurements. From the nmr data, it is clear that this compound is the monomeric species resulting from the redistribution of chloro and methoxyl groups according to the equation

$$\text{CH}_3\text{P}(\text{OCH}_3)\text{Cl} + \text{CH}_3\text{P}(\text{OCH}_3)_2 \rightarrow 2\text{CH}_3\text{P}(\text{OCH}_3)\text{Cl} \quad (1)$$

When there was an excess of dimethoxymethylphosphine in the reagent mixture, the proton-decoupled  $^{31}\text{P}$  nmr patterns resulting from the reaction were relatively simple. In addition to the single resonances at  $-182.5$  ppm for  $\text{CH}_3\text{P}(\text{OCH}_3)_2$ ,  $-192.1$  ppm for  $\text{CH}_3\text{P}(\text{OCH}_3)\text{Cl}$ , and  $-204.5$  ppm for  $\text{CH}_3\text{P}(\text{OCH}_3)\text{Cl}$ , there are a series of 12 peaks in the region from  $-64$  to  $-56$  ppm (with chemical shifts of  $-63.8$ ,  $-63.29$ ,  $-63.22$ ,  $-62.57$ ,  $-61.94$ ,  $-61.86$ ,  $-59.9$ ,  $-58.17$ ,  $-58.09$ ,  $-57.3$ ,  $-56.74$ , and  $-56.62$  ppm) and a series of 12 peaks in the region from  $+70$  to  $+86$  ppm (which appear at  $+70.65$ ,  $+74.98$ ,  $+75.73$ ,  $+75.96$ ,  $+76.45$ ,  $+80.02$ ,  $+80.22$ ,  $+81.04$ ,  $+81.15$ ,  $+81.42$ ,  $+85.23$ , and  $+86.13$  ppm). There was also a small peak at  $-140$  ppm (ca. 1-2% of the total P), which appeared early in the reaction and did not change thereafter. Since the areas of the peaks at  $-64$  to  $-56$  ppm and at  $+70$  to  $+86$  ppm were found to increase in proportion to the formation of the methyl chloride (as determined from the proton nmr spectrum), it was clear that they corresponded



**Figure 1.** The course of the reaction at room temperature of an excess of dimethoxymethylphosphine with dichloromethylphosphine. Curve A corresponds to  $\text{CH}_3\text{P}(\text{OCH}_3)_2$ , B to  $\text{CH}_3\text{P}(\text{OCH}_3)\text{Cl}$ , C to  $\text{CH}_3\text{P}(\text{OCH}_3)\text{Cl}$ , D to the  $^{31}\text{P}$  resonances at  $-64$  to  $-56$  ppm, and E to the resonances at  $+70$  to  $+86$  ppm.



**Figure 2.** The course of the reaction at room temperature of an excess of dichloromethylphosphine with dimethoxymethylphosphine. Curve A corresponds to  $\text{CH}_3\text{P}(\text{OCH}_3)_2$ , B to  $\text{CH}_3\text{P}(\text{OCH}_3)\text{Cl}$ , C to  $\text{CH}_3\text{P}(\text{OCH}_3)\text{Cl}$ , D to the  $^{31}\text{P}$  resonances at  $-64$  to  $-56$  ppm, E to the resonances at  $+70$  to  $+86$  ppm, F to the resonance at  $-40$  ppm, G to that at  $-23$  ppm, and H to that at  $-16$  ppm.

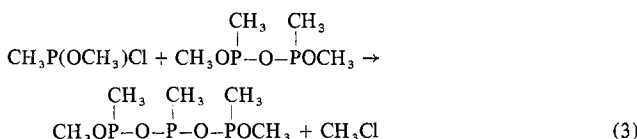
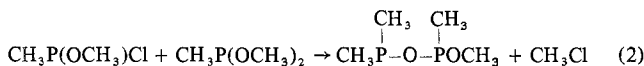
to condensation products. A plot showing the variation of the areas of the various groups of  $^{31}\text{P}$  nmr peaks with time is presented in Figure 1 for a  $\text{CH}_3\text{P}(\text{OCH}_3)_2:\text{CH}_3\text{P}(\text{OCH}_3)\text{Cl}$  reagent ratio of 2.3. As depicted in this figure, the dichloromethylphosphine is promptly exhausted, while it takes about 5 hr for the  $\text{CH}_3\text{P}(\text{OCH}_3)\text{Cl}$  to be used up. Even with this initial 2.3:1 excess of dimethoxymethylphosphine reagent, it should be noted in Figure 1 that very little of this compound remains after ca. 3 hr. Indeed, for any initial  $\text{CH}_3\text{P}(\text{OCH}_3)_2:\text{CH}_3\text{P}(\text{OCH}_3)\text{Cl}$  mole ratio less than ca. 2.1, all of the dimethoxymethylphosphine is found to be incorporated into the condensation products within the first few hours of reaction.

As illustrated by Figure 2, the  $^{31}\text{P}$  nmr spectra show that the first part of the reaction is very much the same when there is an excess of dichloromethylphosphine as when there is an excess of dimethoxymethylphosphine. However, after about 1.5 hr, an additional reaction sets in whereby the condensation products corresponding to the peaks in the region of  $-64$  to  $-56$  ppm and those in the region of  $+70$  to  $+86$  ppm react with the excess dichloromethylphosphine to give a peak at  $-40$  ppm, a pair at  $-23$  ppm, and a very broad one (ca. 100 Hz at half-height) at  $-16$  ppm. Note in Figure 2 that a large excess of dichloromethylphosphine remains when condensation is essentially complete. The preliminary data indicated that for any initial  $\text{CH}_3\text{P}(\text{OCH}_3)_2:\text{CH}_3\text{P}(\text{OCH}_3)\text{Cl}$  mole ratio less than ca. 1.9, there is an excess of dichloromethylphosphine. Thus, the condensation reaction being studied here is somewhat peculiar in that both the  $\text{CH}_3\text{P}(\text{OCH}_3)_2$  and  $\text{CH}_3\text{P}(\text{OCH}_3)\text{Cl}$  are all used up only when their initial

(8) V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5**, 227 (1967).

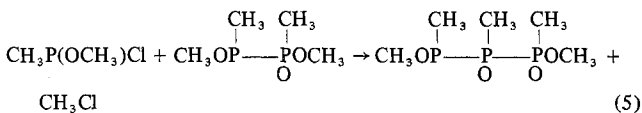
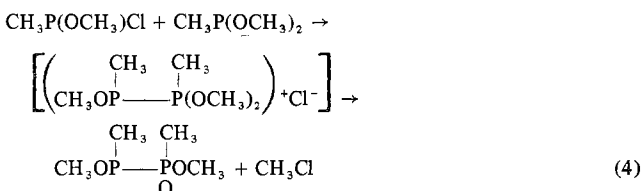
mole ratio is about 2:1. This corresponds to the condensation product being methoxyl-terminated chains averaging around three phosphorus atoms per molecule. It should be noted that we have not observed the formation of any red-to-orange precipitates in any of the compositions studied herein.

From the course of the reaction as shown in the curves of Figures 1 and 2, it is clear that an important condensation step involves the interaction of the  $\text{CH}_3\text{P}(\text{OCH}_3)\text{Cl}$  monomer with the dimethoxymethylphosphine and that the  $\text{CH}_3\text{P}(\text{OCH}_3)\text{Cl}$  further reacts with the resulting condensation products. One possible set of contributing reactions is shown in eq 2 and 3. These reactions which are analogous to



the reactions discussed<sup>5</sup> for the equivalent phosphoryl system  $\text{CH}_3\text{P}(\text{O})\text{PCl}_2-\text{CH}_3\text{P}(\text{O})(\text{OCH}_3)_2$  do not seem to be taking place to any appreciable extent, since a phosphorus atom bearing an electron pair, a methyl group, and two oxygen atoms bridging to other groups ought to exhibit a far-downfield resonance not far from that of the  $\text{CH}_3\text{P}(\text{OR})_2$  resonances which lie in the range of  $-200$  to  $-150$  ppm. Except for the insignificant  $^{31}\text{P}$  resonance appearing at  $-140$  ppm when there is a large excess of  $\text{CH}_3\text{P}(\text{OCH}_3)_2$ , the most negative resonance ( $-64$  ppm) observed for the condensation products is simply not sufficiently downfield to be in accord with the kind of structures represented in eq 2 and 3.

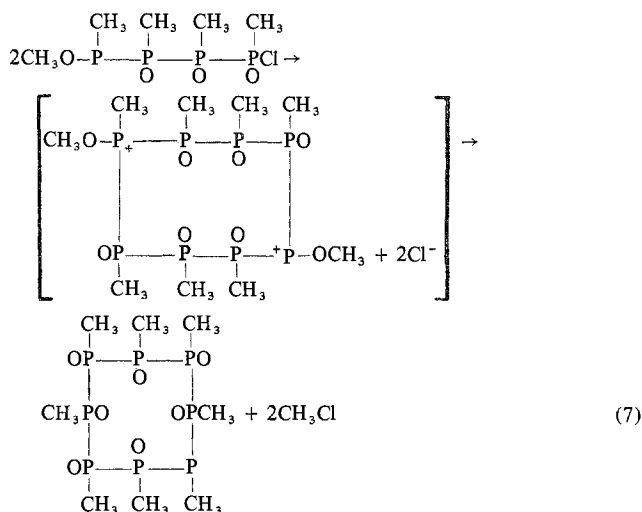
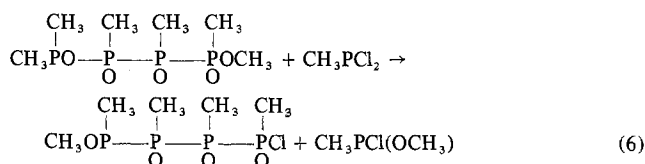
Alternative condensation paths for the reaction between the mixed monomer and the dimethoxymethylphosphine are given in eq 4 and 5. Note that a hypothetical intermediate



is presented in the brackets in eq 4 to show that condensation to give P-P bonded products may exhibit a gross mechanism which is similar to that of the Michaelis-Arbusov<sup>9</sup> rearrangement.

When the condensation between  $\text{CH}_3\text{P}(\text{OCH}_3)_2$  and  $\text{CH}_3\text{P}-\text{Cl}_2$  was carried out with an excess of the latter reagent, there was a slow formation of a crystalline compound exhibiting the empirical formula  $(\text{CH}_3\text{PO})_x$  for  $x = ca. 8$ . (See the Experimental Section for details.) Formation of this compound probably resulted from a cyclization of those suitably sized chain structures which acquired a chlorine termination by exchange with the excess dichloromethylphosphine. Since the average chain length appears to be around 3-4, eq 6 and 7 may be invoked for the formation of  $[\text{CH}_3\text{P}(\text{O})]_8$ .

(9) R. G. Harvey and E. R. De Sombre, *Top. Phosphorus Chem.*, 1, 57 (1964).



As might be expected from the observation that the  $\text{CH}_3\text{P}(\text{OCH}_3)_2:\text{CH}_3\text{P}-\text{Cl}_2$  reagent ratio corresponding to the condensation products remains around 2 even when the proportions of the reagents are widely varied, it is found that the individual  $^{31}\text{P}$  nmr resonances in the  $-64$  to  $-56$  ppm and  $+70$  to  $+86$  ppm regions exhibit area ratios which seem to be quite independent of the degree of condensation or the reagent ratio. In the proton-decoupled  $^{31}\text{P}$  spectra, all of the lines in these two spectral regions appear to be associated with multiplets having coupling constants in the neighborhood of 200 Hz—a value which is commensurate with P-P homonuclear coupling. Except for one example,<sup>2</sup> the published data on phosphorus chemical shifts<sup>8</sup> unfortunately do not encompass a selection of values of the  $^{31}\text{P}$  nmr parameters of phosphorus atoms exhibiting the choice of nearest-neighbor atoms represented by P-P condensation products such as those shown in eq 4 and 5. The exception<sup>2</sup> is found in the compound  $(\text{C}_6\text{H}_5)(\text{CH}_3\text{O})\text{P}_\alpha-\text{P}_\beta(\text{O})(\text{OCH}_3)_2$ , for which  $\delta_\alpha = +50.6$  ppm,  $\delta_\beta = -46.5$  ppm, and  $J_{\text{PP}} = 202$  Hz. From the available  $^{31}\text{P}$  chemical shift information,<sup>2,10</sup> we guess that the region from  $-64$  to  $-56$  ppm may correspond to the methylphosphoryl grouping  $[\text{CH}_3(\text{O})\text{P}<]$  in condensation products of the type shown in eq 4 and 5, whereas the resonances appearing in the region from  $+70$  to  $+86$  ppm are probably due to the methylphosphino ( $\text{CH}_3\text{P}<$ ) grouping. Support for this assignment comes from the fact that the sum of the peak areas in the  $-64$  to  $-56$  ppm region is consistently close to 2.8 times larger than that for the  $+70$  to  $+86$  ppm region. This infers an average of three to four phosphorus atoms per molecule, assuming the kind of structure postulated for the condensation products in eq 4

(10) The following values (ppm) are reported<sup>8</sup> for the methylphosphoryl moiety with the pairs of nearest-neighbor groups indicated:  $ca. -10$  (H, H),  $-63$  ( $\text{CH}_3$ , H),  $-36$  ( $\text{CH}_3$ ,  $\text{CH}_3$ ),  $-41$  ( $\text{CCl}_3$ ,  $\text{OC}_2\text{H}_5$ ),  $-50$  ( $\text{CH}_3$ ,  $\text{OC}_2\text{H}_5$ ),  $-53$  ( $\text{CH}_3$ , OP-),  $-32$  ( $\text{OCH}_3$ ,  $\text{OCH}_3$ ), and  $-23$  ( $\text{OC}_6\text{H}_5$ ,  $\text{OC}_6\text{H}_5$ ). For the methylphosphorus moiety, the following values (ppm) are reported in ref 8:  $+164$  (H, H),  $-20$  (P, P; cyclic),  $+99$  ( $\text{CH}_3$ , H),  $+77$  ( $\text{C}_2\text{H}_5$ , H),  $+60$  [ $\text{CH}_3$ ,  $\text{P}(\text{CH}_3)_2$ ],  $+40$  ( $\text{C}_6\text{H}_5$ , PR<sub>2</sub>),  $+62$  ( $\text{CH}_3$ ,  $\text{CH}_3$ ),  $+34$  ( $\text{C}_2\text{H}_5$ ,  $\text{C}_2\text{H}_5$ ), and  $-201$  ( $\text{OCH}_3$ ,  $\text{OCH}_3$ ). And for the phenylphosphorus moiety the following values are reported in ref 2:  $+64$  ppm,  $J_{\text{PP}} = ca. 163$  Hz ((RO)<sub>2</sub>(O)P-, (RO)<sub>2</sub>(O)P-); and  $+46$  ppm,  $J_{\text{PP}} = ca. 207$  Hz ((RO)(R)(O)P-, (RO)(R)(O)P-).

and 5. The broad singlet at  $-17.1$  ppm for the  $[\text{CH}_3\text{P}(\text{O})]_x$  compound is indicative of a cyclic structure having several conformers with P-P bonding in the ring, *i.e.*, the  $[-(\text{CH}_3)\text{P}(\text{O})-]_{ca.8}$  ring molecule, as previously suggested.

In the  $^1\text{H}$  spectra of the condensation products giving  $^{31}\text{P}$  resonances in the ranges from  $-64$  to  $-56$  ppm and from  $+70$  to  $+86$  ppm, there does seem to be some variation between individual peak areas in the respective  $^1\text{H}$  spectra. For these  $^1\text{H}$  spectra, there are six cleanly identifiable doublets in the methoxyl region while the methylphosphorus region exhibits considerably greater complexity. The coupling constants corresponding to the methoxyl region doublets are in the usual HCOP range around 11 Hz. The ratio of the sum of the methylphosphorus peak areas to that of the methoxyl areas seems to remain quite constant at  $1.44 \pm 0.07$ , regardless of the initial reagent ratio or the reaction time. Assuming only chains with methoxyl termination on each end, this ratio corresponds to an average number of phosphorus atoms per molecule of 2.9.

In order to adduce the structure of the condensation products from chemical evidence, a mixture prepared in the ratio of 2 mol of  $\text{CH}_3\text{P}(\text{OCH}_3)_2$  to 1 of  $\text{CH}_3\text{PCl}_2$  was hydrolyzed after the reaction had proceeded to the point at which the  $^{31}\text{P}$  spectra showed only the condensation products. The results are presented in the second column of Table I. An important feature of the observations reported in Table I is that all of the hydrolysis products correspond to a single methoxyl group bonded directly to a phosphorus. This finding shows that in either the condensation or the hydrolysis reactions, there is no making or breaking of C-P bonds. Furthermore, the hydrolysis results rule out oxygen-bridged condensation products such as indicated in eq 2 and 3, since these products should form nothing but  $\text{CH}_3(\text{O})\text{PH}(\text{OH})$  upon complete hydrolysis. The presence of 9% of  $\text{CH}_3(\text{O})\text{P}(\text{OCH}_3)(\text{OH})$  in the observed hydrolysis products indicates that the P-O-C linkage is somewhat less readily hydrolyzable than the P-P linkage in the condensation products. Increasing the hydrolysis rate by boiling the samples caused all of the  $\text{CH}_3(\text{O})\text{P}(\text{OCH}_3)(\text{OH})$  to convert to  $\text{CH}_3(\text{O})\text{P}(\text{OH})_2$ . Assuming no redistribution to occur during hydrolysis, we have figured out that the products resulting from a random attack by the water on a  $\text{CH}_3\text{O}(\text{CH}_3)\text{P}[-(\text{CH}_3)\text{P}(\text{O})-]_n\text{OCH}_3$  chain of any length or any sized  $[-(\text{CH}_3)\text{P}(\text{O})-]_n$  ring gives the same proportions of hydrolysis products, as shown in third column of Table I. Obviously the hydrolysis reaction deviates from random kinetics.

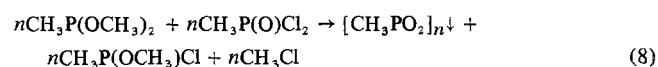
**Reaction of  $\text{CH}_3\text{P}(\text{OCH}_3)_2$  with  $\text{CH}_3\text{X}$ .** Since methyl chloride is formed during the condensation process, it seemed desirable to carry out an exploratory study of the rate at which it would bring about the Michaelis-Arbusov rearrangement<sup>7</sup> of dimethoxymethylphosphine to give methyl dimethylphosphinate which exhibits a  $^{31}\text{P}$  nmr chemical shift of  $-50.5$  ppm. When 6.1 mmol of dimethoxymethylphosphine was combined with 9.3 mmol of methyl chloride at room temperature, about 14 days was required for complete conversion of the  $\text{CH}_3\text{P}(\text{OCH}_3)_2$  to  $(\text{CH}_3)_2\text{P}(\text{O})\text{OCH}_3$ . The rate data indicated that the reaction is formally zero-order and exhibits a conversion rate of  $7.4 \pm 0.9\%$ /day. When methyl iodide was substituted for the methyl chloride, the reaction was found to be complete before the first nmr measurement could be made. Because of the rapid rate involved, considerable heating of the reaction mixture was observed.

**Reaction between the  $\text{CH}_3\text{P}(\text{O})\text{<}$  and  $\text{CH}_3\text{P}<$  Moieties.** When an excess of dimethoxymethylphosphine with di-

Table I. Hydrolysis Products Resulting from the Primary Condensation Products

Hydrolysis product	% obsd	% calcd
$\text{CH}_3(\text{O})\text{PH}_2$	28	25
$\text{CH}_3(\text{O})\text{PH}(\text{OH})$	32	50
$\text{CH}_3(\text{O})\text{P}(\text{OH})_2$	31	} 25
$\text{CH}_3(\text{O})\text{P}(\text{OCH}_3)(\text{OH})$	9	

chloromethylphosphine oxide is warmed to room temperature after mixing at  $-78^\circ$ , it is seen that the solid  $\text{CH}_3\text{-POCl}_2$  dissolves in the  $\text{CH}_3\text{P}(\text{OCH}_3)_2$  with concomitant heating of the resulting neat mixture to *ca.*  $80-90^\circ$  in a 5-mm nmr tube. A  $^1\text{H}$  nmr measurement made 10 min after mixing shows the presence of only  $\text{CH}_3\text{P}(\text{OCH}_3)\text{Cl}$  and  $\text{CH}_3\text{-Cl}$ . On careful examination, it was seen that a transparent solid coating had uniformly covered the surface of the nmr tube exposed to the liquid, thus effectively thickening the tube wall without affecting the nmr spectrum of the liquid phase. This film, which may be broken into little pieces by shaking of the tube, is slightly soluble in chloroform and exhibits a broad  $^1\text{H}$  resonance at  $-2.1$  ppm. Upon its complete hydrolysis, only methylphosphonic acid is observed. These data show that the transparent solid coating formed during the reaction consists of polymeric<sup>5</sup>  $\text{CH}_3\text{PO}_2$ . This means that the rapid part of the overall reaction consists of redistribution of Cl vs.  $\text{OCH}_3$  plus a fast condensation of the resulting  $\text{CH}_3(\text{O})\text{P}(\text{OCH}_3)\text{Cl}$ , as shown in eq 8. The  $\text{CH}_3\text{P-}$



$(\text{OCH}_3)\text{Cl}$  thus formed undergoes further condensation with the  $\text{CH}_3\text{P}(\text{OCH}_3)_2$  as described earlier. As would be expected, rearrangement of  $\text{CH}_3\text{P}(\text{OCH}_3)_2$  into  $(\text{CH}_3)_2\text{P}(\text{O})(\text{OCH}_3)$  was observed when the reaction had proceeded for a period of days. The rate of this rearrangement was consistent with the rate observed in the reaction of pure  $\text{CH}_3\text{P}(\text{OCH}_3)_2$  with methyl chloride.

Upon mixing the two liquids dichloromethylphosphine with dimethyl methylphosphonate, there was no immediate reaction, and less than 10% of the reagent present in the smaller amount was found to have reacted within 24 hr at room temperature. There was no evidence for redistribution of the chloro and methoxyl groups between the  $\text{CH}_3\text{P}<$  and the  $\text{CH}_3\text{P}(\text{O})\text{<}$  moieties. However, the observed slow condensation led to a series of  $^{31}\text{P}$  and  $^1\text{H}$  nmr peaks which were different from those observed previously. At the beginning of the reaction, a series of four peaks (two large and two small) appeared in the region from  $-20$  to  $-25$  ppm in the  $^{31}\text{P}$  spectrum. As these peaks continued to grow, they were joined by a number of resonances in the range from  $-12$  to  $-16$  ppm and later by some peaks in the  $-35$  to  $-50$  ppm region. During the progress of this reaction, it was observed that the  $\text{CH}_3\text{P}(\text{O})(\text{OCH}_3)_2$  was used up to approximately twice the rate as the  $\text{CH}_3\text{PCl}_2$ . Furthermore, this system exhibited the normal behavior whereby the relative areas of the nmr peaks varied with the ratio of the reagents employed.

It seems from this set of studies that at equilibrium the redistribution of chloro and methoxyl groups between the  $\text{CH}_3\text{P}<$  and the  $\text{CH}_3\text{P}(\text{O})\text{<}$  moieties corresponds to essentially all of the methoxyl groups on the latter. When  $\text{CH}_3\text{P}(\text{OCH}_3)_2$  and  $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$  are the reagents, the condensation following the redistribution reaction leads to condensation products based on the  $\text{CH}_3\text{P}<$  moiety which are entirely separate from those based on the  $\text{CH}_3\text{P}(\text{O})\text{<}$  moieties. This

partitioning of the products results, at least in part, from the observed phase separation as well as from the large difference in the condensation rates. On the other hand, it appears that when  $\text{CH}_3\text{PCl}_2$  undergoes condensation with  $\text{CH}_3\text{P}(\text{O})(\text{O}-\text{CH}_3)_2$ , mixed products are formed. However, these molecular structures do not seem to correspond to regular alternation,<sup>11</sup> since more of the  $\text{CH}_3\text{P}(\text{O})$  than the  $\text{CH}_3\text{P}$  moiety is consistently incorporated into the products formed during condensation.

**Acknowledgment.** We wish to thank the National Science Foundation (Grant GP-28698X) for partial financial support of this work.

**Registry No.**  $\text{CH}_3\text{PCl}_2$ , 676-83-5;  $\text{CH}_3\text{P}(\text{O})(\text{OCH}_3)_2$ , 20278-51-7;  $\text{CH}_3\text{P}(\text{O})(\text{OCH}_3)\text{Cl}$ , 51934-48-6;  $\text{CH}_3\text{OP}(\text{CH}_3)\text{P}(\text{O})(\text{CH}_3)\text{OCH}_3$ , 51934-49-7;  $(\text{CH}_3\text{PO})_8$ , 51934-50-0;  $\text{CH}_3\text{Cl}$ , 74-87-3;  $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$ , 676-97-1;  $\text{CH}_3\text{P}(\text{O})(\text{OCH}_3)_2$ , 756-79-6.

(11) J. R. Van Wazer and S. H. Cook, *Inorg. Chem.*, **12**, 909 (1973).

Contribution from the School of Chemistry,  
Georgia Institute of Technology, Atlanta, Georgia 30332

## Reaction of Alkali Metal Hydrides with Zinc Halides in Tetrahydrofuran. A Convenient and Economical Preparation of Zinc Hydride

JOHN J. WATKINS and E. C. ASHBY\*

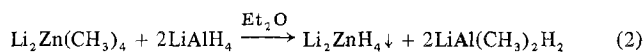
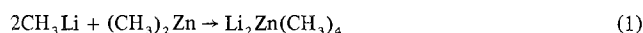
Received March 14, 1974

AIC401760

A convenient and economical preparation of  $\text{ZnH}_2$  is reported. The reaction of  $\text{KH}$  with  $\text{ZnCl}_2$  in 1:2, 1:1, 2:1, and 3:1 molar ratios has been investigated. In these reactions zinc hydride and  $\text{KCl}$  are initially formed; however, the  $\text{KCl}$  reacts further with  $\text{ZnCl}_2$  to form  $\text{KZn}_2\text{Cl}_5$  and  $\text{K}_2\text{ZnCl}_4$ . The reaction of  $\text{NaH}$  with  $\text{ZnCl}_2$  in 1:1 molar ratio forms only  $\text{ZnH}_2$  and  $\text{NaCl}$ . Likewise, the reaction of  $\text{LiH}$  with  $\text{ZnBr}_2$  and  $\text{NaH}$  with  $\text{ZnI}_2$  in 2:1 molar ratio produced only  $\text{ZnH}_2$  and the corresponding alkali metal halide. A more thermally stable form of  $\text{ZnH}_2$ , which is also more reactive than that prepared by any of the known methods, is produced in these reactions.

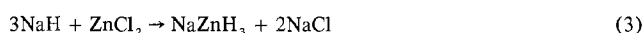
### Introduction

We have been interested for some time in the preparation of complex metal hydrides where the central metal atom is other than boron or aluminum. Since  $\text{NaBH}_4$  and  $\text{LiAlH}_4$  have become such important reagents in synthetic organic chemistry, it would seem important to evaluate complex metal hydrides of other main-group elements for their possible stereoselective properties as reducing agents. In this connection we have reported the preparation of  $\text{KMgH}_3$ ,<sup>1</sup>  $\text{Li}_2\text{ZnH}_4$ ,<sup>2</sup>  $\text{LiCuH}_2$ ,<sup>3</sup> and other complex metal hydrides by the reaction of the corresponding "ate" complex with  $\text{LiAlH}_4$  (e.g., eq 1 and 2).<sup>2</sup> This synthetic scheme has turn-



ed out to be quite good since the complex metal hydride is insoluble in ether and the lithium dimethyldihydroaluminumate is soluble. Thus, the separation of product from by-product is easy and the reaction proceeds in quantitative yield.

It is clear that a more convenient and economical method for the preparation of these compounds would involve the reaction of an alkali metal hydride with the group II metal hydride (e.g., eq 3). This scheme is reasonable since both



$\text{NaBH}_4$  and  $\text{LiAlH}_4$  can be prepared in this manner,<sup>4,5</sup> i.e.

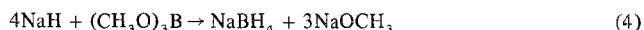
(1) E. C. Ashby, R. Kovar, and R. Arnott, *J. Amer. Chem. Soc.*, **92**, 2182 (1970).

(2) E. C. Ashby and J. J. Watkins, *Inorg. Chem.*, **12**, 2493 (1973).

(3) E. C. Ashby, T. Korenowski, and R. Schwartz, *J. Chem. Soc., Chem. Commun.*, in press.

(4) A. E. Finholt, A. C. Bond, and H. F. Schlesinger, *J. Amer. Chem. Soc.*, **69**, 1199 (1947).

(5) H. F. Schlesinger, H. C. Brown, H. R. Hoekstra, and L. R. Rapp, *J. Amer. Chem. Soc.*, **75**, 199 (1953).



The purpose of this study, therefore, was to prepare complex metal hydrides of zinc (e.g.,  $\text{KZnH}_3$ ,  $\text{K}_2\text{ZnH}_4$ ,  $\text{K}_3\text{ZnH}_5$ , etc.) by the reaction of an alkali metal hydride with zinc chloride, bromide, or iodide. The hope was that even if such complex metal hydrides could not be prepared by this method, it may be possible to prepare  $\text{ZnH}_2$  and/or  $\text{HZnX}$  compounds and, in addition, elucidate the chemistry of reactions of alkali metal hydrides with zinc halides.

### Experimental Section

**Apparatus.** Reactions were performed under nitrogen using Schlenk tube techniques.<sup>6</sup> Filtrations and other manipulations were carried out in a glove box equipped with a recirculating system.<sup>7</sup>

X-Ray powder data were obtained on a Philips-Norelco X-ray unit using a 114.6-mm camera with nickel-filtered  $\text{Cu K}\alpha$  radiation.

Samples were sealed in 0.5-mm capillaries and exposed to X-rays for 6 hr.  $d$  spacings were read on a precalibrated scale equipped with viewing apparatus. Intensities were estimated visually.

**Analytical Work.** Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.<sup>8</sup> Alkali metals were determined by flame photometry. Aluminum was determined by EDTA titration. Zinc in the presence of aluminum was determined by masking the aluminum with triethanolamine and titrating the zinc with EDTA. Zinc alone was determined by EDTA titration. Halide was determined by the Volhard procedure.

**Materials.** Potassium and sodium hydride were obtained from Alfa Inorganics as a slurry in mineral oil. Lithium hydride was prepared by hydrogenolysis of *tert*-butyllithium at 4000 psig for 24 hr. A solution of lithium aluminum hydride (Ventron, Metal Hydride Division) was prepared in tetrahydrofuran in the usual manner. Anhydrous zinc chloride, bromide, and iodide were obtained from Fisher Scientific. Tetrahydrofuran (Fisher Certified reagent grade)

(6) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

(7) E. C. Ashby and R. D. Schwartz, *J. Chem. Educ.*, **51**, 65 (1974).