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Study of the Condensation to Oligomers Containing Oxygen-Bridged Methylphosphonyl and Dimethylsilyl Moieties[1]

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Proton nuclear magnetic resonance has been employed to study the reactions and reaction products resulting from mixing various combinations of the four reagents $(CH_3)_2SiCl_2$, $(CH_3)_2Si(OCH_3)_2$, $CH_3(O)PCl_2$, and $CH_3(O)P(OCH_3)_2$. In these reactions, condensation of a methoxyl group with a chloro group, with elimination of methyl chloride, gives bridging oxygens in oligomeric molecules. It is found that when $(CH_3)_2Si(OCH_3)_2$ is combined with $CH_3(O)PCl_2$, the reaction is slow with the first lengthy step being exchange of a chlorine on the phosphorus for a methoxyl group on the silicon. On the other hand, when $(CH_3)_2SiCl_2$ is combined with $CH_3(O)P(OCH_3)_2$, condensation starts immediately and is essentially complete by the time condensation begins in the other mixture. The products from this latter combination appear to consist of oligomers in which the oxygen-bridged silicon and phosphorus atoms strictly alternate.

Introduction

In spite of the fact that considerable effort has been expended on the study of condensation polymerization of silicon compounds and of phosphorus compounds to give oxygen-bridged oligomers, the literature on condensations to give the mixed species is practically nonexistent.[2,3] In this study we chose to investigate the condensation process in which a methoxyl group on one molecule reacts with a chloro group on another to give methyl chloride plus an oxygen bridge since, in a prior study[4] from our group, the condensation of dimethyl methylphosphonate with methylphosphonic dichloride appeared to reach equilibrium in *ca.* 100 hr at 35° and exhibited unusually interesting reaction products.

Probably the reason that condensation to give oxygen-bridged structures based on the methylphosphonyl, $CH_3(O)P<$, and dimethylsilyl, $(CH_3)_2Si<$, groups has not previously been studied is the complexity of the reaction products. However, this problem has been treated for equilibrated mixtures in previous papers[5-8] from our group, and both equilibrium and kinetics are reasonably approachable with the use of the ideas inherent in stochastic graph theory.[9]

Experimental Section

The reagents and the general procedures used in this study have been previously described.[4,10] The nmr measurements were carried out partly on a Varian A-60 and partly on a Jeol JNM-MH-100 spectrograph, with referencing to tetramethylsilane. The distillations were made in a spinning-band vacuum still at pressures as low as 8 mm. Column chromatography was effected in a 10-ml buret using Merck 71707 aluminum oxide or Fisher S-157 silica gel. In the chromatographic studies, the sample was put on the top of the carbon tetrachloride saturated column, which was eluted with carbon tetrachloride over a period of 2 hr, with about 13 15-ml fractions being collected.

Results and Discussion

Nmr Assignments. The various nmr peaks which can be resolved are reported in Table I for the system under study. Note that the nmr spectrum is divided into three major groups: In the region from +0.5 to −1.0 ppm are found the proton resonances corresponding to the methyl groups bonded to silicon; from −1.3 to −2.5 ppm the resonances are due to methyl groups bonded to phosphorus, and from −3.0 to −4.0 ppm to the methoxyl groups. Furthermore, the methyl phosphorus region is also divided into two separate groups, with the upfield one corresponding to phosphorus with two bridging oxygens and the lower to phosphorus with one or two chlorine atoms bonded to it.

Because of coupling to the phosphorus atom, all of the proton resonances corresponding to methyl groups directly bonded to phosphorus show up as doublets, with a coupling constant of 16.4–18.5 Hz. This splitting clearly delineates the CH_3P region of the spectra from the other two regions. Although some of the resonances listed in Table I were specified by use of pure isolated compounds, many of the assignments given in this table were made through material-balance calculations on spectra that did not show a large number of peaks. Thus, when a sharp resonance was observed along with other previously identified resonances, intercomparison of the measured amounts of reagents, the amount of methyl chloride formed in the sealed nmr tube, and the nmr peak areas were often sufficient to identify the unknown peak with respect to the arrangement of oxygen-bridged neighboring $(CH_3)_2Si<$ and $CH_3(O)P<$ groups.

With due allowance for small changes due to differing molecular environments (solvent effects), the chemical shifts given in Table I agree with those previously published, the values of which were helpful in making our nmr assignments. From one composition to another, the "solvent effect" was never more than ±0.08 ppm, with the presence of chloro end groups tending to cause the chemical shifts to appear downfield as compared to the presence of methoxyl end groups.

Kinetic Studies. When an excess of dimethoxydimethylsilane is combined with methylphosphonic dichloride at 26°, the proton nmr shows that the process during the first 12 hr consists practically exclusively of an exchange of chloro for methoxyl groups to form the compounds chloromethoxydimethylsilane and methyl methylphosphonochloridate, according to eq 1. Starting about the time when condensa-

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[2] T. Alfrey, F. J. Honn, and H. Mark, *J. Polym. Sci.*, 1, 102 (1946); M. G. Voronkov, *Zh. Obshch. Khim.*, 25, 469 (1955); A. P. Kreshkov and D. A. Karateyev, *ibid.*, 27, 2715 (1957).

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[5] J. R. Van Wazer and K. Moedritzer, *J. Amer. Chem. Soc.*, 90, 47 (1968).

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[8] K. Moedritzer, *Ann. N. Y. Acad. Sci.*, 156 (1), 299 (1969).

[9] D. W. Matula, L. C. D. Groenweghe, and J. R. Van Wazer, *J. Chem. Phys.*, 41, 3105 (1964).

[10] K. Moedritzer and J. R. Van Wazer, *J. Amer. Chem. Soc.*, 86, 802 (1964).

Table I. Proton Nmr Data[a]

Structure	δ_H	$^2J_{PH}$
CH_3Si Spectral Region		
$(CH_3)_2Si(OCH_3)_2$	+0.20	
$(CH_3O)(CH_3)_2Si$- end	−0.25	
$(CH_3)_2Si<$ middle	−0.42	
$Cl(CH_3)_2Si$- end	−0.67	
$(CH_3)_2SiCl_2$	−0.77	
CH_3P Spectral Region		
$CH_3(O)P(OCH_3)_2$	−1.38	17.9
$(CH_3O)(CH_3)(O)P$- end (to Si)[b]	−1.44	18.2
$CH_3(O)P<$ middle (to 2Si)	−1.51	18.3
$(CH_3O)(CH_3)(O)P$- end (to P)	−1.60	18.8
$[(CH_3O)_2(CH_3)(O)P]_2O$ (end)	−1.60	18.4
$CH_3(O)P<$ middle (to 2P)	−1.65	18.5
$CH_3(O)P<$ middle (to P and to Si)	−1.64	18.5
$Cl(CH_3)(O)P$- end (to Si)	−1.98	18.2
$Cl(CH_3)(O)P$- end (to P)	−2.25	18.2
$CH_3(O)PCl_2$	−2.53	16.4
CH_3O Spectral Region		
$(CH_3)_2Si(OCH_3)_2$	−3.25	
$(CH_3O)(CH_3)_2Si$- end	−3.42	
$CH_3(O)P(OCH_3)_2$	−3.65	11.4
$(CH_3O)(CH_3)(O)P$- end (to Si)	−3.66	12.5
$(CH_3O)(CH_3)(O)P$- end (to P)	−3.72	13.5

[a] δ is the proton chemical shift in ppm referenced to tetramethylsilane with positive values being upfield and $^2J_{PH}$ refers to the coupling constant in Hz for the coupling between the phosphorus and the hydrogen of the immediately bonded methyl group. [b] The note in parentheses indicates that the particular group is connected by an oxygen bridge to either a silicon or phosphorus as specified.

$$(CH_3)_2Si(OCH_3)_2 + CH_3(O)PCl_2 \rightarrow (CH_3)_2Si(OCH_3)Cl + CH_3(O)P(OCH_3)Cl \qquad (1)$$

tion begins (*ca.* 12 hr in Figure 1), there is a further scrambling of methoxyl for chlorine groups, as indicated by eq 2, to form dimethyl methylphosphonate.

$$(CH_3)_2Si(OCH_3)_2 + CH_3(O)P(OCH_3)Cl \rightarrow (CH_3)_2Si(OCH_3)Cl + CH_3(O)P(OCH_3)_2 \qquad (2)$$

The first building unit of a condensed species to become significant is the methoxyl-terminated silicon end group, $(CH_3O)(CH_3)_2Si$-, which seems necessarily to be attributable to the following reaction at the beginning of the process when it first appears in appreciable quantities

$$(CH_3)_2Si(OCH_3)_2 + (CH_3)_2Si(OCH_3)Cl \rightarrow (CH_3O)(CH_3)_2SiOSi(CH_3)_2(OCH_3) + CH_3Cl \qquad (3)$$

The chloro-terminated phosphorus end group, $Cl(CH_3O)P$–, appears early in the condensation process but never grows to represent an appreciable fraction of the total number of building units present. It may be accounted for by reactions such as those of eq 4 and 5. The methoxyl-terminated phosphorus end group may be formed from the reactions of eq 6 and 7. It should be noted in Figure 1 that at about 21 hr, the concentration of dimethyl methylphosphonate drops off. A reaction which may well contribute to this is presented as eq 8.

$$2CH_3(O)P(OCH_3)Cl \rightarrow (Cl)(CH_3)(O)POP(O)(CH_3)(OCH_3) + CH_3Cl \qquad (4)$$

$$(CH_3)_2Si(OCH_3)Cl + CH_3(O)P(OCH_3)Cl \rightarrow (CH_3O)(CH_3)_2SiOP(O)(CH_3)Cl + CH_3Cl \qquad (5)$$

$$(CH_3)_2Si(OCH_3)_2 + CH_3(O)P(OCH_3)Cl \rightarrow (CH_3O)(CH_3)_2SiOP(O)(CH_3)(OCH_3) + CH_3Cl \qquad (6)$$

$$CH_3(O)P(OCH_3)_2 + CH_3(O)P(OCH_3)Cl \rightarrow (CH_3O)CH_3(O)POP(O)CH_3(OCH_3) + CH_3Cl \qquad (7)$$

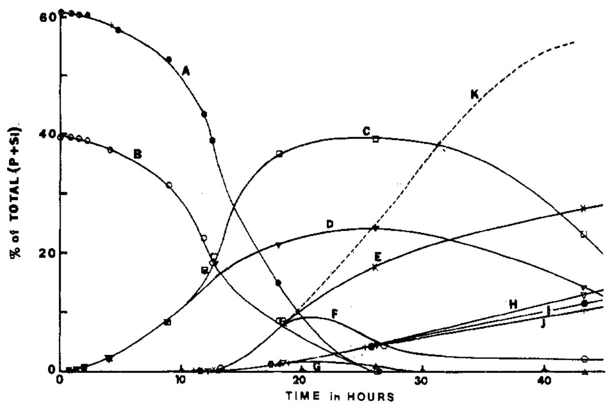
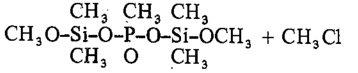


Figure 1. The condensation of methylphosphonic dichloride with an excess of dimethoxydimethylsilane at 26°, as determined by proton nmr: A, $(CH_3)_2Si(OCH_3)_2$; B, $CH_3(O)PCl_2$; C, $(CH_3)_2Si(OCH_3)Cl$; D, $CH_3(O)P(OCH_3)Cl$; E, $(CH_3O)(CH_3)_2Si$- end group; F, $CH_3(O)P(OCH_3)_2$; G, $Cl(CH_3)(O)P$- end group; H, $(CH_3O)CH_3(O)P$- end group; I, $CH_3(O)P$ middle group; J, $(CH_3)_2Si$ middle group. Curve K corresponds to the degree of condensation as calculated from the methyl chloride eliminated.

$$(CH_3)_2Si(OCH_3)Cl + CH_3P(O)(OCH_3)_2 \rightarrow (CH_3O)(CH_3)_2SiOP(O)(CH_3)(OCH_3) + CH_3Cl \qquad (8)$$

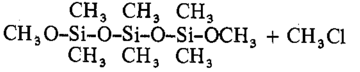
One of the many reactions which can be written to account for the build-up of phosphorus middle groups, $CH_3(O)P<$, is given as eq 9. This reaction was chosen so that it would not only explain the build-up of the phosphorus middle groups but also the continuing increase in the concentration of the methoxyl-terminated silicon end groups. One of the many reactions which might be postulated to account for the build up of silicon middle-groups, $(CH_3)_2Si<$, is shown as eq 10, which was chosen so as to contribute also to the increase in methoxyl-terminated silicon end groups.

$$(CH_3O)(CH_3)_2SiOP(O)(CH_3)(OCH_3) + (CH_3)_2Si(OCH_3)Cl \rightarrow$$



$$\mathrm{CH_3O{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}\underset{O}{\overset{CH_3}{P}}{-}O{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}OCH_3 + CH_3Cl} \qquad (9)$$

$$(CH_3O)(CH_3)_2SiOSi(CH_3)_2(OCH_3) + (CH_3)_2Si(OCH_3)Cl \rightarrow$$



$$\mathrm{CH_3O{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}OCH_3 + CH_3Cl} \qquad (10)$$

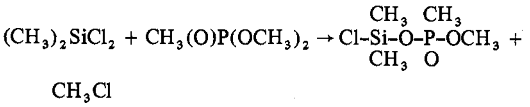
It is obvious that, in order to account fully for the concentration changes in the various silicon- and phosphorus-based building units occurring after 25 hr in Figure 1, a large number of condensation reactions will have to be invoked. Furthermore, the curves of Figure 1 offer no strong qualitative argument as to whether or not there are methoxyl-terminated methylphosphonodimethylsiloxane oligomers (*i.e.*, mixed-backbone structures). Indeed, the rapid early rise of the proportion of silicon present as methoxyl-terminated silicon end groups might possibly lead one to believe that the products resulting from the overall condensation process are a mixture of methoxyl-terminated dimethylsiloxanes and methoxyl-terminated methylphosphonoxanes, so that there would be no molecules having mixed silicon-phosphorus backbones. Careful inspection of the proton nmr spectra indicates that this is not true, because resonances corresponding to phosphorus atoms bonded to one or two silicons through bridging oxygens can be observed. However, as soon as condensation had proceeded appreciably, most of the nmr resonances broadened considerably to exhibit a peak width at half-height of 2-3 Hz, so that it was not possible to determine what proportion of the molecules had such mixed backbones.

Although there is surprisingly little literature on the condensation polymerization of siloxanes with elimination of an alkyl halide, the available evidence[11] indicates that this is a slow process at room temperature in the absence of a catalyst such as ferric or aluminum chloride. This information casts doubt on those reactions (such as are shown in eq 3 and 10) which form phosphorus-free siloxanes, since it seems very difficult to conceive of a catalytic action of the phosphorus-based structures that would not result in the addition to or presence in the silicon-containing molecule of a phosphorus group. Since the early prominence of the methoxyl-terminated silicon end group in the plot of Figure 1 does not seem to be explainable by a reaction other than the silane condensation of eq 3, it would be desirable to carry out a detailed investigation of the reaction between dimethoxydimethylsilane and dichlorodimethylsilane, particularly in view of the fact that the reported work[11] deals with elimination of ethyl chloride, with phenyl as well as methyl substitution on the silicon.

The dotted line in Figure 1 represents the degree of condensation as calculated from the amount of methyl chloride observed in the sealed nmr tube in which the reaction was carried out. A degree of condensation of 100% corresponds to elimination of all possible methyl chloride.

The kinetic data presented in Figure 2 represent a situation (also studied at 26°) in which initially the chlorine is on the phosphorus and the methoxyl on the silicon. Again, there is an excess of methoxyl over chlorine, so that all chain molecules obtained after complete condensation are methoxyl terminated.

Unlike the situation of Figure 1, it should be noted that there is no evidence in the reaction of Figure 2 for the scrambling of methoxyl with chloro groups. Instead condensation starts immediately! The condensation process which appears to account completely for the initial rate process is shown as eq 11. This equation explains the con-



$$\mathrm{(CH_3)_2SiCl_2 + CH_3(O)P(OCH_3)_2 \rightarrow Cl\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\underset{O}{\overset{CH_3}{P}}\text{-}OCH_3 +}$$
$$\mathrm{CH_3Cl} \qquad (11)$$

comitant build-up of the methoxyl-terminated phosphorus end group and the chloro-terminated silicon end group. Since the nmr resonance for these two end groups is very sharp in the first 0.5 hr of reaction and since the CH_3P chemical shift is different from that obtained from the symmetrical $[(CH_3O)(CH_3)(O)P]_2O$ molecule, it seems quite convincing that the first species to be formed by this pair of reagents is the mixed silicon-phosphorus di molecule shown as the product of eq 11, which may be called chlorodimethylsilyl methyl methylphosphonate. Because the chloro-terminated silicon end group does not continue to rise as does the methoxyl-terminated phosphorus end group, it is clear that chlorodimethylsilyl methyl methylphosphonate must react further at the silicon-bonded chloro group.

Because the rate of diminution of dimethyl methylphosphonate is faster than that of the dichlorodimethylsilane in the region of 1 hr of elapsed time in Figure 1, we assume that chlorodimethylsilyl methyl methylphosphonate further reacts with dimethyl methylphosphonate as shown in eq 12.

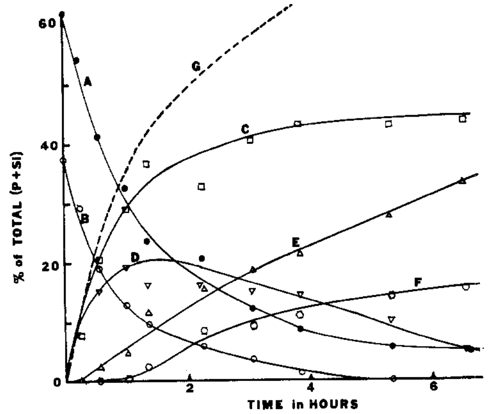
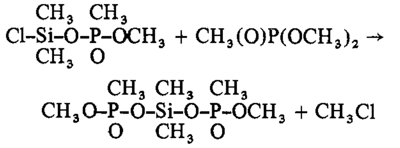
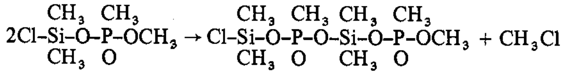


Figure 2. The condensation of dichlorodimethylsilane with an excess of dimethyl methylphosphonate at 26° as determined by proton nmr: A, $CH_3(O)P(OCH_3)_2$; B, $(CH_3)_2SiCl_2$; C, $(CH_3O)(CH_3)$-(O)P- end group attached through a bridging oxygen to silicon; D, $Cl(CH_3)_2Si$- end-group; E, $(CH_3)_2Si$ middle group; F, $CH_3(O)P$ middle group attached on both sides through bridging oxygens to silicon. Curve G corresponds to the degree of condensation as calculated from the methyl chloride eliminated.

Another possible reaction at the beginning of this process is the self-condensation of chlorodimethylsilyl methyl methylphosphonate, as indicated in eq 13.



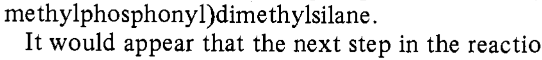
$$\mathrm{Cl\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\underset{O}{\overset{CH_3}{P}}\text{-}OCH_3 + CH_3(O)P(OCH_3)_2 \rightarrow}$$
$$\mathrm{CH_3O\text{-}\underset{O}{\overset{CH_3}{P}}\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\underset{O}{\overset{CH_3}{P}}\text{-}OCH_3 + CH_3Cl} \qquad (12)$$



$$\mathrm{2Cl\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\underset{O}{\overset{CH_3}{P}}\text{-}OCH_3 \rightarrow Cl\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\underset{O}{\overset{CH_3}{P}}\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\underset{O}{\overset{CH_3}{P}}\text{-}OCH_3 + CH_3Cl} \qquad (13)$$

In the nmr measurement made about 0.5 hr after the reaction of Figure 2 was started, the CH_3Si nmr resonance corresponding to the silicon middle group was found to be very sharp, exhibiting a peak width at half-height about 0.2 Hz wider than the narrowest peak width measurable on the spectrometer. This is an indication that the product molecule of eq 12, a molecule which may be called bis(*O,P*-dimethylphosphonyl)dimethylsilane, is indeed a separate structure. Thus at 0.5-1 hr in Figure 2, the reaction mixture consists of essentially only the original reagents plus chlorodimethylsilyl methyl methylphosphonate and bis(*O,P*-dimethylphosphonyl)dimethylsilane.

It would appear that the next step in the reaction sequence involves the further condensation of the product of eq 13 with dimethyl methylphosphonate, as shown in eq 14.



$$\mathrm{Cl\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\underset{O}{\overset{CH_3}{P}}\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\underset{O}{\overset{CH_3}{P}}\text{-}OCH_3 + CH_3(O)P(OCH_3)_2 \rightarrow}$$
$$\mathrm{CH_3O\text{-}\underset{O}{\overset{CH_3}{P}}\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\underset{O}{\overset{CH_3}{P}}\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\underset{O}{\overset{CH_3}{P}}\text{-}OCH_3 + CH_3Cl} \qquad (14)$$

Note that in eq 11-14 the product molecules all have structures in which the oxygen-bridged silicon and phosphorus atoms are present in alternating sequence. The small number and simple form of the curves shown in Figure 2 suggest that the condensation process throughout its entire course produces oligomeric structures with alternating silicon and phosphorus atoms. This idea is supported by the fact that the phosphorus middle groups all seem to be of the same kind, corresponding to the nearest neighbors being

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[11] K. A. Andrianov, "Metalorganic Polymers," Interscience, New York, N. Y., 1965, pp 163-167. Also see W. Noll, "Chemie und Technologie der Silicone," Verlag Chemie, Weinheim/Bergstr., 1960, pp 126-127, for some patent literature.

oxygen-bonded silicons. Furthermore, the nmr peak widths of the silicon and phosphorus middle groups of the reaction of Figure 2 consistently remained more narrow than the peak widths observed in the measurements for Figure 1.

Separation Studies. Vacuum distillation was attempted on the compositions resulting from the reactions of Figures 1 and 2 after several hundred hours had elapsed. In both of these cases, as well as in the case of other compositions, distillation always produced rearrangements. Thus, the product of the reactions of Figure 2, when heated at 225° and 8 Torr, gave in a couple of hours a small amount of distillate consisting of dimethyl methylphosphonate plus a complicated molecular mixture made up of methoxyl-terminated phosphorus end groups with silicon and phosphorus middle groups. The nmr peaks corresponding to these end and middle groups were very broad; and, in addition, two sharp resonances peeped out of the broad resonance corresponding to phosphorus middle groups. The nmr resonances of the still-pot residue were also very broad. We attribute the sharp resonances to cyclic phosphorus species and conclude that the distillation caused considerable rearrangement of the original oligomers, since both the distillate and the still residue as well as their recombination exhibited nmr patterns which were different from that of the unheated starting material.

When this same product from the reaction of Figure 2 was chromatographed on a silica column, the first species to be isolated was a small amount of dimethyl methylphosphonate. The second species to come out of the column appeared from the nmr analysis to be quite pure bis(*O,P*-dimethylphosphonyl)dimethylsilane (the product of eq 12). The additional fractions were obviously mixtures of molecules, with more and more middle groups appearing in these mixtures as the column continued to be eluted. Similar results, but with poorer resolution, were obtained by chromatography with alumina. The chromatographic data on the composition resulting from the reaction of Figure 1, as well as from reactions involving combinations of three or four of the original starting materials, gave uninteresting results, with only the monophosphorus or monosilicon compounds being resolved.

Long-Term Studies. Since we originally hoped to achieve equilibrium with respect to the scrambling of the various building units between the oligomeric molecules, considerable effort was put on the nmr measurement of compositions which had been stored for several months at 26°. However, we now believe that none of these compositions were at all near equilibrium. The chief evidence for this lies in the results obtained on approximately 1:1 mixtures of $(CH_3)_2SiCl_2 + CH_3(O)P(OCH_3)_2$ and of $(CH_3)_2Si(O)(CH_3)_2 + CH_3(O)PCl_2$ which exhibited quite different nmr patterns after 2–3 months of standing. The first of these two mixtures gave patterns which were consistent with alternation of the silicon and phosphorus atoms, whereas the second corresponded to more complicated mixtures. These results would be expected from extrapolation of the reactions of Figures 2 and 1, respectively. A half dozen samples made from various combinations of $(CH_3)_2Si(OCH_3)_2$ with $CH_3(O)P(OCH_3)_2$ and $CH_3(O)PCl_2$, so adjusted as to have methoxyl end groups upon complete condensation, exhibited predominantly phosphorus end groups with apparently no preference for alternation of silicon and phosphorus atoms. Likewise, mixtures of $CH_3(O)P(OCH_3)_2$ with $(CH_3)_2Si(OCH_3)_2$ and $(CH_3)_2SiCl_2$, corresponding to methoxyl termination at complete condensation, showed the silicon to be preferentially placed in the terminal positions; with again no signs of undue emphasis on silicon–phosphorus alternation.

When the starting ratios were so adjusted as to give chlorogroup termination at complete condensation, there always seemed to be some preference for silicon end groups. Although the evidence is not complete, it appears that the same general behavior observed with methoxyl termination is found for the reactions leading to chloro-terminated products upon complete condensation.

Conclusions

There seems to be sufficient evidence reported here to support the claim that the condensation of dichlorodimethylsilane with dimethyl methylphosphonate leads to alternation of the oxygen-bridged silicon and phosphorus atoms in the molecular backbone. Although this type of behavior has naively been postulated for inorganic heteropolymerizations in the past, the usual procedures for making such oligomers result in complicated mixtures, with scrambling of building units often dominating the chemistry. In other words, the common situation is closer to the random sorting of structural building units rather than to ABABABA sequencing.

The methoxyl-terminated oligomers exhibiting oxygen-bridged silicon–phosphorus alternation appeared to be reasonably stable molecules. Thus, condensation products stored at room temperature for 8 months showed essentially no change in their nmr patterns as compared to the time immediately after condensation (*ca.* 12 hr). A sample of such alternating backbone oligomers with methoxyl termination was mixed with water and found not to react immediately, even with shaking. After 3 days at room temperature with occasional stirring, there appeared to be little hydrolysis.

Registry No. $(CH_3)_2Si(OCH_3)_2 \cdot CH_3(O)P(OCH_3)_2$ polymer, 38117-51-0; $(CH_3)_2Si(OCH_3)Cl \cdot CH_3(O)P(OCH_3)Cl$ polymer, 38117-52-1.

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