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Preparation and Characterization of Dimethoxyphosphine

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Dimethoxyphosphine, $(CH_3O)_2PH$, has been obtained from the reaction of PF_2H, CH_3OH, and pyridine and from the carefully controlled reduction of $(CH_3O)_2PCl$ by $(C_4H_9)_3SnH$. The new ligand was characterized by ir, mass, and nmr spectra. Methoxyphosphine, H_2POCH_3, could not be prepared, but the borane adduct was synthesized by reported methods. The borane adduct of $HP(OCH_3)_2$ was also prepared and characterized. The P-B coupling constants indicate that the basicity order toward borane is $P(OCH_3)_3 > HP(OCH_3)_2 > H_2POCH_3 > H_3P$. The nmr spectrum of $HP(OR)_2\cdot BH_3$ is found to be temperature dependent. The observed changes can be explained by quadrupolar spin-lattice relaxation.

Introduction

A survey of the known phosphines revealed few stable derivatives of the unknown phosphorus acid, $HP(OH)_2$. Early attempts to prepare Cl_2PH, the logical starting material for this series of compounds, have been unsuccessful;[1] however, the preparation of HPF_2[2] and the availability of selective reducing agents[3] (*i.e.*, tin hydrides) offer routes to these compounds. Lutsenko, *et al.*,[4] utilizing the hydrides, have reported the preparation of $(RO)_2PH$ compounds, where R is a large alkyl group, but they were unsuccessful in their efforts to prepare $HP(OCH_3)_2$, the simplest member of the series.

Recently there has been considerable interest in the basicity toward boranes of certain phosphines,[5-7] and of particular interest is the unusual basicity of HPF_2 in the series $PF_{3-x}H_x$. The base strength order in the series is $PF_2H > PF_3 \gtrsim PH_3$. In other phosphine series a monotonic increase or decrease occurs: a comparison of the $F_{3-x}PH_x$ series with the somewhat analogous $(CH_3O)_{3-x}PH_x$ series would be of interest. We report herein the preparation of $HP(OCH_3)_2$ and the investigation of the basicity of this compound and other members of the $(CH_3O)_{3-x}PH_x$ series.

Experimental Section

Material and General Techniques. Standard high-vacuum techniques were used throughout.[8] Mass spectra were obtained on a Varian M66 (70 eV). Infrared spectra were recorded on a Perkin-Elmer 137 NaCl spectrophotometer and a 421 grating spectrophotometer using a 10-cm gas cell with KBr windows. Phosphorus nmr were recorded at 40.4 MHz and boron at 32.1 MHz on a Varian HA-100. Proton spectra were observed at 100 MHz on a Jeol MH-100.

PF_2H,[2] B_2H_6,[9] $HSn(C_4H_9)_3$,[10] and $H_2POCH_3BH_3$[1] were prepared by literature methods. Pyridine, PCl_3, $P(OCH_3)_3$, and CH_3OH were obtained from Matheson Coleman and Bell. All were distilled prior to use. $LiBH_4$ was obtained from Alfa Inorganics.

Preparation of $ClP(OCH_3)_2$. The alkoxychlorophosphines can be readily prepared by mixing stoichiometric amounts of PCl_3 and the desired trialkyl phosphite. In a typical preparation of $ClP(OCH_3)_2$, 250 g (2 mol) of $P(OCH_3)_3$ was mixed with 106 g (1 mol) of PCl_3 at room temperature. The temperature of the mixture rapidly increased as the exchange occurred. After sitting overnight at room temperature, a proton nmr indicated better than 90% purity. Attempts to purify $ClP(OCH_3)_2$ further by distillation led to decomposition. The product obtained from the exchange was used directly in the synthesis of $HP(OCH_3)_2$. The CH_3OPCl_2 used in the preparation of $H_2POCH_3BH_3$ was prepared by an analogous reaction.

As the size of the alkyl group increases, the rate of exchange decreases rapidly. For large alkyl groups heating and refluxing are necessary to isolate the mixed alkoxychlorophosphine. Trimethyl phosphite and PCl_3 must be mixed at room temperature and may require cooling during reaction. In one experiment $P(OCH_3)_3$ and PCl_3 were heated prior to and after mixing. A violent reaction and fire occurred.

Reaction of PF_2H, CH_3OH, and Pyridine. In a typical experiment 1.06 mmol of PF_2H was condensed with 1.08 mmol of CH_3OH and 2 ml of pyridine in a 75-cm^3 reaction vessel and allowed to warm slowly to room temperature. During warming a vigorous reaction occurred. The products of the reaction were rapidly distilled through traps held at −35, −100, and −196°. Excess pyridine at −35° and PF_3, PH_3, and SiF_4 at −196° were discarded. The −100° trap contained $HP(OR)_2$ and pyridine. The pyridine was removed by distilling the mixture through traps at −50 and −196°. The pyridine stopped at −50° and was discarded. The −196° trap contained 0.21 mmol of $HP(OR)_2$ for a 19% yield based on the amount of alcohol used.

Reaction of $(CH_3O)_2PCl$ with Tributyltin Hydride. In a typical experiment 13 g (100 mmol) of $(CH_3O)_2PCl$ dissolved in 10 g of $P(OCH_3)_3$ was slowly added to 35 g of $(C_4H_9)_3SnH$ (117 mmol, slight excess) dissolved in 20 g of $P(OCH_3)_3$ in a 200-cm^3 reaction vessel. Tributyltin hydride must always be in excess; thus $(CH_3O)_2PCl$ must always be added to the tin hydride. The mixture was kept at room temperature about 5 min. The vessel was then opened to the vacuum system and the products were pumped through traps held at −25 and −196°. This was continued until the volatile material contained no PH stretch (2222 cm^{-1}). The volatile components consisted of H_2, $HP(OCH_3)_2$, $P(OCH_3)_3$, and PH_3. The $P(OCH_3)_3$ at −25° was discarded while the material at −196° was distilled through traps at −35 and −196°. The $P(OCH_3)_3$ at −35° was again discarded. The impure product at −196° was finally purified by passing through traps held at −40, −90, and −196°. $P(OCH_3)_3$ at −50° and PH_3 at −196° were discarded. The −90° trap contained 1.5 g of $HP(OCH_3)_2$ (16.3 mmol) for a 16% yield, based on the amount of $(CH_3O)_2PCl$ used. In order to find the best method of mixing the above compounds the reaction was examined *via* proton nmr under varying conditions.

On mixing $(C_4H_9)_3SnH$ with $(CH_3O)_3P$ no PH peak was observed in the proton nmr. At room temperature tributyltin hydride will not reduce $P(OCH_3)_3$. Mixing $(C_4H_9)_3SnH$ with excess $(CH_3O)_2PCl$ resulted in a large amount of yellow solids. On examining the proton nmr, no PH peaks were observed. Excess $(CH_3O)_2PCl$ must be avoided since it will further react with the $(CH_3O)_2PH$ produced. Tributyltin hydride was dissolved in $P(OCH_3)_3$, and PCl_3 was slowly added. A reaction occurred with the formation of yellow solids. Again on examining the proton nmr, no PH peak was observed. The reaction of PCl_3 with R_3SnH occurred before exchange between $P(OCH_3)_3$ and PCl_3 could occur.

Reaction of $HP(OCH_3)_2$ and B_2H_6. In a typical experiment 1.25 mmol of $HP(OCH_3)_2$ was mixed with 1.53 mmol of B_2H_6 in a

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75-cm^3 reaction vessel. The mixture was allowed to sit at room temperature for several minutes. An immediate reaction occurred with the formation of a yellow oil. The products were distilled through traps held at −60, −125, and −196°. The material at −125° (0.4 mmol, unidentified) and the B_2H_6 (1.0 mmol) at −196° were discarded. A 0.4-mmol sample (32% yield) of $HP(OCH_3)_2BH_3$ was found at −60°. The material has several millimeters of pressure at room temperature and flames immediately on exposure to air.

Reaction of $LiBH_4$ and $ClP(OCH_3)_2$. A 4.0-g (31-mmol) sample of $ClP(OCH_3)_2$ was condensed on a 0.78-g (35-mmol) sample of $LiBH_4$ in a 200-cm^3 reaction vessel. The mixture was allowed to warm slowly to room temperature. An immediate reaction occurred producing yellow solids and hydrogen. The volatile components were distilled through traps held at −78 and −196° The $HP(OCH_3)_2$, B_2H_6, and PH_3 found at −196° were discarded. The material at −78° was distilled through traps held at 0, −40, and −196°. Small amounts of material at 0 and −196° were discarded. The −40° trap contained 1.0 g of $(CH_3O)_2PHBH_3$ for a 30% yield.

Reaction of $HP(OCH_3)_2$ and CH_3OH. Equimolar (∿2 mmol) amounts of $HP(OCH_3)_2$ and CH_3OH were condensed and sealed in an nmr tube. The proton nmr of the mixture only exhibited peaks which could be assigned to the two free compounds. No adduct peaks were observed down to −70°.

Results and Discussion

A. Preparation and Characterization of $HP(OCH_3)_2$.

Using vacuum-line techniques[8] dimethoxyphosphine has been prepared by the reaction of methyl alcohol, difluorophosphine, and pyridine

$$PF_2H + 2CH_3OH + 2C_5H_5N \rightarrow HP(OCH_3)_2 + 2C_5H_5NHF$$

With careful distillation, yields of the product were usually about 19%. A slight excess of PF_2H was usually used because of the difficulty of separating CH_3OH and $(CH_3O)_2PH$.

A more practical route to the ligand is the reaction of tributyltin hydride and dimethoxychlorophosphine. Earlier workers[4] were unable to isolate the methoxy compound using this route

$$ClP(OCH_3)_2 + (C_4H_9)_3SnH \xrightarrow{P(OCH_3)_3} HP(OCH_3)_2 + (C_4H_9)_3SnCl$$

The phosphine can be prepared by this method by carefully controlling the conditions and using standard vacuum-line techniques.[8] Using equimolar amounts of $ClP(OCH_3)_2$ and $HSn(C_4H_9)_3$ and using $P(OCH_3)_3$ as a solvent, yields of product have been about 15%.

It appears that the method of addition is very important. No $HP(OCH_3)_2$ was produced if $ClP(OCH_3)_2$ is in excess, indicating reaction between $HP(OCH_3)_2$ and $ClP(OCH_3)_2$. Therefore, the tin hydride must always be in excess. This can be accomplished by the addition of the chlorophosphite to the tributyltin hydride so that the hydride is always in excess. Attempts to prepare CH_3OPH_2 by an analogous reaction were unsuccessful.

Dimethoxyphosphine is a colorless liquid at room temperature, but decomposition occurs rapidly to give methyl alcohol and unidentified oils. $HP(OCH_3)_2$ was characterized by its mass, infrared, and nmr spectra. The gas-phase infrared spectrum showed a strong peak at 2222 cm^{-1} which can be assigned to the phosphorus-hydrogen symmetric stretching vibration. This peak strongly indicates that trivalent phosphorus is present. The PH stretches for phosphine oxides and pentavalent phosphorus are in the 2500-2400-cm^{-1} region. Other peaks include 3000 (b, w), 2940 (m), 2840 (m), 2140 (w), 1172 (b, w), 1075 (m), 1040 (s), 984 (m), 931 (m) (PQR), 747 (s) (PQR) cm^{-1}.

The proton and phosphorus nmr spectra showed the expected splitting patterns. The phosphorus spectrum consisted of a doublet, $J_{PH} = 203$ Hz, $\delta(H_3PO_4)$ −171 ppm. Each doublet was further split into a septet, $J_{POCH} = 9.4$ Hz. The proton spectrum confirmed the phosphorus spectrum. It consisted of a doublet ($J_{PH} = 200$ Hz, δ(TMS) 6.8 ppm) with a relative area of 1 and a second doublet ($J_{POCH} = 9.2$ Hz, δ(TMS) 3.7 ppm) with a relative area of 6.[11]

The mass spectrum is relatively simple and can be fitted very nicely to the compound. Following are the mass numbers (species) and relative abundances of the ions in the mass spectrum of $HP(OCH_3)_2$: 94 ($HP(OCH_3)_2^+$), 44; 93 ($P(OCH_3)_2^+$), 100; 79 ($HPO_2CH_3^+$), 34; 77 ($PO_2CH_2^+$), 3; 64 (HPO_2^+), 6; 63 ($HPOCH_3^+$, PO_2^+), 41; 62 ($POCH_3^+$), 7; 50 (H_3PO^+), 4; 49 (H_2PO^+), 9; 48 (HPO^+), 6; 47 (PO^+), 37; 45 (PCH_3^+), 7; 33 (PH_2^+), 4; 32 (PH^+), 11; 31 (P^+, H_3CO^+), 6; 29 (HCO^+), 7; 28 (CO^+), 26; 18 (H_2O^+), 3; 15 (CH_3^+), 26.

B. Chemistry of the Series $H_xP(OCH_3)_{3-x}$.

The borane adducts of the series $H_xP(OCH_3)_{3-x}$, except for the unknown CH_3OPH_2, can be prepared by the action of B_2H_6 on the free ligand or in the case of $H_2POCH_3BH_3$ and $HP(OCH_3)_2 \cdot BH_3$ by the action of $LiBH_4$ on the corresponding alkoxychlorophosphine

$$LiBH_4 + ClP(OCH_3)_2 \xrightarrow{P(OCH_3)_3} LiCl + HP(OCH_3)_2BH_3$$

$$HP(OCH_3)_2 + {}^1/_2B_2H_6 \rightarrow HP(OCH_3)_2BH_3$$

The previously unreported dimethoxyphosphine-borane was prepared by both methods. The direct reaction of the ligand gave a 32% yield of product. A more practical route for the preparation of the borane adduct was the reaction of $LiBH_4$ with $ClP(OCH_3)_2$. The reaction gave only a 30% yield, but large amounts can be prepared since the reactants are readily available. The product was a slightly volatile oil which flames immediately in air. No noticeable decomposition occurred at room temperature or when heating *in vacuo* to about 40°.

$HP(OCH_3)_2BH_3$ was characterized by its proton and boron nmr spectra. The proton nmr spectrum consists of three sets of peaks at 30°. A broad upfield 1:1:1:1 quartet assigned to the BH protons ($J_{BH} = 96$ Hz, δ(TMS) 0.4 ppm) each member of which was further split into a doublet ($J_{PBH} = 16$ Hz). Two doublets were also observed, one with a relative area of 6 which could be assigned to the methoxy protons in $HP(OCH_3)_2BH_3$ ($J_{POCH} = 11$ Hz, δ 3.7 ppm). The other doublet with a relative area of 1 could be assigned to the PH proton ($J_{PH} = 448$, δ 6.8 ppm). The ^{11}B nmr confirmed the proton spectrum. It consisted of a quartet ($J_{BH} = 96$ Hz, $\delta(BF_3O(C_2H_5)_2)$ 41.6 ppm) split into a doublet; $J_{PB} = 75$ Hz.

The various nmr spectra of $HP(OCH_3)_2BH_3$ exhibited a temperature dependence. The most dramatic temperature effects are seen when observing the BH protons (Figure 1). At room temperature and above the spectrum consists of a 1:1:1:1 quartet each member of which is split into a doublet (J_{BH} and J_{PBH}, respectively). As the temperature is lowered, collapse of the J_{PBH} doublets occurs at about −10°. As the temperature is lowered further, the 1:1:1:1 quartet begins to collapse. The outer two members of the quartet collapse at a faster rate than the inner members. At −60° the outer members are barely discernible. Further cooling causes complete decoupling and at −90° a singlet with a line width of 60 Hz is observed. The sample began to freeze on cooling below −90°. Line widths for the PH proton peaks also decreased on cooling. Nmr temperature dependence of various boron-hydrogen compounds has been observed by

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(11) Conventions from IUPAC International Bulletin No. 4, Appendices on Tentative Nomenclature, Symbols, Units and Standards, 1970. Signals downfield from tetramethylsilane are reported as positive.

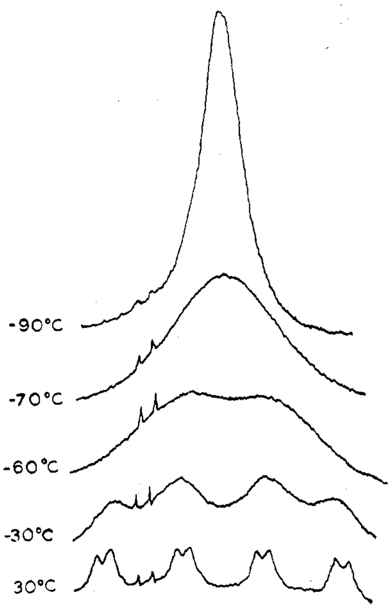

Figure 1. A portion of the 100-MHz pmr spectra of $HP(OCH_3)_2$-BH_3 showing the temperature dependence of the borane protons. The small doublet is an impurity.

other authors.[12-14] In most cases, the effects usually involve a broadening of the proton peaks. Complete decoupling is seldom observed for boron compounds under normal laboratory conditions. Recently Marks and Shrimp[12] have carried out an extensive study of the temperature dependence of the proton nmr spectra of $Zr(BH_4)_4$ and $Hf(BH_4)_4$. They concluded that temperature effects in these molecules were the result of the variable rate of ^{10}B and ^{11}B quadrupolar spin-lattice relaxation. This effect would also explain the temperature dependence of the nmr spectra of $HP(OCH_3)_2$-BH_3.

Methoxyphosphine-borane was also prepared by the reaction of $LiBH_4$ and $Cl_2P(OCH_3)_2$ and characterized *via* nmr. $CH_3OPH_2BH_3$ is unstable at room temperature giving off H_2, PH_3BH_3, and yellow solids. The proton nmr consisted of three sets of peaks: a high field 1:1:1:1 quartet (J_{BH} = 96 Hz, δ(TMS) 0.4 ppm), an intense doublet (J_{POCH} = 12 Hz, δ(TMS) 3.8 ppm), and a weaker doublet (J_{PH} = 388, δ(TMS) 6.5 ppm) each member of which was split into a 1:3:3:1 quartet (J_{HBPH} = 6 Hz). HBPH coupling has been observed in PF_2HBH_3 and PH_3BH_3.[5]

C. Base Strength of the Series $H_xP(OCH_3)_{3-x}$ toward BH_3. Attempts to determine the base strength of the members of this family using displacement reactions were unsuccessful because of the instability of $HP(OCH_3)_2$ and H_2POCH_3. Recently Cowley[6] and Rudolph[7] have examined the use of J_{PB} as a measure of the base strength of the phosphine. Rudolph found that the correlation did not hold with several fluorophosphines (*e.g.*, F_2POPF_2); also, it did not hold if there were drastic changes in the acid. Cohn[15] has recently observed that the J_{PB} of PF_2CH_3 cannot be correlated to its base strength. In a series such as $H_xP(OCH_3)_{3-x}$, J_{BP} is expected to correlate with the basicity of the series. On examining the J_{BP} for this series we find the following values: $P(OCH_3)_3$, 97 Hz; $HP(OCH_3)_2BH_3$, 75 Hz; $H_2P(OCH_3)BH_3$, 55 Hz; H_3PBH_3, 27 Hz. Thus J_{BP} suggests that the base strength order is $P(OCH_3)_3 > HP(OCH_3)_2 > H_2POCH_3 > H_3P$.

This is in contrast to the somewhat analogous H_xPF_{3-x} system.[5] The base strength is found to be $PF_2H > PF_3 \gtrsim PH_3$. A more available electron pair is expected on the oxygen in the methoxy group than on the fluorine. π bonding between the oxygen and phosphorus should enhance the basicity of the phosphorus. In the fluorophosphines little or no π bonding would occur between fluorine and phosphorus.[16] Thus the predominant effect in the basicity of the alkoxyphosphines is electron drift from the oxygen π system. The unusual trend observed in the H_xPF_{3-x} series has been difficult to explain. The high basicity of PF_2H may be the result of a weak coulombic interaction between the PH and BH protons.[17] The large contribution to the basicity from the electron drift from oxygen to phosphorus should overwhelm this effect giving a monotonic increase in basicity for the series $H_xP(OCH_3)_{3-x}$.

It is interesting to note that $HP(OCH_3)_2$ will not form adducts with CH_3OH, whereas $PF_2H_2OCH_3$ can be isolated from the reaction of PF_2H and CH_3OH.[18] This could be attributed to the high deformation energy for $HP(OCH_3)_2$ which is required in converting pyramidal $HP(OCH_3)_2$ to trigonal bipyramidal $H_2P(OCH_3)_3$. Increased deformation energy would result from increased π bonding. If the deformation energy exceeds the bonding energy, no adduct would form. The formation of the borane adduct would not be affected by the deformation energy of the phosphine, since it requires only minor geometric change.

Registry No. PF_2H, 14984-74-8; CH_3OH, 67-56-1; C_5H_5N, 110-86-1; $(CH_3O)_2PCl$, 3743-07-5; $(C_4H_9)_3SnH$, 688-73-3; B_2H_6, 19287-45-7; $LiBH_4$, 16949-15-8; $HP(OCH_3)_2$, 20502-63-0; $Cl_2P(OCH_3)$, 3279-26-3; $HP(OCH_3)_2BH_3$, 38496-22-9; $CH_3OPH_2BH_3$, 38496-23-0.

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