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Condensation Reactions Giving Rise to P–P Bonded Compounds

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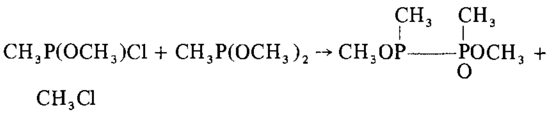
The room-temperature condensation of $CH_3P(OCH_3)_2$ with an equimolar amount of $(C_6H_5)_2PCl$ leads to the new compound $(C_6H_5)_2P{-}P(O)(CH_3)OCH_3$, whereas the related reaction between CH_3PCl_2 and $(C_6H_5)_2POCH_3$ leads first to exchange of the chloro and methoxyl groups followed by slow self-condensation of the resulting $CH_3P(OCH_3)Cl$ molecules. When $CH_3P(OCH_3)_2$ is combined with an excess of $(C_6H_5)_2PCl$, the product is found to react further with this excess reagent to give $(C_6H_5)_2P{-}P(C_6H_5)_2$. Furthermore, the room-temperature reaction of $CH_3P(OCH_3)_2$ with $C_6H_5PCl_2$ leads to condensation products apparently based on the combination of the $C_6H_5(CH_3O)P{-}$ end group with $CH_3P(O){<}$ and $C_6H_5P(O){<}$ middle groups terminated with a $CH_3(CH_3O)P(O){-}$ group. The new compound $(C_6H_5)_2P{-}P(O)(OCH_2)_2C(CH_3)_2$ was obtained by reaction of $(C_6H_5)_2POCH_3$ with $(CH_3)_2C(CH_2O)_2PCl$, whereas, also at room temperature, only exchange of chloro for methoxyl group was observed in the reaction between *o*-$C_6H_4O_2PCl$ and $(C_6H_5)_2POCH_3$. At 140°, the reagents underwent exchange and condensation to give what appeared to be a P–O–P bridged structure, $[C_6H_4O_2P]_2O$.

Introduction

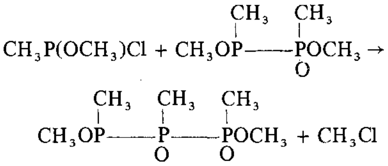
About 20 years ago it became apparent that redistribution or scrambling reactions played a dominant role in or at least were deeply interwoven into the fabric of synthetic inorganic chemistry. As a result there has been a long-term effort by this group to clarify redistribution reactions[1-3] and their resulting equilibria[4,5] in the chemistry of both simple compounds and polymers or oligomers. Recently we have returned to the study of the role of scrambling in practical synthetic chemistry and this paper, which is a continuation of a recent study,[6] represents an example of this kind of approach applied to condensation reactions.

In the prior paper[6] we reported that the room-temperature reaction between CH_3PCl_2 and $CH_3P(OCH_3)_2$ consisted of redistribution, condensation, and rearrangement processes—with the redistribution of chloro and methoxyl groups being the first to dominate the reaction sequence. Furthermore, it appeared that the condensation process involved rearrangement to give products based on $CH_3(O)P{<}$ units connected by P–P bonds, as shown in eq 1–3. This paper

$$CH_3PCl_2 + CH_3P(OCH_3)_2 \rightarrow 2CH_3P(OCH_3)Cl \qquad (1)$$



$$CH_3P(OCH_3)Cl + CH_3P(OCH_3)_2 \rightarrow CH_3O\overset{CH_3}{\overset{|}{P}}{-\!-\!-}\underset{O}{\overset{CH_3}{\overset{|}{P}}}OCH_3 + CH_3Cl \qquad (2)$$



$$CH_3P(OCH_3)Cl + CH_3O\overset{CH_3}{\overset{|}{P}}{-\!-\!-}\underset{O}{\overset{CH_3}{\overset{|}{P}}}OCH_3 \rightarrow CH_3O\overset{CH_3}{\overset{|}{P}}{-\!-\!-}\underset{O}{\overset{CH_3}{\overset{|}{P}}}{-\!-\!-}\underset{O}{\overset{CH_3}{\overset{|}{P}}}OCH_3 + CH_3Cl \qquad (3)$$

describes the results of our continued work in this general area.

Experimental Section

The ^{31}P nuclear magnetic resonance (nmr) measurements were carried out using a Varian XL-100-15 spectrometer equipped with Fourier-transform accessories supplied by Nicolet Technology Corp. The ^1H nmr measurements were run on 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 could be employed in the ^{31}P studies and the chemical shifts for this nucleus were referenced by the tube-interchange method to 85% H_3PO_4, with negative shifts being downfield. Tetramethylsilane was used as the ^1H nmr reference standard, again with negative shifts being downfield.

The dichloromethylphosphine was obtained from Edgewood Arsenal and some of it was converted to dimethoxymethylphosphine according to the method of Maier.[7] Chlorodiphenyl- and dichlorophenylphosphines were purchased from Orgmet, Inc., Hampstead, N.H. The methoxydiphenylphosphine was prepared from its chloride according to literature.[8] The 2-methoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane, 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane, and 2-chloro-1,3,2-benzodioxaphosphole were obtained from our laboratory stores. All of these compounds were repurified by distillation in a nitrogen atmosphere and each exhibited the proper boiling point.

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, where 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. A drybag or a drybox, filled with predried nitrogen and containing phosphorus pentoxide as the dehydrating agent, was employed wherever appropriate. Some of the reactions also were carried out in sealed glass tubes and, in such cases, the filtration and transfer of the products were done strictly under dry nitrogen.

Synthesis of $(C_6H_5)_2P{-}P(O)(CH_3)OCH_3$. In a typical preparation, 0.5 g (4.6 mmol) of $CH_3P(OCH_3)_2$ was mixed with a solution of 0.95 g (4.3 mmol) of $(C_6H_5)_2PCl$ in 1 ml of CH_2Cl_2 in a sealed, evacuated glass tube. Thorough mixing of the reagents was achieved by shaking the tube. After about 1 hr, the volatile products were removed *in vacuo* to obtain $(C_6H_5)_2P{-}P(O)(CH_3)OCH_3$ as a viscous liquid; yield 1.16 g (96.7% based on the $(C_6H_5)_2PCl$ used). *Anal.* Calcd for $C_{14}H_{16}P_2O_2$: C, 60.4; H, 5.7; P, 22.3. Found: C, 60.1; H, 5.7; P, 22.2. Nmr: proton spectrum $\delta_{C_6H_5}$ −7.75, −7.45 ppm (complex multiplet, 10 H), δ_{OCH_3} −3.79 ppm (doublet, 3 H), J_{POCH} = 11.5 Hz, δ_{CH_3} −1.4 ppm (doublets of doublets, 3 H), J_{PCH} = 12.1 Hz, J_{PPCH} = 2.3 Hz; phosphorus spectrum (proton decoupled, in CH_2Cl_2) δ_{P_A} +29.94 ppm (doublet), δ_{P_B} −59.42 ppm (doublet), $J_{P_AP_B}$ = 209.05 Hz. Ir: 3050 (m), 3000 (w), 2948 (m), 2905 (w), 2840 (w), 1580 (m), 1478 (s), 1430 (s), 1282 (s), 1200 (vs), 1180 (s, sh), 1080 (w), 1030 (vs), 995 (m), 880 (s), 860 (s), 798 (s), 746 (vs), 690 (vs) cm^{-1}.

Synthesis of $(C_6H_5)_2P{-}P(C_6H_5)_2$. In a typical reaction, 1.55 g (7.04 mmol) of $(C_6H_5)_2PCl$ in about 1 ml of CH_2Cl_2 was mixed with 0.35 g (3.24 mmol) of $CH_3P(OCH_3)_2$ in a sealed tube and occasionally shaken for about 5 hr. During this time, white crystalline $(C_6H_5)_2P{-}P(C_6H_5)_2$ precipitated. It was filtered and the crude solid product was dissolved in about 5 ml of benzene and an analytically pure sample was recrystallized from this solvent; mp 119–121°; yield 1.15 g (83% based on the $(C_6H_5)_2PCl$ used). Its ^{31}P nmr in CH_2Cl_2 exhibited a singlet at +15.7 ppm and addition of a known sample of $(C_6H_5)_2P{-}P(C_6H_5)_2$ did not lead to any spectral variation.

The filtrate was analyzed from its ^{31}P and ^1H nmr spectra and was found to contain, in addition to the solvent and dissolved $(C_6H_5)_2P{-}P(C_6H_5)_2$, $CH_3P(O)(OCH_3)Cl$ and small amounts of some other phosphorus compounds (see Results and Interpretation for details).

Reaction of CH_3PCl_2 with $(C_6H_5)_2POCH_3$. In a representative reaction, 0.56 g (4.78 mmol) of CH_3PCl_2 was mixed with 1.07 g (4.95 mmol) of $(C_6H_5)_2POCH_3$ in 0.65 g of CH_2Cl_2 in a 5-mm nmr tube at −78°. The tube was promptly sealed and the reaction mixture was warmed to room temperature. The nmr spectra were recorded at this temperature in intervals of 15 min for 6 hr. The experiment was then repeated with various molar ratios of the two reagents (see Results and Interpretation for details of product identification).

Reaction of $CH_3P(OCH_3)_2$ and $C_6H_5PCl_2$. A typical reaction mixture containing 0.74 g (6.9 mmol) of $CH_3P(OCH_3)_2$ and 0.51 g (2.84 mmol) of $C_6H_5PCl_2$ in 0.5 g of CH_2Cl_2 in a 5-mm nmr tube was sealed at −78°. It then was warmed to room temperature and nmr spectra were recorded at intervals of 15 min for 5 hr and thereafter at intervals of 1 day for 2 weeks. The experiment was repeated for several other reaction mixtures containing the two reagents in various molar ratios (see Results and Interpretation for details of product characterization).

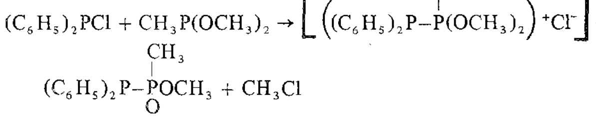
Reaction of $C_6H_4O_2PCl$ with $(C_6H_5)_2POCH_3$. A reaction mixture containing 1.04 g (6 mmol) of $C_6H_4O_2PCl$ and 1.18 g (5.3 mmol) of $(C_6H_5)_2POCH_3$ was sealed in a 5-mm nmr tube at −78°. After warming to room temperature it was examined with ^1H and ^{31}P nmr for 24 hr. Thereafter the spectra were recorded, first after heating for 20 hr at 80° and then after heating for 2 hr at 140°. The nmr data are given in the Results and Interpretation section.

Reaction of $C_6H_4O_2PCl$ with $CH_3P(OCH_3)_2$. Experiments were carried out in 5-mm nmr tubes and a representative reaction mixture contained 1.15 g (6.6 mmol) of $C_6H_4O_2PCl$ and 0.49 g (4.5 mmol) of $CH_3P(OCH_3)_2$. Nmr spectra were taken at room temperature. On heating the mixture for about 4 hr at 70°, a large amount of an orange-yellow solid melting above 200° and insoluble in common organic solvents was obtained.

Synthesis of $(C_6H_5)_2P–P(O)(OCH_2)_2C(CH_3)_2$. In a reaction, 2.17 g (12.9 mmol) of $(CH_3)_2C(CH_2O)_2PCl$ and 2.33 g (10.6 mmol) of $(C_6H_5)_2POCH_3$ were combined in a 50-ml three-necked flask containing 5 ml of *n*-hexane under nitrogen. After stirring the mixture for 3 hr at room temperature, the white solid obtained was filtered, washed five times with 10-ml portions of *n*-hexane, and dried *in vacuo*; mp 98–99°; yield 3.42 g (92.45% based on the $(C_6H_5)_2POCH_3$ employed in the reaction). *Anal.* Calcd for $C_{17}H_{20}O_3P_2$: C, 61.07; H, 5.98; P, 18.56; O, 14.37. Found: C, 60.5; H, 6.1; P, 18.0. Nmr: proton spectrum $\delta_{C_6H_5}$ −7.8 ppm (complex multiplet, 10 H), δ_{CH_2} −3.61 ppm (complex multiplet, 4 H), δ_{CH_3} −0.98, −0.47 ppm (6 H); phosphorus spectrum (proton decoupled, in CH_2Cl_2) δ_{P_A} +46.42 ppm (doublet), δ_{P_B} −20.53 ppm (doublet), $J_{P_AP_B}$ = 204.47 ppm. The same compound is obtained using a similar procedure by treating $(CH_3)_2C(CH_2O)_2POCH_3$ with $(C_6H_5)_2PCl$ at room temperature.

Results and Interpretation

Reactions of $CH_3P(OCH_3)_2$ with $(C_6H_5)_2PCl$. Preliminary experiments using various proportions of dimethoxymethylphosphine and chlorodiphenylphosphine showed that the nature of the reaction products depended upon the quantity of the two reagents present initially as well as upon the extent of time they were in contact. Thus, when $(C_6H_5)_2PCl$ and $CH_3P(OCH_3)_2$ were present either in equimolar ratio or with the latter phosphine in excess, the two react rapidly with elimination of methyl chloride. The ^1H and ^{31}P nmr spectra of the liquid condensation product were in agreement with a single phosphorus-containing product, the new compound $(C_6H_5)_2P–P(O)(CH_3)OCH_3$, I, and the material balance was in accord with the stoichiometry shown in eq 4. The pair of doublets observed in the proton-decoupled ^{31}P nmr spectrum at −59.42 and +29.94 ppm, with a P–P coupling constant of 209.05 Hz, is clearly indicative of the P–P(O) backbone.[6,9] In the proton-undecoupled spectrum, each resonance in the −59.42-ppm doublet was observed as a septet with a coupling constant of 11.90 Hz, and hence they are assignable to the $CH_3P(O)(OCH_3)–$ moiety, whereas, in the same spectrum, the two peaks centered at +29.94 ppm were seen as poorly resolved quintets characteristic of the $(C_6H_5)_2P–$ group. In the ^1H nmr spectrum, the methoxyl groups gave a doublet centered at −3.79 ppm (J_{POCH} = 11.5 Hz) and the methyl resonances were observed as doublets of a doublet (the $P_A–P_B–CH_3$ coupling pattern) with J_{P_ACH} = 2.3 Hz and J_{P_BCH} = 12.1 Hz. The new compound, I, though air and moisture sensitive, is stable in sealed tubes for over 1 month.



$$(C_6H_5)_2PCl + CH_3P(OCH_3)_2 \rightarrow \left[\left((C_6H_5)_2P–\overset{\overset{\large CH_3}{|}}{P}(OCH_3)_2\right)^+Cl^-\right] \rightarrow (C_6H_5)_2P–\underset{O}{\overset{\overset{\large CH_3}{|}}{P}}OCH_3 + CH_3Cl \qquad (4)$$

When this reaction was run with $CH_3P(OCH_3)_2$ and $(C_6H_5)_2PCl$ in a molar ratio of 1:2, the initial reaction, as evidenced by nmr data, was the same as shown in eq 4 producing $(C_6H_5)_2P–P(O)(CH_3)OCH_3$. However, the excess of $(C_6H_5)_2PCl$ did not condense with the methoxyl group on the biphosphine monoxide to give the direct condensation product $(C_6H_5)_2P–P(O)CH_3–O–P(C_6H_5)_2$; instead, there was a cleavage reaction, as depicted in eq 5, to form $(C_6H_5)_2P–P(C_6H_5)_2$ and methoxymethylphosphonyl chloride, $CH_3P(O)(OCH_3)Cl$. Identification of the tetraphenylbiphosphine was achieved by comparing the properties of the separated product with an authentic sample. Evidence for the formation of $CH_3P(O)(OCH_3)Cl$ was obtained from ^1H and ^{31}P nmr spectra. The ^1H nmr data—δ_{CH_3} −1.99 ppm, J_{PCH} = 17.8 Hz; δ_{CH_3O} −3.83 ppm, J_{POCH} = 17.1 Hz—of $CH_3P(O)(OCH_3)Cl$ observed here agreed well with values reported previously.[10] Moreover, the proton-undecoupled ^{31}P spectrum exhibited a pseudoseptet centered at −40.82 ppm, indicating the $CH_3(CH_3O)P(O)–$ group. It should be noted that, as the reaction shown in eq 5 progressed, the ^{31}P nmr spectrum of the reaction mixture exhibited, in addition to the resonances of $(C_6H_5)_2P–P(C_6H_5)_2$ and $CH_3P(O)(OCH_3)Cl$, a gradual buildup of two peaks at −23.56 and −23.87 ppm. It seemed from material-balance calculations that these resonances are due to decomposition products of $CH_3P(O)(OCH_3)Cl$. The formation of $(C_6H_5)_2P–P(C_6H_5)_2$ can be explained by assuming that $(C_6H_5)_2PCl$ first attacks the $(C_6H_5)_2P–$ moiety in I to form the intermediate $[(C_6H_5)_2P–P^+(C_6H_5)_2P(O)(CH_3)OCH_3]Cl^-$, which then eliminates $CH_3P(O)(OCH_3)Cl$ to produce $(C_6H_5)_2P–P(C_6H_5)_2$.

$$(C_6H_5)_2P–P(O)(CH_3)OCH_3 + (C_6H_5)_2PCl \rightarrow (C_6H_5)_2P–P(C_6H_5)_2 + CH_3P(O)(OCH_3)Cl \qquad (5)$$

Reaction of CH_3PCl_2 with $(C_6H_5)_2POCH_3$. When dichloromethylphosphine was combined with methoxydiphenylphosphine at room temperature, they reacted immediately giving off a noticeable amount of heat. As in the reaction between $(C_6H_5)_2PCl$ and $CH_3P(OCH_3)_2$, the nature of the products depended upon the amount of the reactants taken initially. In all cases, however, the direct condensation product, $CH_3(Cl)P–P(O)(C_6H_5)_2$, did not form since the exchange of the chloro and methoxyl groups between the two phosphorus moieties occurred, as shown in eq 6 and 7. The chloromethoxymethylphosphine, $CH_3P(OCH_3)Cl$, was identified from its previously reported[6] nmr chemical shifts. All the other compounds were available in pure form and thus were readily characterized from their nmr spectra.

$$CH_3PCl_2 + (C_6H_5)_2POCH_3 \rightarrow CH_3P(OCH_3)Cl + (C_6H_5)_2PCl \qquad (6)$$

$$CH_3P(OCH_3)Cl + (C_6H_5)_2POCH_3 \rightarrow CH_3P(OCH_3)_2 + (C_6H_5)_2PCl \qquad (7)$$

When an equimolar amount or an excess of CH_3PCl_2 was present, only the reaction shown in eq 6 to produce $CH_3P(OCH_3)Cl$ and $(C_6H_5)_2PCl$ was observed at the beginning. There was no further condensation between the products $(C_6H_5)_2PCl$ and $CH_3P(OCH_3)Cl$; instead the latter disappeared through self-condensation processes producing oligomers containing P–P bonds.[6] On the other hand, when the reaction between CH_3PCl_2 and $(C_6H_5)_2POCH_3$ was run with an excess of the latter, both of the reactions shown in eq 6 and 7 came into play in the early stages with the latter one progressing more slowly. In this case, however, there were two condensation processes which succeeded these redistribution reactions. Both of these involved the products of eq 6 and 7. Thus, $CH_3P(OCH_3)_2$ and $(C_6H_5)_2PCl$ produced $(C_6H_5)_2P$-

$P(O)(CH_3)OCH_3$, I, according to eq 4 and $CH_3P(OCH_3)_2$ reacted with $CH_3P(OCH_3)Cl$ forming the oligomers described in eq 2 and 3. Because of these two competing condensation processes, the amount of $CH_3P(OCH_3)_2$ available to convert all of the $(C_6H_5)_2PCl$ to I was not sufficient. This left some uncondensed $(C_6H_5)_2PCl$ which, however, reacted with I, converting the latter eventually to $(C_6H_5)_2P–P(C_6H_5)_2$ and $CH_3P(O)(OCH_3)Cl$ (eq 5).

Reaction of $CH_3P(OCH_3)_2$ with $C_6H_5PCl_2$. When dimethoxymethylphosphine and dichlorophenylphosphine were combined at room temperature, the two compounds reacted very rapidly, giving off a noticeable amount of heat. The condensation as measured by methyl chloride elimination was essentially complete in the first hour. The easily identifiable product in the ^{31}P nmr spectrum of the reaction mixture (containing either $C_6H_5PCl_2$ or $CH_3P(OCH_3)_2$ in excess) was $CH_3P(OCH_3)Cl$ which exhibited the chemical shifts (δ_P −204.5 ppm) and coupling constants ($J_{PCH} = J_{POCH} = 13.2$ Hz) reported previously.[6] This methoxyphosphine, which never amounted to more than 5% of the total phosphorus, should have been formed according to eq 8.

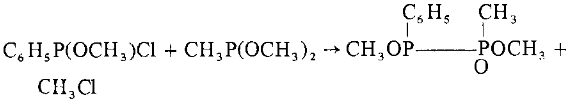
$$C_6H_5PCl_2 + CH_3P(OCH_3)_2 \rightarrow C_6H_5P(OCH_3)Cl + CH_3P(OCH_3)Cl \qquad (8)$$

However, no $C_6H_5P(OCH_3)Cl$ was ever observed, so that it seems to have been used up as soon as it was formed.

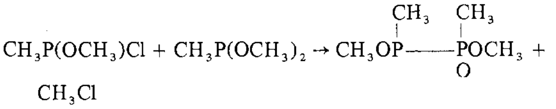
When there was an excess of $CH_3P(OCH_3)_2$ in the reaction mixture, the proton-decoupled ^{31}P nmr spectra showed, in addition to the single resonances of $CH_3P(OCH_3)_2$ at −182.5 ppm and $CH_3P(OCH_3)Cl$ at −204.5 ppm, a series of 16 peaks between −62 and −53 ppm (with chemical shifts of −62.41, −62.22, −60.98, −60.92, −60.83, −60.64, −59.44, −59.29, −57.63, −57.48, −55.97, −55.86, −55.78, −55.63, −54.09, and −53.97 ppm) and another series of 12 peaks between +44 and +63 ppm (at +44.81, +48.77, +50.01, +50.28, +52.51, +53.67, +53.89, +55.48, +57.28, +57.51, +58.79, and +62.29 ppm). The rather close similarity between these chemical shifts and those observed for the products resulting from the interaction of CH_3PCl_2 with $CH_3P(OCH_3)_2$ suggests that the products of condensation between $C_6H_5PCl_2$ and $CH_3P(OCH_3)_2$ also contain P–P bonds rather than P–O–P linkages. Another similarity to the condensation between CH_3PCl_2 and $CH_3P(OCH_3)_2$ was seen in the fact that a fixed ratio of the reagents always seems to be involved in condensation whether or not one or the other is present in excess. Study of the reaction products corresponding to a series of seven different $CH_3P(OCH_3)_2$:$C_6H_5PCl_2$ mole ratios ranging from 0.25 to 4.0 showed that the condensation product corresponded consistently to a value of this mole ratio equal to 2.0.

The compound $C_6H_5P[P(O)(CH_3)OCH_3]_2$ produced by the direct condensation of the two reagents can be ruled out as a product, since it should exhibit a relatively simple ^{31}P nmr pattern similar to that of $C_6H_5P[P(O)(OCH_3)_2]_2$[9]—the latter exhibits a doublet at −33.7 ppm and triplet at +64.9 ppm; J_{PP} = 168 Hz. It is quite evident that the important condensation steps involve the interaction of the monomers $C_6H_5P(OCH_3)Cl$ and $CH_3P(OCH_3)Cl$ with dimethoxymethylphosphine and that these monomers further react with the resulting condensation products to form oligomers containing P–P bonds.

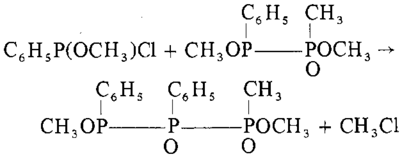
In the system $CH_3P(OCH_3)_2$ *vs.* CH_3PCl_2, where the condensation involved the interaction of the $CH_3P(OCH_3)Cl$ monomer with $CH_3P(OCH_3)_2$, the 12 peaks observed between −64 and −56 ppm were assigned to $CH_3P(O)<$ and $CH_3(CH_3O)P(O)–$ moieties, the phosphorus atom in each moiety being directly connected to another phosphorus atom. In the ^{31}P spectrum of the compound $C_6H_5(CH_3O)P(O)–P(C_6H_5)–P(O)(OCH_3)C_6H_5$,[9] the resonance due to the $C_6H_5(CH_3O)P(O)–$ group appears at −45.7 ppm and that due to $C_6H_5P<$ appears at +64.9 ppm, whereas the resonance of $C_6H_5(CH_3O)P–$ in $C_6H_5(CH_3O)P–P(O)(OCH_3)_2$ is found at +50.6 ppm.[9] No data are available for the ^{31}P resonance associated with the group $C_6H_5P(O)<$. From these published shifts, it is reasonable to assume that the 16 peaks between −62 and −53 ppm are most probably attributable to the $CH_3P(O)(OCH_3)–$ and $CH_3P(O)<$ moieties, although $C_6H_5P(O)<$ cannot be ruled out unequivocally. The 12 resonances between +44 and +63 ppm are in the range found for either $C_6H_5(OCH_3)P–$ or $C_6H_5P<$ groups, but they are not at a sufficiently low field to be assigned to the $C_6H_5(Cl)P–$ group—since the resonance of $C_6H_5(Cl)P–$ moiety in $C_6H_5(Cl)P–P(O)(C_6H_5)_2$ is found[9] at +26.6 ppm. Thus it seems reasonably satisfactory to assume the triply connected moiety in the condensation product arises from $C_6H_5PCl_2$ and appears as the $C_6H_5(CH_3O)P–$ end group, whereas the quadruply connected phosphorus moieties are mostly derived from $CH_3P(OCH_3)_2$ and to some extent from $C_6H_5PCl_2$, probably appearing as the $CH_3(CH_3O)P(O)–$, $CH_3P(O)<$, and $C_6H_5P(O)<$ groups. Reactions in agreement with these ideas are shown in eq 9–12. As might be expected from the



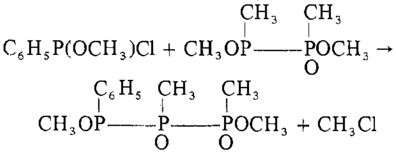
$$C_6H_5P(OCH_3)Cl + CH_3P(OCH_3)_2 \rightarrow CH_3O\overset{C_6H_5}{\overset{|}{P}}\text{———}\underset{O}{\overset{CH_3}{\overset{|}{P}}}OCH_3 + CH_3Cl \qquad (9)$$



$$CH_3P(OCH_3)Cl + CH_3P(OCH_3)_2 \rightarrow CH_3O\overset{CH_3}{\overset{|}{P}}\text{———}\underset{O}{\overset{CH_3}{\overset{|}{P}}}OCH_3 + CH_3Cl \qquad (10)$$



$$C_6H_5P(OCH_3)Cl + CH_3O\overset{C_6H_5}{\overset{|}{P}}\text{——}\underset{O}{\overset{CH_3}{\overset{|}{P}}}OCH_3 \rightarrow CH_3O\overset{C_6H_5}{\overset{|}{P}}\text{———}\underset{O}{\overset{C_6H_5}{\overset{|}{P}}}\text{———}\underset{O}{\overset{CH_3}{\overset{|}{P}}}OCH_3 + CH_3Cl \qquad (11)$$



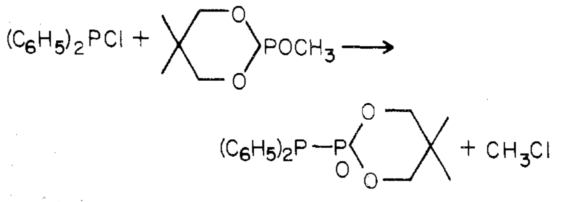
$$C_6H_5P(OCH_3)Cl + CH_3O\overset{CH_3}{\overset{|}{P}}\text{——}\underset{O}{\overset{CH_3}{\overset{|}{P}}}OCH_3 \rightarrow CH_3O\overset{C_6H_5}{\overset{|}{P}}\text{——}\underset{O}{\overset{CH_3}{\overset{|}{P}}}\text{——}\underset{O}{\overset{CH_3}{\overset{|}{P}}}OCH_3 + CH_3Cl \qquad (12)$$

observation that the $CH_3P(OCH_3)_2$:$C_6H_5PCl_2$ 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}P resonances in the −62 to −53 and +44 to +63 ppm regions exhibit area ratios which are quite independent of the degree of methyl chloride elimination or the reagent ratio. It should be noted that in the proton-decoupled ^{31}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 commensurate with P–P homonuclear coupling.

In reactions resulting from an excess of $CH_3P(OCH_3)_2$ (*i.e.*, no more $C_6H_5PCl_2$ is present on completion of condensation), the nmr spectra showed no evidence for structural changes in the products, even after standing for several months at room temperature. When there was an excess of $C_6H_5PCl_2$, however, it was seen to react further with the initial condensation products so as to result in a slow, gradual disappearance of all the peaks in the two regions at −62 to −53 and +44 to +63 ppm, with a concurrent buildup of a new series of eight peaks between −24 and −21 ppm and another series of more than 20 peaks between −2 and +5 ppm. It may be that this reaction of $C_6H_5PCl_2$ with the condensation products bears some similarity to the reaction of $(C_6H_5)_2PCl$ with I (see eq 5).

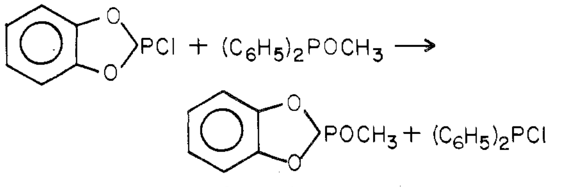
Related Reactions Involving Cyclic Phosphines. Another example of the significance of substituent exchange in synthetic phosphorus chemistry is clearly found in the reactions of either

2-methoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane, $(CH_3)_2C(CH_2O)_2POCH_3$, with $(C_6H_5)_2PCl$ or 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane, $(CH_3)_2C(CH_2O)_2PCl$, with $(C_6H_5)_2POCH_3$. Both reactions produce the same new compound: $(CH_3)_2C(CH_2O)_2P(O)$-$P(C_6H_5)_2$. Evidently, when $(CH_3)_2C(CH_2O)_2PCl$ is combined with $(C_6H_5)_2POCH_3$, the chloro and methoxyl groups first exchange and the resulting phosphines then condense, whereas only condensation occurs in the companion reaction (eq 13) involving $(C_6H_5)_2PCl$ and $(CH_3)_2C(CH_2O)_2POCH_3$.



(13)

In order to gain further insight into the nature of reactions being studied, we also examined the condensation of 2-chloro-1,3,2-benzodioxaphosphole, $C_6H_4O_2PCl$, with either $(C_6H_5)_2POCH_3$ or $CH_3P(OCH_3)_2$. Thus when 6 mmol of $C_6H_4O_2PCl$ was combined with 5.5 mmol of $(C_6H_5)_2POCH_3$, the ^{31}P nmr spectrum (15 min after mixing at room temperature) showed three peaks, one at −171.4 ppm for $C_6H_4O_2PCl$, another at −80.01 ppm for $(C_6H_5)_2PCl$, and a third peak at −125.60 ppm, which was identified as due to $C_6H_4O_2POCH_3$ from stoichiometric calculations and from the proton-undecoupled ^{31}P spectrum where this peak appeared as a quartet with $J_{POCH} = 9.37$ Hz. Obviously the redistribution reaction depicted in eq 14 has taken place. Standing at room temperature for 24 hr or heating at 80° for 20 hr did not lead to further reaction. However, upon heating at 140°, the reaction products gradually acquired an orange-yellow coloration. After 2 hr of heating at this temperature, the proton-decoupled ^{31}P spectrum exhibited some additional resonances which include a prominent peak at −127.38 ppm, two small peaks of about equal intensity at −126.2 and −120.06 ppm, and small single resonances at −30.2, −20.4, and +15.7 ppm. None of the above peaks are characteristic of compounds containing P–P(O) bonds. The ^{31}P spectrum without proton decoupling showed that the structure associated with the resonance at −127.38 ppm contained no hydrogen capable of coupling with the phosphorus atom. Furthermore the intensities of the resonances of $C_6H_4O_2PCl$ and $C_6H_4O_2POCH_3$ were seen to decrease more or less in proportion to the growing intensity of this peak at −127.38 ppm. Therefore it is reasonable to assume that this peak is due to $C_6H_4O_2POPO_2C_6H_4$. Note that by analogy this compound should exhibit a ^{31}P resonance close to that of $C_6H_4O_2POCH_3$ which is in fact the case. By similar reasoning, the peaks at −126.2 and −120.06 ppm may be due to $(C_6H_5)_2POC_6H_4OPCl_2$. The resonance observed at +15.7 ppm and its proton-undecoupled spectrum correspond to tetraphenylbiphosphine.



(14)

Treatment of $C_6H_4O_2PCl$ with $CH_3P(OCH_3)_2$ has led to additional interesting results. The two compounds reacted exothermally, when a reaction mixture containing 6.6 mmol of $C_6H_4O_2PCl$ and 4.53 mmol of $CH_3P(OCH_3)_2$ was warmed to room temperature from −78°. The resulting ^{31}P nmr spectrum exhibits the resonances of $CH_3P(OCH_3)Cl$ at −204.5 ppm, $C_6H_4O_2PCl$ at −171.4 ppm, and $C_6H_4O_2POCH_3$ at −125.60 ppm. In addition, there are a series of 12 peaks in the range from −64 to −56 ppm and another series of 12 peaks between +70 and +86 ppm. These 24 peaks exhibited the chemical shifts and intensities characteristic of the condensation products from CH_3PCl_2 and $CH_3P(OCH_3)_2$ described in eq 2 and 3. There was no evidence for the formation of $C_6H_4O_2P$–$P(O)(CH_3)OCH_3$ and all of the *o*-$C_6H_4(O-)_2$ difunctional group was accounted for in the compounds $C_6H_4O_2PCl$ and $C_6H_4O_2P(OCH_3)$. The only room-temperature reactions observed after the initial fast reaction were the scrambling of chloro and methoxyl groups to produce CH_3PCl_2. Heating of the mixture for about 4 hr at 70° resulted in the formation of a large amount of orange-yellow solid which had a melting range lying above 200° and which was insoluble in common organic solvents.

Discussion

Although the reactions treated in this paper are obviously under kinetic rather than thermodynamic control, the qualitative rate data do suggest the direction of the redistribution equilibria which would be achieved if the condensation processes could be inhibited. Thus, it seems clear that for the scrambling of methoxyl and chloro groups between the methylphosphino, $CH_3P<$, and the diphenylphosphino, $(C_6H_5)_2P$–, moieties, the equilibrium situation should correspond to a rather strong preference for the methoxyl group to be on the methylphosphino moiety. In the case of the scrambling between the methylphosphino and phenylphosphino, $C_6H_5P<$, moieties, the experimental data reported herein might be interpreted to mean that the chloro group goes preferentially to the methylphosphine moiety; however, the very rapid condensation observed makes such a conclusion questionable. For the exchanges involving either of the cyclic phosphino moieties, $(CH_3)_2C(CH_2O)_2P$– or $C_6H_4O_2P$–, the methoxyl group ought to be preferentially found at equilibrium on the cyclic phosphino moiety, with the chlorine on the diphenylphosphino or the methylphosphino moiety (with the latter only having been determined *vs.* the $C_6H_4O_2P$– moiety). This implies that, for the scrambling of methoxyl and chloro groups on triply connected phosphorus, the inferred equilibria are in accord with the previously noted[11] clumping of oxygen-bonded substituents [*i.e.*, a high stability for $C_6H_4O_2POCH_3$ and for $(CH_3)_2C(CH_2O)_2POCH_3$] and perhaps also in accord with the preferential placement of methoxyl on alkyl- instead of aryl-substituted phosphines.

Although we were greatly surprised to find that chlorodiphenylphosphine reacted with 2-methoxy-2-methyl-1,1-diphenylbiphosphine 2-oxide to give tetraphenylbiphosphine, this reaction (eq 5) appears straightforward if the proposed onium intermediate is assumed. It is yet another example of the apparently dominant role of Arbusov-type onium intermediates in the chemistry of triply connected phosphorus. We are now studying the role of chloro group donating agents other than chlorodiphenylphosphine in the formation of biphosphines from this biphosphine monoxide reagent.

The formation of a P–O–P bridge between a pair of triply connected phosphorus atoms in the compound $[C_6H_4O_2P]_2O$ shows that it is indeed possible to obtain[6] bridging oxygens between triply connected phosphorus atoms which are properly substituted. Presumably, the appearance of this oxygen-bridged structure is related to the thermodynamic tendency toward the clumping of oxygen atoms which was noted above and which is commonly observed for the scrambling of the chloro substituent and an oxygen-bridged substituent on any single kind of moiety based on a main-group element.[2]

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Registry No. $(C_6H_5)_2P$–$P(O)(CH_3)OCH_3$, 54166-36-8; $(C_6H_5)_2P$–$P(C_6H_5)_2$, 1101-41-3; $CH_3P(OCH_3)_2$, 20278-51-7; (C_6-

$H_5)_2PCl$, 1079-66-9; CH_3PCl_2, 676-83-5; $(C_6H_5)_2POCH_3$, 4020-99-9; $C_6H_5PCl_2$, 644-97-3; $C_6H_4O_2PCl$, 1641-40-3; $(C_6H_5)_2P-P(O)(OCH_2)_2C(CH_3)_2$, 54166-37-9; $(CH_3)_2C(CH_2O)_2PCl$, 2428-06-0; $C_6H_4O_2POCH_3$, 20570-25-6; $C_6H_4O_2POPO_2C_6H_4$, 16421-86-6; $(C_6H_5)_2POC_6H_4OPCl_2$, 54166-38-0.

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The NF_3^+ Radical Cation. Electron Spin Resonance Studies of Radiation Effects in NF_4^+ Salts

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Exposure of $NF_4^+AsF_6^-$ and $NF_4^+SbF_6^-\cdot 0.8SbF_5$ to ^{60}Co γ rays at 77°K gave two paramagnetic centers, one of which is shown by ESR spectroscopy to contain one nitrogen atom and three equivalent fluorine atoms. Based on its magnetic properties it is identified as pyramidal $\dot{N}F_3^+$, a novel radical cation. The other center exhibits strong interaction of the electron with two fluorine atoms, weaker interaction with the antimony or arsenic central atom, and small interaction with several other fluorine atoms. It is tentatively assigned to the electron-loss species $As\dot{F}_6$, $Sb\dot{F}_6$, or $Sb_2\dot{F}_{11}$ with the unpaired electron largely confined to two fluorine ligands. Irradiation of $NF_4^+BF_4^-$ did not result in well-defined magnetic centers. An improved synthesis of $NF_4^+BF_4^-$ is reported.

Introduction

Although carbon readily forms tetrahedral molecules with electronegative ligands, such as the halogens, the synthesis of the isoelectronic nitrogen compounds has been achieved only recently.[1] Attempts to prepare NF_4^+ salts had been discouraged by theoretical computations[2,3] showing that these salts should be thermodynamically unstable and by the nonexistence of the parent compound NF_5. Once the principle was recognized[1] that NF_4^+ salts can be prepared from NF_3, F_2, and a strong Lewis acid in the presence of a suitable activation energy source, a number of synthetic methods became available. These involve the use of different activation energy sources such as glow discharge,[4,5] elevated temperature and pressure,[6,7] γ irradiation,[8] and uv photolysis.[9]

On exposure to high-energy radiation, CF_4 undergoes the dissociative electron-capture process

$$CF_4 + e^- \rightarrow \dot{C}F_3 + F^- \qquad (1)$$

to give $\dot{C}F_3$ radicals which have been detected both in the liquid[10] and solid[10-12] phase. The fact that no evidence for the existence of the $\dot{C}F_4^-$ radical anion was observed is not surprising in view of the validity of the octet rule for first-row elements of the periodic system. A study of the corresponding NF_4^+ system appeared interesting, particularly in view of the recent suggestion[9] that $\dot{N}F_3^+$ and the radicals derived from the Lewis acid–fluorine interaction, such as $As\dot{F}_6$, are the key intermediates in the formation mechanism of NF_4^+ salts. By analogy with CF_4, one might expect that $\dot{N}F_3^+$ might be prepared by γ irradiation of NF_4^+ salts according to

$$NF_4^+ + e^- \rightarrow \dot{N}F_3^+ + F^- \qquad (2)$$

In this paper we report ESR spectroscopic evidence for the existence of the novel radicals $\dot{N}F_3^+$ and $M\dot{F}_6$, in addition to an improved synthesis of $NF_4^+BF_4^-$ by metathesis in HF solution.

Experimental Section

Syntheses of NF_4^+ Salts. A sample of $NF_4^+SbF_6^-\cdot 0.8SbF_5$ was prepared as previously described[7] by heating a 1:1.2:1 molar mixture of NF_3, F_2, and SbF_5 in a Monel cylinder to 120° for 2 days under an autogenous pressure of 200 atm. The resulting white solid, having the composition $NF_4^+SbF_6^-\cdot 1.9SbF_5$, was converted to $NF_4^+SbF_6^-\cdot 0.8SbF_5$ by heating under a dynamic vacuum to 200° for 3 days. The compound was analyzed as previously described.[13] The only detectable impurities were small amounts of Ni (0.066 wt %) and Cu (0.03%) in the form of their salts. The synthesis of $NF_4^+AsF_6^-$ has previously been described.[13] Again, the only detectable impurities were Ni (0.98%) and Cu (0.27%).

For the synthesis of $NF_4^+BF_4^-$ by metathesis, commercial HF was dried by shaking it overnight in a 1-l. Monel cylinder with fluorine (10 l./0.7 kg of HF) after which oxygen and residual fluorine (ca. 210 psi) were removed under vacuum at −78°. The metathesis apparatus, fabricated entirely from Teflon and Kel-F, consisted of four identical 1-l. vessels connected in series through valves and filters with a fitting carrying a vacuum line connection, a 60-psi pressure relief valve, and a compound pressure–vacuum gauge (Kel-F-coated diaphragm) between the last two vessels. In addition, each vessel was stirred with a Teflon-coated magnetic stirring bar and equipped with a valve which by-passed the filter for introduction or removal of gaseous or liquid materials. All manipulations of reagents and products were conducted either in an inert-atmosphere glove box or by standard high-vacuum techniques.

A 251.5-g (1.94-mol) quantity of silver fluoride (Cationic, Inc.), which contained 2.1% HF-insoluble impurities, was loaded into the first vessel and 284 g of HF was added. Into the second vessel were placed 400.5 g (0.822 mol) of $NF_4SbF_6\cdot 0.8SbF_5$ and 148 g of HF. The $AgHF_2$ solution in the first vessel was pressurized to 30 psi with nitrogen and passed through a filter into the stirred NF_4^+ salt–HF solution under autogenous pressure in the second vessel. The resulting NF_4HF_2 solution was separated from the $AgSbF_6$ precipitate by filtration into the evacuated third reaction vessel. After brief pumping to remove the nitrogen pressurizing gas, BF_3 (68 g, 1.0 mol) was added to the third vessel until the total pressure above the liquid remained constant at 19–20 psi. The NF_4BF_4 solution was separated from the precipitated $AgBF_4$ by filtration into the evacuated fourth vessel. After removal of excess BF_3 and solvent HF the residual solid product (101.9 g) was isolated. The composition of the solid (in mole percent) was NF_4BF_4 (89), $NF_4Sb_2F_{11}$ (7.9), and $AgBF_4$ (3.1).

γ Irradiation and ESR Spectra. The NF_4^+ salts were transferred in the dry nitrogen atmosphere of a glove box into passivated 4-mm o.d. quartz tubes which were flame-sealed in vacuo. For the solution study, a 0.24 *M* solution of $NF_4^+SbF_6^-\cdot 0.8SbF_5$ in anhydrous HF was heat-sealed in a Teflon FEP tube.

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