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REACTIONS OF OXYL GROUPS ON THE TRIMETHYLSILYL MOIETY WITH DIPHENYL- OR DICYCLOHEXYL-CHLOROPHOSPHINES

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Summary

Treatment of either $(C_6H_5)_2PCl$ with $(CH_3)_3SiOCH_3$, or $(C_6H_5)_2POCH_3$ with $(CH_3)_3SiCl$ results in the formation of $(C_6H_5)_2P—P(O)(C_6H_5)_2$. On the other hand, reaction of $(C_6H_{11})_2PCl$ with $(CH_3)_3SiOCH_3$ produces $(C_6H_{11})_2$-$P(O)CH_3$. When $(C_6H_5)_2PCl$ is allowed to react with $(CH_3)_3SiOSi(CH_3)_3$, $(C_6H_5)_2P—P(O)(C_6H_5)_2$ and $(C_6H_5)_2P—P(C_6H_5)_2$ are produced. But $(C_6H_{11})_2PCl$ shows little reaction with $(CH_3)_3SiOSi(CH_3)_3$ even after heating for five days at ca. 150°.

Introduction

Although several reactions of hexamethyldisiloxane, $(CH_3)_3SiOSi(CH_3)_3$ (I) or methoxysilanes with phosphorus(V) halides have been reported [1, 2], a study of the interaction of these silicon reagents with phosphorus(III) halides has received little attention. Recently, we have reported [3] on the reactions of methoxytrimethylsilane, $(CH_3)_3SiOCH_3$ (II), and dimethoxydimethylsilane, $(CH_3)_2Si(OCH_3)_2$, with dichloromethylphosphine, CH_3PCl_2. We found that when CH_3PCl_2 and $(CH_3)_2Si(OCH_3)_2$ or $(CH_3)_3SiOCH_3$ are combined at room temperature, the chloro and methoxyl groups initially undergo redistribution reactions to give $CH_3P(OCH_3)Cl$ and $CH_3P(OCH_3)_2$. The methoxyphosphines thus formed then condense to form oligomeric molecules apparently based on a phosphorus backbone and possessing P—P bonds. The silyl group becomes attached to the phosphorus oligomers only at a later stage in the reaction, and its assimilation into the oligomeric structures is dependent upon the availability of reactive end groups (Cl or OCH_3) on the terminal phosphorus atom. Thus it became apparent that phosphorus(III) and phosphorus(V) chlorides react with methoxysilanes through different pathways, with the latter chlorides producing siloxyphosphorus(V) species as the primary reaction product. The interaction of $(CH_3)_3SiOSi(CH_3)_3$ with phosphorus(V) halides often proceeds with the scission of the Si—O—Si linkage and with the subsequent attachment of the $(CH_3)_3SiO$ group onto the phosphorus atom. Recently it was reported [4] that the phosphorane $(CF_3)_3P[OSi(CH_3)_3]_2$ was formed when compound I was treated with *tris*(-trifluoromethyl)phosphine oxide, $(CF_3)_3PO$. In this paper we report the results of our further studies in this area: the reactions of I and II with chlorodiphenylphosphine, $(C_6H_5)_2PCl$ (III), and with chlorodicyclohexylphosphine, $(C_6H_{11})_2PCl$ (IV), two suitable reactive phosphorus(III) chlorides.

Experimental

The ^{31}P nuclear magnetic resonance (NMR) measurements were run using a Varian XL-100-15 spectrometer equipped with Fourier transform accessories supplied by Nicolet Technology Corporation; ^1H NMR studies were done with a JEOLCO JNM-MH-100 spectrometer. The phosphorus spectra, with or without broad-band decoupling, 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 averaging. The ^{31}P chemical shifts were referenced by the tube-interchange method to 85% H_3PO_4 and the ^1H chemical shifts were referenced to internal $(CH_3)_4Si$, with negative shifts being downfield for both the nuclei.

Chlorodiphenylphosphine and chlorodicyclohexylphosphine were purchased from Strem Chemicals Inc., Danvers, Massachusetts. Methoxydiphenylphosphine was prepared from $(C_6H_5)_2PCl$ according to ref. 5. The silicon compounds employed in this study were obtained from Peninsular Chemical Research Inc., Gainesville, Florida. All of the reagents were finally purified by distillation under nitrogen and exhibited proper boiling points, with no evidence of impurities according to both ^{31}P and ^1H NMR spectra.

To avoid moisture and air, the reagents were handled under a nitrogen atmosphere in a glove bag containing phosphorus pentoxide as the dehydrating agent. The reactions were carried out either in sealed, evacuated glass tubes or three-necked flasks and the filtration and transfer of the products were done strictly under nitrogen employing the Shlenk tube technique.

Synthesis of $(C_6H_5)_2P{-}P(O)(C_6H_5)_2$

In a typical preparation, 4.5 g (0.043 mol) of $(CH_3)_3SiOCH_3$ was added to 6.4 g (0.029 mol) of $(C_6H_5)_2PCl$ under nitrogen in a 100 ml three-necked flask containing an inlet tube, reflux condenser and dropping funnel. The mixture was heated at ca. 70° for one hour with constant stirring. During this time a white crystalline solid precipitated. Thereafter, it was cooled to room temperature and the volatile materials were removed under vacuum. The crystalline solid was identified as tetraphenylbiphosphine monoxide (m.p. 157-160° lit. [6] 158-161° and [7] 155-158°). Yield 5.39 g (96%). Its ^{31}P NMR spectrum (^1H broad-band decoupled) in CH_2Cl_2 exhibited a doublet centered at -35.25 and another doublet centered at $+23.16$ ppm; $J(PP)$ 224.3 Hz. Addition of a known sample of $(C_6H_5)_2P{-}P(O)(C_6H_5)_2$, prepared according to ref. 7, did not show any spectral variation.

Synthesis of $(C_6H_5)_2P{-}P(O)(C_6H_5)_2$ *and* $(C_6H_5)_2P{-}P(C_6H_5)_2$

In a reaction, 2.13 g (9.7 mmol) of $(C_6H_5)_2PCl$ and 2.07 g (12.6 mmol) of

$(CH_3)_3SiOSi(CH_3)_3$ were combined in a glass tube and which was then promptly evacuated and sealed. It was then heated for four days between 140-145°. Thereafter, the reaction mixture was cooled and kept in a refrigerator for more than two weeks. During this time a white crystalline solid precipitated. The resulting solid-liquid mixture was filtered and the solid was washed with ether and dried in vacuum (1.42 g). It was then heated in an evacuated sublimation apparatus at ca. 100° and 1 torr. The white crystalline sublimate was identified as $(C_6H_5)_2P{-}P(C_6H_5)_2$, from its melting point (118-120°) and by comparing its ^{31}P NMR spectrum with that of an authentic sample obtained from Strem Chemicals, Inc. The ^{31}P NMR spectrum of this compound in CH_2Cl_2 exhibited a singlet at $+15.7$ ppm. Yield 0.52 g, (29%). The unsublimed material was similarly identified as tetraphenylbiphosphine monoxide. Its ^{31}P resonance was identical with that for the sample prepared from $(CH_3)_3SiOCH_3$ and $(C_6H_5)_2PCl$. Yield 0.89 g (47.5%).

The NMR spectra of the filtrate showed that it consisted of CH_3SiCl, unreacted $(C_6H_5)_2PCl$ and $(CH_3)_3SiOSi(CH_3)_3$ and some other phosphorus-containing products.

Synthesis of $(C_6H_{11})_2P(O)CH_3$

In a reaction, 0.79 g (3.4 mmol) of $(C_6H_{11})_2PCl$ and 0.51 g (4.7 mmol) of $(CH_3)_3SiOCH_3$ were combined in a sealed, evacuated glass tube and heated for 65 h at 95-100°. Removal of the volatile materials left a white crystalline solid identified as dicyclohexylmethylphosphine oxide, $(C_6H_{11})_2P(O)CH_3$ (m.p. 79-81°). (Found: C, 68.1; H, 10.8; P, 13.5; O, 7.6 (by difference). $C_{13}H_{25}OP$ calcd.: C, 68.4; H, 10.96; P, 13.59; O, 7.00 %.) Its ^{31}P NMR (CH_2Cl_2) spectrum exhibited a singlet at -52.61 ppm and its ^1H NMR spectrum exhibited two broad peaks (cyclohexyl protons) at -1.79 and -1.25 ppm and a sharp doublet centered at -1.24 ppm. (This doublet overlaps the broad upfield peak due to cyclohexyl protons.) The hygroscopic solid, $(C_6H_{11})_2P(O)CH_3$ is soluble in CH_2Cl_2, $(CH_3)_3SiCl$ and $(CH_3)_3SiOCH_3$. Yield 0.72 g (94.5%).

$(C_6H_{11})_2PCl$ *with* $(CH_3)_3SiOSi(CH_3)_3$

When a mixture of 0.73 g (3.14 mmol) of $(C_6H_{11})_2PCl$ and 3.9 g (3.95 mmol) of $(CH_3)_3SiOSi(CH_3)_3$ was heated for 5 days at ca. 150° in a sealed, 5 mm NMR tube, there was no evidence of any reaction according to the NMR spectra.

Results and discussion

When chlorodiphenylphosphine is treated with methoxytrimethylsilane, tetraphenylbiphosphine monoxide is formed according to eqn. 1. An NMR

$$2\,\underset{\text{(III)}}{(C_6H_5)_2PCl} + \underset{\text{(II)}}{(CH_3)_3SiOCH_3} \rightarrow \underset{\text{(V)}}{(C_6H_5)_2P{-}P(O)(C_6H_5)_2} + CH_3Cl + (CH_3)_3SiCl \quad (1)$$

investigation has revealed that the initial reaction process involves the redistribution of chloro and methoxyl groups between the $(C_6H_5)_2P$ and $(CH_3)_3Si$ moieties (eqn. 2). The $(C_6H_5)_2POCH_3$ thus formed reacts with the $(C_6H_5)_2PCl$ to produce $(C_6H_5)_2P{-}P(O)(C_6H_5)_2$ (V) (eqn. 3). Chlorotrimethylsilane and methyl chloride were identified from their characteristic ^1H chemical shifts of -0.49

and —3.05 ppm respectively, as measured for known samples. Their amounts were in agreement with the stoichiometry shown in eqn. 1. Methoxydiphenyl-

$$\underset{\text{(III)}}{(C_6H_5)_2PCl} + \underset{\text{(II)}}{(CH_3)_3SiOCH_3} \rightarrow (C_6H_5)_2POCH_3 + (CH_3)_3SiCl \qquad (2)$$

$$(C_6H_5)_2POCH_3 + \underset{\text{(III)}}{(C_6H_5)_2PCl} \rightarrow \underset{\text{(V)}}{(C_6H_5)_2P{-}P(O)(C_6H_5)_2} + CH_3Cl \qquad (3)$$

phosphine was similarly identified from its ^{31}P chemical shift of —116.1 ppm. Although V is formed slowly at room temperature, rapid conversion can be achieved by heating the mixture for 1 h at ca. 70°. The yield of V is practically quantitative and it is easily purified by removing the volatile $(CH_3)_3SiCl$, $(CH_3)_3SiOCH_3$ and CH_3Cl in vacuo. It was found that the presence of an excess of $(CH_3)_3SiOCH_3$, large enough to convert all of the chlorophosphine initially to the methoxyl derivative, did not hinder the yield of V. This implies that a probable secondary process involving the redistribution of methoxyl and chloro groups between $(C_6H_5)_2POCH_3$ and $(CH_3)_3SiCl$ also comes into play. Proof for this was obtained from an independent reaction between $(C_6H_5)_2POCH_3$ and $(CH_3)_3SiCl$. When 3.8 mmol of $(C_6H_5)_2POCH_3$ was combined with 3.3 mmol of $(CH_3)_3SiCl$ in 0.7 g of methylene chloride, a quantitative yield of V was obtained in ca. 4 h at room temperature. The reaction was found to follow the stoichiometry shown in eqn. 4.

$$2\,(C_6H_5)_2POCH_3 + (CH_3)_3SiCl \rightarrow (C_6H_5)_2P{-}P(O)(C_6H_5)_2 + CH_3Cl + (CH_3)_3SiOCH_3 \qquad (4)$$

Unlike III, dicyclohexylchlorophosphine showed very little reaction with $(CH_3)_3SiOCH_3$ at room temperature. The ^{31}P NMR spectrum of a sample containing 3.57 mmol $(C_6H_{11})_2PCl$ and 4.7 mmol $(CH_3)_3SiOCH_3$ after 4 days at room temperature showed, in addition to the resonance of $(C_6H_{11})_2PCl$ at —125.14 ppm, only a small peak (ca. 4% of total P) at —150.84. Since a comparable amount of $(CH_3)_3SiCl$ was observed in its ^1H NMR spectrum, this new ^{31}P resonance may be attributed to $(C_6H_{11})_2POCH_3$, produced according to eqn. 5.

$$(C_6H_{11})_2PCl + (CH_3)_3SiOCH_3 \rightarrow (C_6H_{11})_2POCH_3 + (CH_3)_3SiCl \qquad (5)$$

On heating the two at ca. 100°, they react quantitatively to produce dicyclohexylmethylphosphine oxide, $(C_6H_{11})_2P(O)CH_3$ (VI) as shown in eqn. 6.

$$\underset{\text{(IV)}}{(C_6H_{11})_2PCl} + \underset{\text{(II)}}{(CH_3)_3SiOCH_3} \rightarrow \underset{\text{(VI)}}{(C_6H_{11})_2P(O)CH_3} + (CH_3)_3SiCl \qquad (6)$$

The structure of VI was proved from its ^1H and ^{31}P NMR spectra. The ^{31}P resonance at —52.61 is very close to the chemical shifts reported [8] for other known cyclohexylphosphine oxides, (viz. $\delta(C_6H_{11})_3PO$ at —50 ppm; $\delta(C_6H_{11})_2P(O)CH(C_6H_5)OH$ at —53 ppm). Furthermore, methoxyl protons, which usually exhibit ^1H resonances in the region —3 to —4 ppm, were not observed. The observed doublet centered at —1.24 ppm is clearly in the range found for CH_3P groups. Either the $(C_6H_{11})_2POCH_3$, formed as a primary product rearranges to $(C_6H_{11})_2P(O)CH_3$ at the temperature range employed in the experiment or the rearrangement may be catalysed by the silicon compounds present in the reaction mixture. An alternative possibility is the initial formation of $(C_6H_{11})_2POSi(CH_3)_3$ and CH_3Cl and the subsequent reaction of the two via an Arbusov-type rearrangement to form VI. It should be noted that a small amount of CH_3Cl (ca. 5% of the total CH_3O group present initially) was observed as a reaction product, although no evidence for $(C_6H_{11})_2POSi(CH_3)_3$ was obtained.

When hexamethyldisiloxane and chlorodiphenylphosphine were combined at room temperature, no reaction was observed. However, the ^{31}P and ^{1}H NMR spectra of a mixture containing the two in about a 1/1 ratio, when heated for four days at 140-145°, revealed the presence of several reaction products. Upon holding this mixture in a refrigerator, white crystalline material precipitated over a period of two weeks. This solid consisted entirely of a mixture of tetraphenylbiphosphine, $(C_6H_5)_2P{-}P(C_6H_5)_2$ (VII) and its monoxide, V. The filtrate from the reaction contained, in addition to some starting materials, $(CH_3)_3SiCl$ and some other phosphorus-containing products. The ^{31}P NMR spectrum of the filtrate showed a major peak at +6.7 ppm and a minor resonance at —41.2 ppm.

The presence of diphenyl trimethylsiloxyphosphine, $(C_6H_5)_2POSi(CH_3)_3$, an obvious product following a reaction course shown in eqn. 7, was not observed.

$$\underset{(III)}{(C_6H_5)_2PCl} + \underset{(I)}{(CH_3)_3SiOSi(CH_3)_3} \not\rightarrow (C_6H_5)_2POSi(CH_3)_3 + (CH_3)_3SiCl \quad (7)$$

This compound was prepared recently by Issleib and co-workers [9] and was identified as a liquid having b.p. of 103-106°/0.5 torr and exhibiting a ^{31}P chemical shift of —94.1 ppm. The formation of $(C_6H_5)_2P{-}P(O)(C_6H_5)_2$ as the major phosphorus-containing product could be explained by assuming that if $(C_6H_5)_2POSi(CH_3)_3$ were initially formed, it would react with another mole of $(C_6H_5)_2PCl$ via an Arbusov-type rearrangement, as depicted in eqn. 8.

$$(C_6H_5)_2POSi(CH_3)_3 + (C_6H_5)_2PCl \rightarrow \underset{(V)}{(C_6H_5)_2P{-}P(O)(C_6H_5)_2} + (CH_3)_3SiCl \quad (8)$$

Note that this reaction is similar to that between $(C_6H_5)_2PCl$ and $(C_6H_5)_2POCH_3$. A reasonable reaction to account for the formation of VII is shown in eqn. 9.

$$\underset{(III)}{3(C_6H_5)_2PCl} \rightarrow \underset{(VII)}{(C_6H_5)_2P{-}P(C_6H_5)_2} + (C_6H_5)_2PCl_3 \quad (9)$$

Although the ^{31}P chemical shift of $(C_6H_5)_2PCl_3$ varies considerably with the nature of the solvent[10], the assignment of the ^{31}P NMR peak observed at +6.7 ppm in the spectrum of the filtrate to $(C_6H_5)_2PCl_3$ is not unreasonable when one compares this value with the chemical shifts of other halophosphoranes [8]. This is supported by the fact that the ratio of 2.1/1 for the peak at +15.7 ppm with respect to that at +6.7 ppm in the ^{31}P NMR spectrum of a reaction mixture before precipitation of the crystals is in good agreement with the expected value of 2/1 from eqn. 9. The observed higher yield of $(C_6H_5)_2$-$P{-}P(C_6H_5)_2$, when $(C_6H_5)_2PCl$ was present in large excess, also substantiates the disproportionation reaction described in eqn. 9.

It may be noted that, when $(C_6H_5)_2PCl$ was heated alone for five days at 145°, no detectable reaction products were observed. Probably the silicon compounds present in the reaction mixture has some catalytic effect in promoting the reaction proposed in eqn. 9. An alternative possibilty described in eqn. 10 cannot be ruled out.

$$\underset{(V)}{(C_6H_5)_2P{-}P(O)(C_6H_5)_2} + \underset{(III)}{(C_6H_5)_2PCl} \rightarrow \underset{(VII)}{(C_6H_5)_2P{-}P(C_6H_5)_2} + (C_6H_5)_2P(O)Cl \quad (10)$$

The minor resonance in the ^{31}P NMR spectrum of the filtrate at -41.2 ppm is close to the chemical shift reported for $(C_6H_5)_2P(O)Cl$ [8]. Of course, the $(C_6H_5)_2P{-}P(C_6H_5)_2$ may be formed via both of the pathways described above.

Unlike $(C_6H_5)_2PCl$, dicyclohexylchlorophosphine did not react with hexamethyldisiloxane even after heating for five days at 150°.

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